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Abstract

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Abstract

The rejection behaviours of 41 trace organic chemicals (TrOCs) by a hollow fibre cellulose triacetate (CTA) reverse osmosis (RO) membrane for potable water reuse were evaluated. Results reported here suggest that the rejection behaviours of TrOCs by the CTA RO membrane are mostly similar to those previously reported for polyamide (PA) RO membrane. However, in comparison to PA based RO membrane, hydrophobic interaction plays a greater role while electrostatic interaction is less significant in governing the rejection of TrOCs by the CTA RO membrane. No difference in rejection between positively and negatively charged compounds by the CTA RO membrane could be observed. The rejection of neutral TrOCs by the CTA RO membrane varied significantly from 25% to over 95%. Molecular size (i.e. minimum projection area) was found to be an important factor governing the rejection of neutral TrOCs. Further investigation using N-nitrosamines reveals that in addition to molecular size, hydrophobicity could significantly influence their rejection by the CTA RO membrane, while N-nitrosamine rejection by PA RO membrane was mostly governed by molecular size. In contrast to the neutral TrOCs, most charged TrOCs selected in this investigation exhibited over 90% rejection, regardless of molecular size.

Keywords: Potable water reuse, trace organic chemicals, N-nitrosamines, reverse osmosis, cellulose triacetate membrane.

1. Introduction

Wastewater reclamation for potable reuse is an important practice to enhance the security of water supplies in many arid or densely populated areas [1]. This practice is in contrast to the conventional approach whereby potable water is to be sourced from a protected natural water body. Thus, potable water reuse is commonly subjected to very stringent treatment requirements to achieve satisfactory removal of a diverse range of contaminants known to occur in raw and conventionally treated wastewater. These include many trace organic chemicals (TrOCs) that may cause chronic health impacts to the public.

In a growing number of modern water reclamation plants, the removal of TrOCs is achieved mostly by the reverse osmosis (RO) filtration process. In fact, RO membrane has been recognised as reliable barrier for removing most TrOCs that may occur in secondary treated effluent [2]. Most, if not all, of these water reclamation plants use polyamide (PA) or PA-derivative RO membranes that can offer high permeate flux and adequate salt rejection [3]. However, PA RO membranes are not chemically resilient to strong oxidising agents such as free chlorine which has a high potential of controlling biofouling. For example, PA RO membrane can be degraded by chlorine [4, 5]. All PA RO membrane manufacturers have specified a chlorine limit of about 200 – 1,000 mg/L-hours. As a result, monochloramine which is a less powerful oxidant than chlorine in terms of disinfection performance is used to control biofouling. Thus, their applications to feed solution with a high fouling potential may entail undesirable complications. Moreover, depending on the system configuration, N-nitrosodimethylamine (NDMA) and other N-nitrosamines, which are an important group of disinfection by-products, can be formed during the formation of chloramines from chlorine [6]. At several full-scale water reclamation plants using RO, the concentrations of NDMA in the RO permeate were detected at concentrations higher than value (e.g. 10 ng/L) regulated or recommended by health authorities, leading to the installation of advanced oxidation post treatment for further NDMA removal [6, 7]. It is also noteworthy that NDMA rejections by PA RO membranes reported from pilot- and full-scale RO systems were low and variable in the range from 10% to 60% [6-10]. In this instance, chlorine resistant membranes would allow for the use of chlorine to control biofouling with significantly less NDMA formation [11].

In recent years, cellulose acetate (CA) and cellulose triacetate (CTA) have re-emerged as an attractive material to fabricate RO membranes especially for feed water with high

fouling potential. In comparison to CTA RO membranes, PA membranes usually have high permeability and can be operated in a much wider pH range [12]. Nevertheless, CTA RO membranes are chlorine-resistant and thus residual chlorine can be maintained at up to 1 mg/L in the RO feed [13]. In fact, the CTA RO filtration in combination with chlorination can suppress biological growth on RO membrane surfaces and prevent an increase in feed pressure caused by membrane fouling in seawater desalination applications [14-17]. Thus, RO filtration using CTA RO membranes potentially has an advantage over PA-based thin-film composite RO membranes with respect to the control of biofouling and N-nitrosamine formation during water treatment. Despite its potential, knowledge regarding the rejection of TrOCs by CTA RO membranes remains scarce. There have only been a few studies on the rejection of TrOCs by CA [18, 19] and CTA [20] membranes. Only six TrOCs were investigated in these studies and the experiments were conducted using small flat sheet membrane samples. Given the need for chlorine resistant RO membranes, CTA based membranes are expected to play a greater role in water recycling applications. Thus, a comprehensive understanding of TrOC rejection by CTA RO membranes is essential for their application for potable water reuse.

The aim of this work was to assess the rejection behaviour of TrOCs by a CTA RO membrane. The rejection of a range of TrOCs by a hollow fibre CTA RO membrane was examined using a laboratory-scale RO filtration unit. The study also aimed to elucidate physicochemical properties of these compounds governing their rejection by the CTA RO membrane. The rejection results obtained here were directly compared with those observed for a PA RO membrane.

2. Materials and methods

2.1. RO membrane and Bench-scale filtration system

A cellulose triacetate hollow fibre RO membrane module for brackish water desalination (HKC3023V) supplied by Toyobo Co., Ltd. (Osaka, Japan) was used in this investigation. The hollow fibres were operated in an outside-in configuration and were bundled inside the module with a horseshoe shape (Figure 1a). Each hollow fibre was about 1 m in length, with outer and inner diameters of 165 μm and 70 μm , respectively. Because of the very small fibre diameter, the contact angle and zeta potential of this membrane could be measured. However, it can be inferred from measurement using a flat sheet CTA material [21] that this hollow fibre membrane is hydrophilic and only slightly negatively charged.

The module housing was made of a polyvinyl chloride pipe reinforced specially by steel rings. According to the manufacturer, the applied feed pressure of this module should not exceed 1.1 MPa. The HKC3023V membrane module has a total outer surface area of 22 m². According to the manufacturer, the nominal NaCl rejection of this membrane evaluated under test operating conditions (500 mg/L NaCl, feed pressure = 0.5 MPa, feed temperature = 25.0 °C, and recovery = 30%) is 94% (feed salinity basis). Pure water permeability of the CTA membrane determined using Milli-Q water at 1.0 MPa was 0.38 L/m²hbar.

A laboratory-scale cross flow RO filtration system was used in this study (Figure 1b). The filtration system comprises a stainless steel reservoir with a 12 L solution capacity, high pressure pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN, USA) and membrane module. Permeate and cross flow rates were monitored using variable area flow meters. These flow rates were adjusted using a back pressure regulating valve and bypass valve. Feed temperature was controlled by a temperature control unit (Neslab RTE 7, Thermo Scientific Inc., Waltham, MA, USA) which is connected to a stainless steel heat exchanger coil.

[Figure 1]

2.2. Chemicals

A set of 41 organic chemicals was selected to represent major TrOC groups that occur widely in treated wastewater effluent. They include pharmaceutically active compounