Rejection of trace organic chemicals by a nanofiltration membrane: the role of molecular properties and effects of caustic cleaning

Manuscript submitted to

Environmental Science: Water Research & Technology

July 2015

Takahiro Fujioka [1,*], Stuart J. Khan [2], James A. McDonald [2], Long D. Nghiem [3]

[1] Division of Chemistry and Materials Science, Graduate School of Engineering, Nagasaki University, Nagasaki 852-8521, Japan

[2] UNSW Water Research Centre, School of Civil and Environmental Engineering, The University of New South Wales, NSW 2052, Australia

[3] Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, The University of Wollongong, NSW 2522, Australia

_____

* Corresponding author: Takahiro Fujioka, Email: tfujioka@nagasaki-u.ac.jp

1   **Abstract**

2   The aim of this study was to provide further insights to the rejection mechanisms of trace
3   organic chemicals (TrOCs) by nanofiltration (NF). The separation mechanisms of TrOCs by
4   an NF membrane were elucidated by assessing the role of molecular properties and the
5   impact of caustic cleaning on their rejection. All charged TrOCs were rejected by the NF270
6   membrane by more than 80%. However, the rejection of positively charged TrOCs was lower
7   than that of their negatively charged TrOCs with similar molecular sizes and was similar to
8   the rejection of natural TrOCs. The results suggest that size interaction, rather an electrostatic
9   repulsion, was a major factor attributing to the rejection of these positively charged TrOCs.
10   The results also showed that the minimum projection area was a better surrogate parameter
11   for molecular dimensions than molecular weight. Our study highlight the need to monitor the
12   rejection of neutral and positively charged TrOCs (particularly those that are normally
13   moderately rejected by the membrane) following caustic cleaning.

14   **Keywords:** Chemical cleaning; nanofiltration; potable water treatment; trace organic
15   chemicals (TrOCs).

16

1. Introduction

Population growth, climate change and contamination of natural freshwater sources present major threats to clean water availability in many parts of the world. As a consequence, it has been predicted that water scarcity will continue to increase in densely populated regions around the world [1]. In particular, the pollution of freshwater bodies with anthropogenic and low molecular weight trace organic chemicals (TrOCs) has been a worldwide issue over the past few decades [2-5]. These TrOCs are biologically active and can present a potential hazard to human health and the environment. TrOCs can be classified into pharmaceutical and personal care products, endocrine disruptors, pesticides, and industrial chemicals such as plastic additives. A concerning increase of the numbers and concentrations of TrOCs in drinking water has been noted by the World Health Organization [6].

There are two major factors contributing to the public awareness of TrOCs in the environment. Firstly, the increasing number and concentration of TrOCs that are released into the aquatic environment, in particular since World War II, due to the large quantities of produced and consumed pharmaceuticals in modern societies [1, 3]. Secondly, there has been tremendous technological progress in the field of analytical chemistry, which has allowed the quantification of TrOCs at trace levels [7]. TrOCs can be detected in a water sample at concentrations as low as 1 nanogram per litre (ng/L) or less. The majority of TrOCs are released into the environment by effluent discharged from private households, hospitals, and industrial and farming activities [8, 9]. These TrOCs are often poorly removed from wastewaters by conventional wastewater treatment facilities [8, 9]. Significant progress in process engineering and materials science have facilitated effective removal of TrOCs by membrane filtration processes such as nanofiltration (NF) and reverse osmosis (RO). Indeed, NF/RO membranes have become an integral part of many water reuse facilities. Water reuse is commonly considered to be more cost effective and environmentally friendly than seawater desalination or long-distance water transfers for regions experiencing regular droughts and water scarcity [1].

The increasing use of NF/RO for drinking water purification and potable water reuse has spurred many dedicated studies to assess the rejection mechanism of TrOCs by these membrane processes. As an example, Mery-sur-Oise is the world's largest NF plant (capacity

47   of 140,000 m^3/day) specifically designed and built for the removal of pesticides from the

48   Paris river for drinking water production [10]. NF process also shows an excellent performance

49   on softening and removing natural organic matter for drinking water applications [10]. On the

50   other hand, RO has been extensively used for potable water reuse applications.

51   Although the distinction between NF and RO membranes is not clear, it is widely accepted

52   that the removal mechanisms of TrOCs by these membranes are similarly. In addition,

53   because TrOC rejection by NF membranes is lower compared to RO membranes, variations

54   in TrOC rejection due to changes in the operating condition can be better observed with NF

55   membranes. Bellona et al., [11] provided an early, and arguably one of the most comprehensive,

56   reviews on the rejection of TrOCs by NF/RO membranes. However, the review by Bellona et

57   al., [11] and most subsequent studies only cover a small number of TrOCs and often heavily

58   rely on investigations with concentrations well above typical for these compounds due to

59   difficulties associated with their analysis. To date, key mechanisms governing the separation

60   of TrOCs by NF membranes, namely size exclusion, electrostatic interaction, and adsorption

61   (e.g., due to hydrophobic interaction or hydrogen bonding), have been discussed [12-14].

62   The lack of comprehensive data obtained from consistent conditions has hindered the

63   identification of more subtle factors that can also influence the rejection of TrOCs by NF

64   membranes. As a notable example, the effects of membrane fouling and chemical cleaning on

65   TrOC rejection have only been recently investigated. It has been observed that membrane

66   fouling can compromising the rejection of TrOCs by altering the surface hydrophobicity,

67   charge, pore size and by hindering back diffusion of the solute [15-17]. Membrane fouling has to

68   be managed by periodic caustic and acidic chemical cleaning, which in turn can compromise

69   the membrane properties temporary or permanently. It has been reported that caustic cleaning

70   may exert considerable impact on the rejection of some TrOCs by NF membranes [18]. Simon

71   et al., [18] suggested that caustic cleaning causes the swelling of the membrane polymer matrix

72   due to the increased electrostatic repulsion among the deprotonated carboxylic functional

73   groups in the polymer matrix, which was identified by zeta potential analysis. The swelling

74   effect caused by caustic cleaning ultimately results in an enlargement of membrane pore

75   structure and an increase in solute and solution permeation. However, in comparison to

76   membrane fouling, studies focusing on the impact of chemical cleaning on TrOC rejection

77   remain very limited [19]. Since fouling and subsequent cleaning (particularly caustic cleaning)

78   to restore the water flux are inevitable in most if not all membrane filtration processes, it is

79   essential to understand the impact of chemical cleaning on TrOC rejection. Thus, the aim of

80   this study was to provide further insights to the rejection mechanisms of TrOCs by an NF

81   membrane, allowing for an estimation of TrOC removal by chemically cleaned NF

82   membranes. By examining the role of molecular properties and the impact of caustic cleaning

83   on their rejection, the separation mechanisms of TrOCs by an NF membrane were assessed.

2. Materials and methods

2.1. NF membranes and laboratory-scale NF filtration system

86   Flat sheet NF270 membrane samples were obtained from Dow Chemical (Midland, Michigan,

87   USA). The NF270 is a polyamide-based thin-film composite NF membrane which can be

88   used for potable water purification and water reuse applications. A laboratory-scale NF

89   filtration system was used in this study (**Figure 1**). The system is comprised of four main

90   components: a stainless steel cross-flow membrane cell with a channel height of 2 mm, a

91   stainless steel reservoir, a temperature control unit (Neslab RTE 7, Thermo Scientific Inc.,

92   USA), and a high pressure pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN,

93   USA). The stainless steel membrane cell can hold one flat sheet membrane sample with an

94   effective membrane surface area of 40 cm^2 (4 cm $\times$ 10 cm). The temperature control unit

95   regulates the feed solution temperature through a stainless steel heat exchanging coil. The

96   filtration system is also equipped with several instruments (i.e., pressure gauges and flow

97   meter) including a digital flow meter (FlowCal, GJC Instruments Ltd., UK) measuring the

98   permeate flow rate.

99
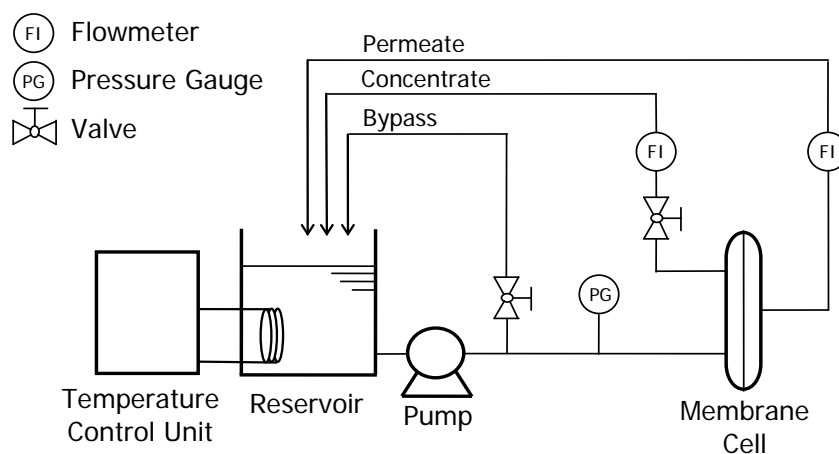
100   **Figure 1:** Schematic diagram of the cross flow NF filtration system.

2.2. Chemicals

A suite of 34 TrOCs was selected for investigation. These organic chemicals were from Sigma-Aldrich (St Louis, MO, USA) and were of analytical grade. They represent major groups of TrOCs that are frequently detected in municipal wastewater, reclaimed water, and to a lesser extent surface water [9]. These chemicals also cover a wide range of physicochemical properties such as molecular size, charge, and hydrophobicity (**Table 1**), which allows a comprehensive evaluation on solute transport through membranes. TrOCs ionised less than 50% at pH 8 were classified as "neutral" chemicals, while chemicals with more than 50% ionisation at pH 8 were classified as "charged" chemicals (**Table 1**). Neutral TrOCs were further categorised into two groups: hydrophilic ($\log D < 2$) and hydrophobic ($\log D \geq 2$) [11, 20]. In this study, Log D represents the logarithm of the apparent (or effective) water-octanol distribution coefficients (D) at pH 8. Charged TrOCs were also classified into negative and positive charge categories. The minimum projection area (MPA), which was calculated based on the van der Waals radius, summarised in Table 1 represents the minimum projected circular area of the chemical as described in **Figure 2**.

A stock solution containing 10 mg/L of each of the selected TrOCs was prepared in methanol. Deuterated analogues of each TrOC were obtained from CDN isotopes (Pointe-Claire, Quebec, Canada) and used as surrogate standards to account for matrix effects and incomplete recoveries during sample preparation and analysis of TrOCs. A surrogate stock solution containing contained 50 µg/L of each deuterated TrOC was also prepared in methanol. Both stock solutions were kept in the dark at -18 ℃. Analytical grade NaCl, CaCl$_2$ and NaHCO$_3$ were purchased from Ajax Finechem (Australia) and were used to prepare the synthetic feed solutions.

Table 1: Physicochemical characteristics of the selected 34 TrOCs.

Compound			Molecular weight [Da]	Log D at pH 8[a]	pKa (pKb)[a]	Ionisation at pH 8[a] [%]	MPA[a] [Å²]	MDL[b] [ng/L]
	Hydrophilic	Paracetamol	151.2	0.91	9.5	3	21.8	5
		Caffeine	194.2	-0.55	(0.9)	0	30.0	10
		Simazine	201.7	1.78	(3.2)	0	35.8	5
		Atrazine	215.7	1.32	(3.2)	0	39.0	5
		Primidone	218.3	1.12	11.5	0	42.7	5
		Meprobamate	218.3	0.93	15.2	0	45.8	5
		Triamterene	253.3	1.11	(1.9)	0	35.2	5
		Trimethoprim	290.3	1.28	(7.2)	12	51.1	5
Neutral	Hydrophobic	N,N-Diethyl-meta-toluamide (DEET)	191.3	2.50	(0.1)	0	40.1	5
		Bisphenol A	228.3	4.04	9.8; 10.4	2	44.0	20
		Diuron	233.1	2.53	13.2	0	28.6	10
		Carbamazepine	236.3	2.77	16.0	0	38.8	5
		Linuron	249.1	2.68	12.0	0	30.8	5
		Dilantin	252.3	2.18	9.5	3	47.3	5
		Diazepam	284.7	3.08	(2.9)	0	47.8	5
		Tris(2-chloroethyl)phosphate (TCEP)	285.5	1.96	n.a.	0	49.9	10
		Diazinon	304.4	4.25	(4.2)	0	50.7	5
		Triclocarban	315.6	4.93	11.4	0	50.1	10
		Clozapine	326.3	3.40	(3.9; 7.8)	36	55.5	5
		Omeprazole	345.4	2.43	(4.8); 9.3	2	43.5	5
		Hydroxyzine	374.9	3.24	(2.1; 7.8)	40	64.7	5
Charged	(-)	Ibuprofen	206.3	0.97	4.9	100	35.4	5
		Naproxen	230.3	-0.16	4.2	100	34.8	5
		Gemfibrozil	250.3	1.33	4.4	100	43.4	5
		Sulfamethoxazole	253.3	0.39	6.2	99	45.2	5
		Ketoprofen	254.3	0.48	3.9	100	41.7	5
		Triclosan	289.5	4.57	7.7	68	38.5	5
		Diclofenac	296.1	1.16	4.0	100	43.3	5
		Enalapril	376.5	-0.91	3.7; (5.2)	100	60.0	5
		Simvastatin hydroxy acid	436.6	0.63	4.2	100	65.1	5
	(+)	Atenolol	266.3	-1.18	(9.7)	98	36.9	5
		Amitriptyline	277.4	3.02	(9.8)	98	58.2	5
		Fluoxetine	309.3	2.46	(9.8)	98	44.3	5
		Verapamil	454.6	3.44	(9.7)	98	81.2	5

126   [a] Chemaxon (http://www.chemicalize.org/).
127   [b] MDL: method detection limit

128
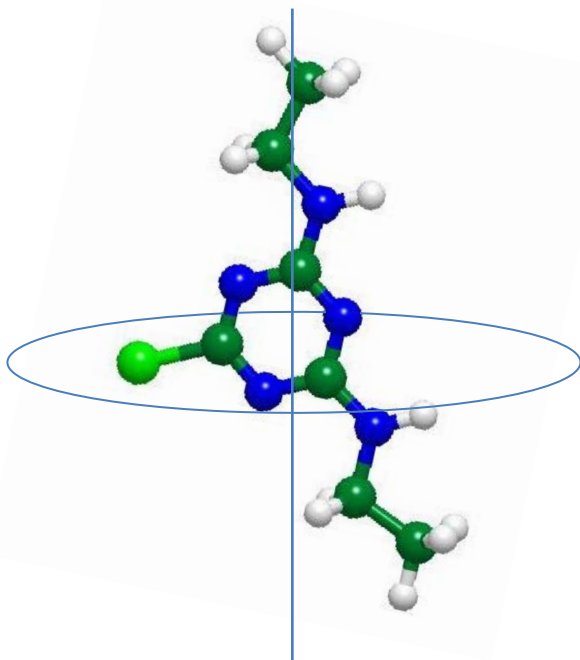
Figure 2: Conceptual figure of minimum projection area. The line perpendicular to the circular disk represents the centre axis of the minimum projection area.

2.3. Filtration protocols

The NF filtration system (Section 2.1) was first operated using Milli-Q water at a constant pressure (i.e., 1,000 kPa) to stabilise permeate flux. The cross flow velocity and solution temperature were adjusted at 0.43 m/s and 20.0±0.1 °C, respectively. Thereafter, electrolytes were added to condition the feed solution with the concentrations of 20 mM NaCl, 1 mM CaCl$_2$ and 1 mM NaHCO$_3$. The stock solutions of TrOCs were also dosed into the feed solution to obtain approximately 500 ng/L of each chemical which was determined based on their concentrations detected in treated wastewater. The pH of the feed solution was adjusted to 8. The permeate flux was set at 42 L/m^{2}h by adjusting the feed pressure of the filtration system. The system was continuously operated for 20 hours, which was followed by collecting 500 mL of the permeate and the feed samples for analysis.

Compound rejection (R) was calculated using $R\ [\%] = \left(1 - \dfrac{C_p}{C_f}\right) \times 100$, where C_p and C_f are measured concentrations in the permeate and feed solutions, respectively. When TrOC

7

144 concentrations in the permeate were detected at below their detection limits, the analytical
145 detection limit was used for the (minimum) rejection calculation.

2.4. Simulated caustic cleaning protocols

147 Simulation of caustic cleaning was performed by immersing membrane samples in a test
148 solution. The cleaning solution was adjusted to pH 11 or 12 by adding a small volume of 1M
149 NaOH solution to Milli-Q water. Prior to the simulated cleanings, flat sheet membrane
150 samples were rinsed with Milli-Q water to remove preservatives from the membrane surface.
151 A membrane sample for each experiment was stored in a 200 mL glass bottle filled with
152 cleaning solution. The bottle was immersed in a water bath (SWB1, Stuart®, Staffordshire,
153 UK) at 30.0±0.3 ℃ for 25 hours. The 25-hour cleaning period was determined based on
154 typical chemical cleaning frequency and cleaning conditions – twice a year and 4 hour
155 cleaning period for each cleaning event [21] – which accounts for the cumulative chemical
156 cleaning period of approximately 3 years filtration system operation. Due to the absence of a
157 fouling layer, this simulated caustic cleaning procedure could significantly overestimate the
158 effect of chemical cleaning. Nevertheless, the evaluation using the experimental protocol
159 described above allowed systematic evaluation of the cleaning effects on TrOC rejections.
160 After chemical cleaning simulation, the membranes were rinsed with Milli-Q water to
161 eliminate residual cleaning solution. These membranes were stored in Milli-Q water at 4 ℃
162 until being used for the following filtration experiments.

2.5. Analytical techniques

164 TrOC concentrations in the feed and permeate samples were determined using an analytical
165 method previously reported by Tadkaew et al. [22] The deuterated surrogate stock solution was
166 added to each sample (500 mL) to obtain 50 ng/L of each surrogate compound. The aqueous
167 samples were then extracted using 6cc Oasis HLB solid phase extraction (SPE) cartridges
168 (Waters, Milford, MA, USA). The SPE cartridges were eluted and the eluents were
169 transferred into acetonitrile for subsequent quantification using an Agilent 1200 series HPLC
170 system (Palo Alto, CA, USA) coupled with an API 4000 triple quadrupole mass spectrometer
171 (Applied Biosystems, Foster City, CA, USA).

172   The pH, electrical conductivity and temperature of permeate and feed solutions were
173   measured by an Orion 4-Star Plus pH/conductivity meter (Thermo Fisher Scientific, Waltham,
174   MA, USA).

3.   Results and discussion

3.1. TrOC rejection

177   The rejection of neutral TrOCs increased as molecular weight increased (**Figure 3**). It is also
178   notable that several hydrophobic and neutral TrOCs (e.g. bisphenol A, diuron, and linuron)
179   exhibited considerably lower rejections compared to the hydrophilic and neutral TrOCs with
180   equivalent molecular weights. All charged TrOCs investigated were highly rejected (>80%)
181   by the NF270 membrane (**Figure 3**). Nevertheless, it is discernible that three positively
182   charged TrOCs (i.e., atenolol, amitriptyline, and fluoxetine) had lower rejections than
183   negatively charged TrOCs with equivalent molecular weights. Verapamil is the only
184   positively charged TrOC that had comparable rejection (>97%) to the negatively charged
185   compounds and this can be attributed to its large molecular weight (454.6 g/mol). These
186   results suggest that the rejection of positively charged TrOCs is not governed by electrostatic
187   repulsion.

188   It is noteworthy that Triclocarban (log D = 4.93) and triclosan (log D = 4.57) were excluded
189   from **Figure 3**. They are the most hydrophobic compound, respectively, among the neutral
190   and negatively charged TrOCs investigated in this study. The concentration of Triclocarban
191   in the feed after 20 hours filtration decreased to below the detection limit (10 ng/L) in all
192   experiments. Similarly, the concentration of triclosan in the feed also decreased to less than
193   40 ng/L after 20 hours filtration. The decrease in feed concentration of these two TrOCs can
194   be attributed to their adsorption onto the membrane due to hydrophobic interaction. The
195   adsorption of hydrophobic TrOCs onto polyamide NF/RO membranes have also been
196   reported in several previous studies [14, 23].

197   Although the rejection of neutral TrOCs did increase as their molecular weight increased, the
198   data are quite scattered. In an early study, Meireles et al., [24] investigated the rejection of
199   several organic solutes (i.e., dextrans, proteins, and polyethylene glycol) by ultrafiltration and
200   microfiltration membranes and suggested that the hydrodynamic volume of these organic
201   solutes rather than molecular weight should be used to characterise their rejection. In their

202 study [24], the hydrodynamic volume parameter is the product between molecular weight and
203 intrinsic viscosity of the solute. It is noteworthy that the intrinsic viscosity of TrOCs may not
204 be readily available. More importantly, Meireles et al., [24] did not account for the 3
205 dimensional nature of the solute and thus their findings are only valid for microporous
206 membranes (i.e. ultrafiltration and microfiltration). As can be seen in **Figure 4**, results
207 reported here show that the minimum projection area is a better surrogate parameter to assess
208 the rejection of neutral TrOCs by the NF270 membrane in comparison to molecular weight.
209 The correlation between minimum projection area and the rejection of neutral TrOCs by the
210 NF270 membrane was generally consistent with that by another NF membrane (NF90,
211 Dow/Filmtec) that was reported in a previous study [25]. However, data presented in **Figure 4**
212 also show three exceptions (or outliners) including bisphenol A, caffeine, and TCEP, and
213 their rejection values do not follow the other neutral compounds investigated here.
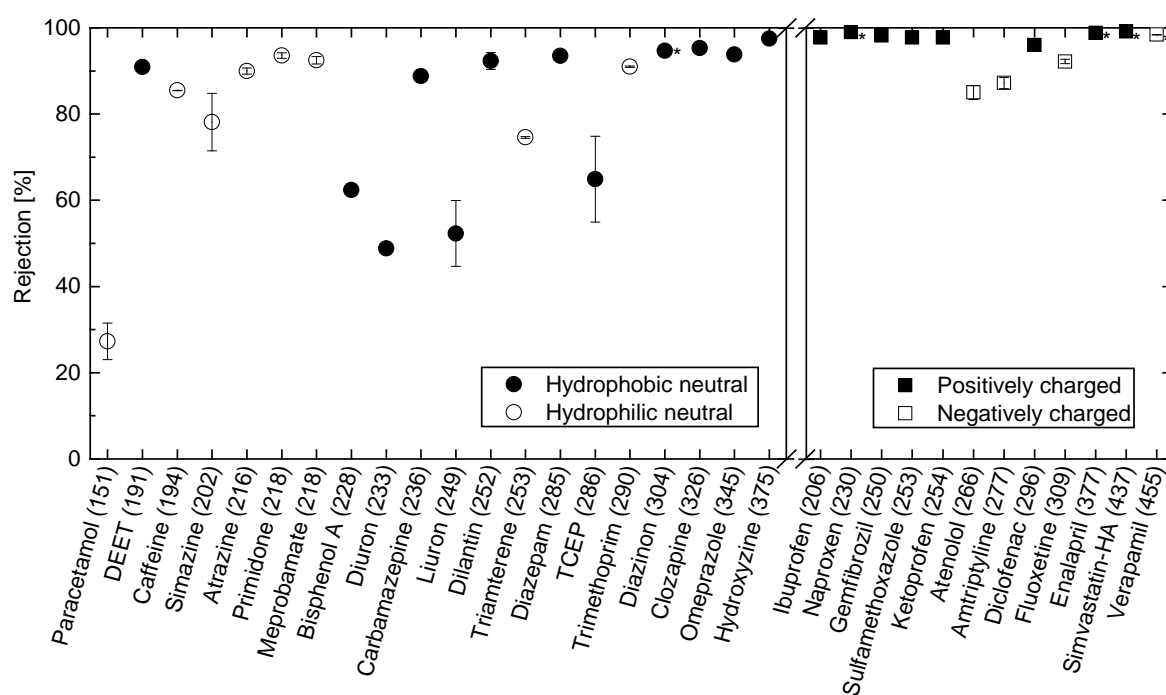
214
215 **Figure 3:** Rejection of TrOCs by a virgin NF270 membrane (20 mM NaCl, 1 mM NaHCO$_3$,
216 1 mM CaCl$_2$, permeate flux 42 L/m^{2}h, feed pH 8.0 ± 0.1, feed temperature $20.0 \pm 0.1°C$). The
217 molecular weight (Da) is shown in the parentheses. Values reported here are the average and
218 ranges of duplicate experiments. The symbol with asterisk (*) indicates that the rejection was
219 calculated based on the detection limit of TrOC in the permeate. Values reported here are the
220 average and ranges of duplicate samples.

10

221 Bisphenol A (log D = 4.0; MPA = 44 Å^2) that showed a lower rejection than the other
222 compounds with equivalent minimum projection areas (**Figure 4**). The rejection of bisphenol
223 A (62%) by the NF270 membrane was much lower than that of omeprazole (94%; log D =
224 2.4; MPA = 44 Å^2). Although bisphenol A is the third most hydrophobic compound among
225 the selected neutral TrOCs, the degree of hydrophobic property is not the only factor
226 explaining its low rejection. In fact, the other hydrophobic and neutral TrOCs including
227 diazinon (log D = 4.3; MPA = 51 Å^2) generally fitted well with the correlation between
228 minimum projection area and rejection (**Figure 4**). There can possibly be mechanisms other
229 than electrostatic, steric and hydrophobic interactions that govern the separation of TrOCs by
230 NF membrane. It is interesting to note that one of the three exceptions involved a hydrophilic
231 and neutral TrOC (i.e., caffeine). Caffeine (log D = -0.6; MPA = 30 Å^2) – the most
232 hydrophilic compound among the selected TrOCs – exhibited a higher rejection than the
233 other neutral TrOCs with equivalent minimum projection area values: diuron (log D = 2.5;
234 MPA = 29 Å^2) and linuron (log D = 2.7; MPA = 31 Å^2).

235
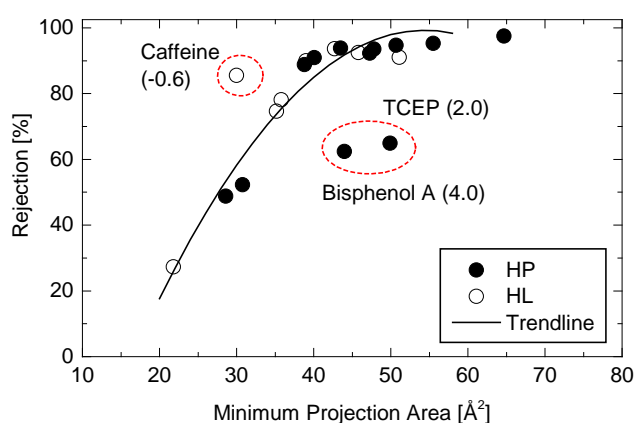
Figure 4: Rejection of neutral TrOCs by the NF270 membrane as a function of the
compound minimum projection area. Experimental conditions are described in Figure 3. The
rejection trendline of neutral TrOCs does not include caffeine, TCEP, and bisphenol A. The
Log D of these three TrOCs is shown in the parentheses.

240 The rejection of positively charged TrOCs generally followed the rejection trend line of
241 neutral TrOCs with an exception of amitriptyline that has a hydrophobic property (log D =
242 3.0) (**Figure 5**). The results suggest that the main mechanism of the rejection of positively
243 charged TrOCs is the size exclusion like neutral TrOCs. By contrast, the rejection of
244 negatively charged TrOCs was high and was independent of their MPA. The observed high
245 rejection of all negatively charged TrOCs can be attributed to the electrostatic repulsion

11

occurred between these negatively charged TrOCs and the negatively charged NF270
membrane surface (zeta potential = –14 mV at pH 8 [18]).
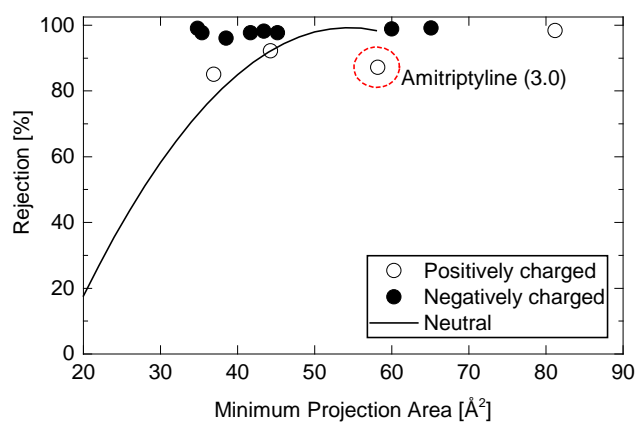
Figure 5: Rejection of charged TrOCs by the NF270 membrane as a function of the
compound minimum projection area. Experimental conditions are described in Figure 3. The
line "Neutral" is the rejection trendline of neutral TrOCs described in Figure 4. The Log *D* of
Amitriptyline is shown in the parentheses.

3.2. Effects caustic cleaning on permeability and conductivity rejection

Table 1: NF membranes used in this study.

Name	Permeability[a] [L/m^{2}hbar]	Conductivity rejection[b] [%]
NF270 Virgin	15.3	38
NF270 cleaned with pH 11	18.2	22
NF270 cleaned with pH 12	23.6	18

[a] Determined with Milli-Q water at 1000 kPa and 20 °C feed temperature. Values reported
here are the average of duplicate experiments.
[b] Determined with feed solution containing 20 mM NaCl, 1 mM NaHCO$_3$, 1 mM CaCl$_2$, at
permeate flux 20 L/m^{2}h, feed pH 8.0 ± 0.1 and feed temperature 20.0 ± 0.1°C.

Permeability of the NF270 membrane increased by 19% and 54% after caustic cleaning with
pH 11 and pH 12 solutions, respectively (**Table 1**). In response to changes in permeability,
conductivity rejection at the permeate flux of 20 L/m^{2}h decreased from 38% down to 18%.
This observation is consistent with findings reported in several previous studies [21, 26, 27] in
which NF and RO membranes were exposed to various caustic commercial cleaning reagents.
Caustic cleaning did not result in any significant changes in the membrane surface charge
(data not shown). Simulated caustic cleaning on polyamide-based membranes with a soaking
period of less than 25 hours does not cause a significant change in surface property (e.g. zeta
potential and surface chemistry) but the change in membrane performance can be reversed

12

268 with acidic cleaning according to previous studies [18, 21]; thus, the observed variation in
269 membrane performance after simulated caustic cleaning is expected to be temporary.

270 *3.3. Effects of caustic cleaning on neutral TrOC rejection*

271 Caustic cleaning led to a notable decrease in the rejection of neutral TrOCs (**Figure 6**). For
272 example, paracetamol rejection decreased from 27% to 11 and 18% after exposing the NF270
273 membrane to pH 11 and pH 12 caustic solutions, respectively. Simon et al. [18] hypothesized
274 that NF membrane pores could be enlarged in caustic solutions due to electrostatic repulsion
275 between the deprotonated carboxylic functional groups on the pore walls of the active skin
276 layer at high pH. The impact of caustic cleaning on the rejections of neutral TrOCs was more
277 severe as the cleaning solution pH increased and was more apparent with compounds that
278 exhibited low or moderate rejection by virgin membranes (**Figure 6**).
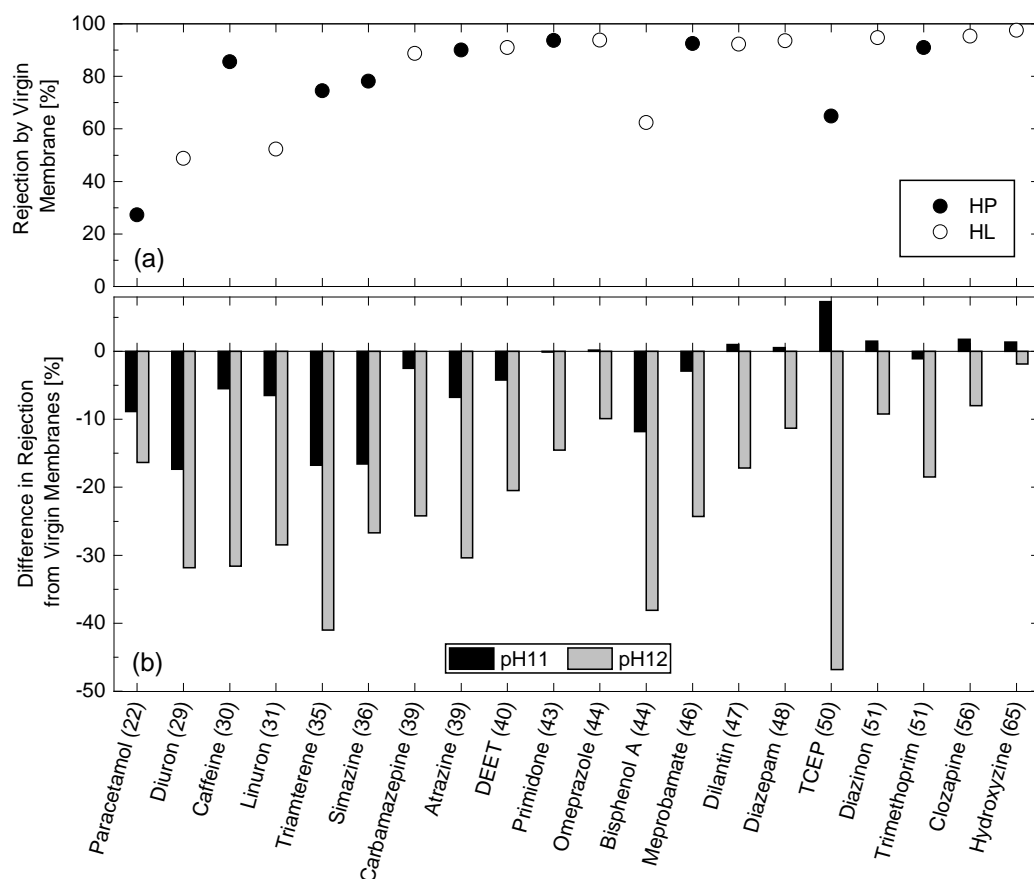
279

280 **Figure 6:** (a) Rejection of neutral and hydrophobic (HP) and hydrophilic (HL) TrOCs by the
281 virgin NF270 membrane, and (b) differences in rejection after being exposed to pH 11 and
282 pH 12 solutions for 25 h at 30 °C. Experimental conditions are described in Figure 3. The
283 minimum projection area (Å^2) is shown in the parentheses.

Minimum projection area also allows for a better assessment of the impact of operating condition variation on TrOC rejections by the NF270 membrane. The strong correlation between minimum projection area of neutral TrOCs and their rejections could still be observed after caustic cleaning (**Figure 7b&c**). Once again, there were three outline TrOCs (i.e., caffeine, bisphenol A, and TCEP) as previously discussed in section 3.1. However, a similar conclusion can be made for these compounds. For example, as can be seen in **Figure 7**, caffeine rejection by the NF270 membrane decreased from 86% (virgin condition) to 54% (immediately after caustic chemical cleaning at pH 12).
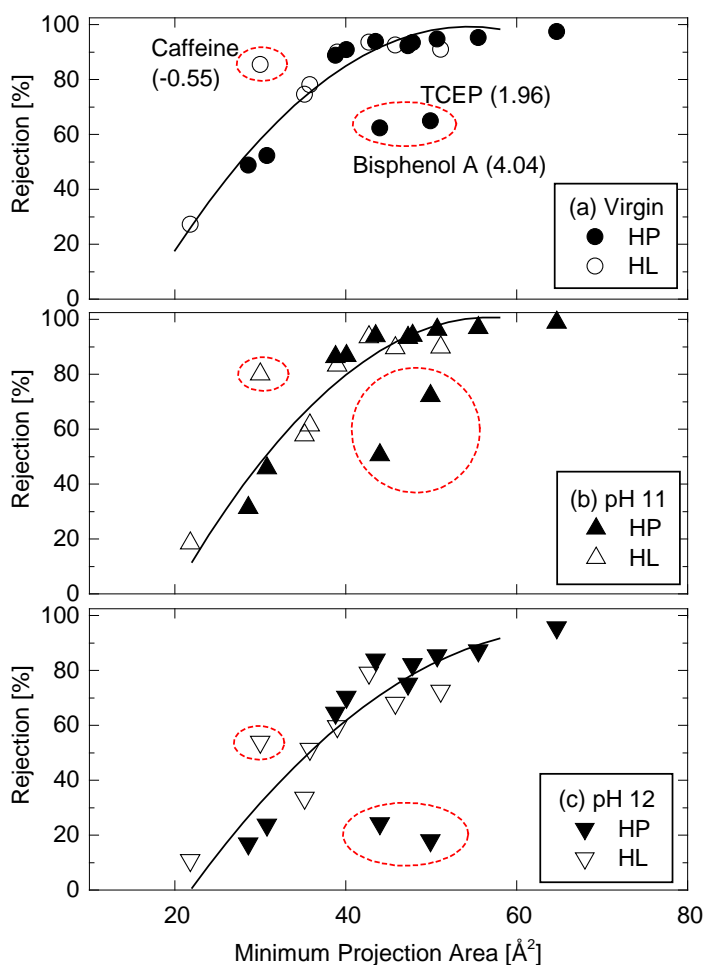
Figure 7: Rejection of neutral and hydrophobic (HP) and hydrophilic (HL) TrOCs by (a) the virgin NF270 membrane, and the NF 270 membranes after being exposed to (b) pH 11 and (c) pH 12 caustic solutions as a function of their minimum projection area. Experimental conditions are described in Figure 3. The rejection trendline of neutral TrOCs does not include caffeine, TCEP, and bisphenol A. The Log D of these three TrOCs is shown in the parentheses.

14

3.4. Effects of caustic cleaning on charged TrOC rejection

300 Charged TrOCs were generally well rejected by the NF270 membrane. Moreover, the impact

301 of caustic cleaning on the rejection of negatively charged TrOCs was rather insignificant

302 (**Figure 8**). On the other hand, significant impacts of caustic cleaning was observed for the

303 rejections of atenolol which has the largest molecular weight among all positively charged

304 TrOCs investigated here. The rejections of atenolol decreased substantially from 85% (by

305 virgin membranes) to 76.4 and 47.8% (after caustic cleaning with pH 11 and 12, respectively).

306 The rejection of positively charged TrOCs increased with increasing minimum projection

307 area and was generally comparable to that of neutral TrOCs even after caustic cleaning was

308 applied (**Figure 9**), indicating that the rejection of positively charged TrOCs could be

309 predicted using minimum projection area regardless of the application of chemical cleaning.

310 By contrast, the rejection of negatively charged TrOCs remained unrelated with minimum

311 projection area.
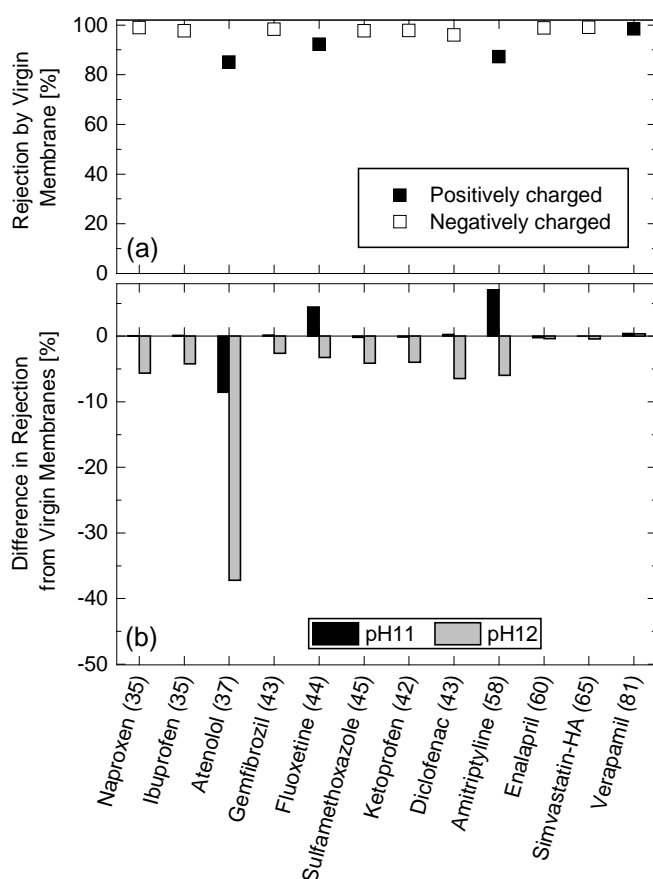
312

313 **Figure 8:** (a) Rejection of positively and negatively charged TrOCs by the virgin NF270
314 membrane, and (b) differences in rejection after being exposed to pH 11 and pH 12 solutions

15

for 25 h at 30 °C. Experimental conditions are described in Figure 3. The minimum projection area (Å^2) is shown in the parentheses.
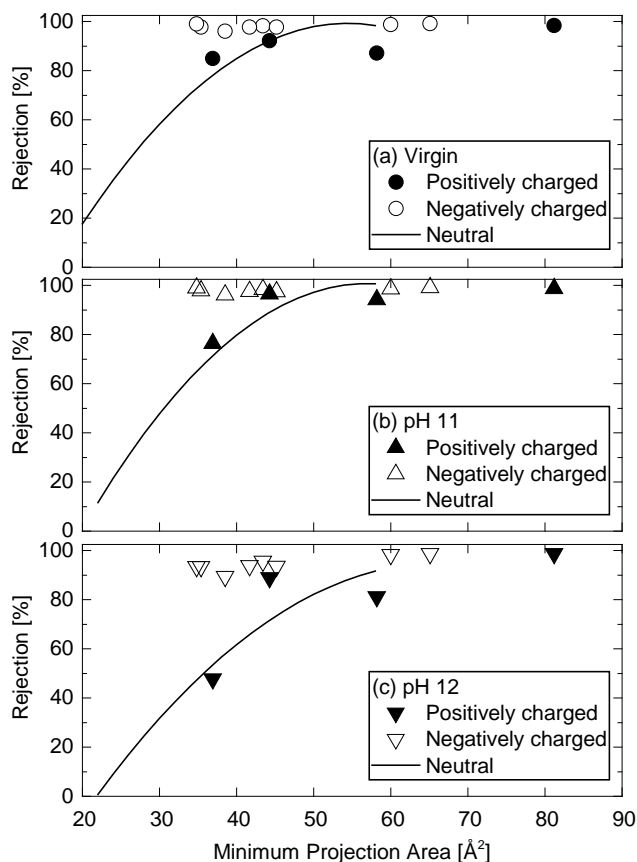
Figure 9: Rejection of Rejection of positively and negatively charged TrOCs by (a) the virgin NF270 membrane, and the NF 270 membranes after being exposed to (b) pH 11 and (c) pH 12 caustic solutions as a function of their minimum projection area. Experimental conditions are described in Figure 3. The rejection trendline of neutral TrOCs does not include caffeine, TCEP, and bisphenol A.

4. Conclusions

Results reported in this study provide further insights to the rejection mechanisms of TrOCs by the NF270 membrane. All charged TrOCs investigated in this study were highly rejected (>80%). However, the rejections of positively charged TrOCs were lower than those of negatively charged TrOCs with equivalent molecular sizes. These results suggest that an electrostatic repulsion between a negatively charged membrane and TrOCs was a major factor contributing to the high rejections of these negatively charged TrOCs. Our results show that the minimum projection area was a better surrogate parameter

16

for molecular dimension than molecular weight. The rejection of most neutral and positively charged TrOCs could potentially be expressed as a function of the minimum projection area. On the other hand, the rejection of negatively charged TrOCs was high and was independent of the minimum projection area. This study highlights the need to consider the rejection of neutral and positively charged TrOCs (particularly those that are moderately rejected by membranes) after caustic cleaning.

5. References

1. M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Marinas and A. M. Mayes, *Nature*, 2008, **452**, 301-310.

2. B. I. Escher, R. Baumgartner, M. Koller, K. Treyer, J. Lienert and C. S. McArdell, *Water Res.*, 2011, **45**, 75-92.

3. R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. von Gunten and B. Wehrli, *Science*, 2006, **313**, 1072-1077.

4. C. G. Pan, G. G. Ying, Y. S. Liu, Q. Q. Zhang, Z. F. Chen, F. J. Peng and G. Y. Huang, *Chemosphere*, 2014, **114**, 16-25.

5. G. G. Ying, J. L. Zhao, L. J. Zhou and S. Liu, *Journal*, 2013, **62**, 453-557.

6. WHO, *Pharmaceuticals in drinking-water*, World Health Organization, 2012.

7. B. J. Vanderford, J. E. Drewes, A. Eaton, Y. C. Guo, A. Haghani, C. Hoppe-Jones, M. P. Schluesener, S. A. Snyder, T. Ternes and C. J. Wood, *Anal. Chem.*, 2014, **86**, 774-782.

8. T. A. Ternes, A. Joss and H. Siegrist, *Environ. Sci. Technol.*, 2004, **38**, 392A-399A.

9. Y. Luo, W. Guo, H. H. Ngo, L. D. Nghiem, F. I. Hai, J. Zhang, S. Liang and X. C. Wang, *Sci. Total Environ.*, 2014, **473-474**, 619-641.

10. B. Van der Bruggen and C. Vandecasteele, *Environ. Pollut.*, 2003, **122**, 435-445.

11. C. Bellona, J. E. Drewes, P. Xu and G. Amy, *Water Res.*, 2004, **38**, 2795-2809.

12. A. R. D. Verliefde, E. R. Cornelissen, S. G. J. Heijman, J. Q. J. C. Verberk, G. L. Amy, B. Van der Bruggen and J. C. van Dijk, *J. Membr. Sci.*, 2008, **322**, 52-66.

13. K. Kimura, G. Amy, J. Drewes and Y. Watanabe, *J. Membr. Sci.*, 2003, **221**, 89-101.

14. Y. Kiso, Y. Sugiura, T. Kitao and K. Nishimura, *J. Membr. Sci.*, 2001, **192**, 1-10.

15. A. R. D. Verliefde, E. R. Cornelissen, S. G. J. Heijman, I. Petrinic, T. Luxbacher, G. L. Amy, B. Van der Bruggen and J. C. van Dijk, *J. Membr. Sci.*, 2009, **330**, 90-103.

362   16.   C. Bellona, M. Marts and J. E. Drewes, *Sep. Purif. Technol.*, 2010, **74**, 44-54.

363   17.   P. Xu, J. E. Drewes, T.-U. Kim, C. Bellona and G. Amy, *J. Membr. Sci.*, 2006, **279**,
364   165-175.

365   18.   A. Simon, W. E. Price and L. D. Nghiem, *J. Membr. Sci.*, 2013, **432**, 73-82.

366   19.   N. Porcelli and S. Judd, *Water Res.*, 2010, **44**, 1389-1398.

367   20.   B. Van der Bruggen, A. Verliefde, L. Braeken, E. R. Cornelissen, K. Moons, J. Q. J.
368   C. Verberk, H. J. C. van Dijk and G. Amy, *J. Chem. Technol. Biotechnol.*, 2006, **81**,
369   1166-1176.

370   21.   T. Fujioka, S. J. Khan, J. A. McDonald, A. Roux, Y. Poussade, J. E. Drewes and L. D.
371   Nghiem, *Desalination*, 2014, **343**, 60-66.

372   22.   N. Tadkaew, F. I. Hai, J. A. McDonald, S. J. Khan and L. D. Nghiem, *Water Res.*,
373   2011, **45**, 2439-2451.

374   23.   V. Yangali-Quintanilla, A. Verliefde, T. U. Kim, A. Sadmani, M. Kennedy and G.
375   Amy, *J. Membr. Sci.*, 2009, **342**, 251-262.

376   24.   M. Meireles, A. Bessieres, I. Rogissart, P. Aimar and V. Sanchez, *J. Membr. Sci.*,
377   1995, **103**, 105-115.

378   25.   T. Fujioka, S. J. Khan, J. A. McDonald and L. D. Nghiem, *Sep. Purif. Technol.*, 2014,
379   **136**, 258-264.

380   26.   R. Liikanen, J. Yli-Kuivila and R. Laukkanen, *J. Membr. Sci.*, 2002, **195**, 265-276.

381   27.   S. Siavash Madaeni, T. Mohamamdi and M. Kazemi Moghadam, *Desalination*, 2001,
382   **134**, 77-82.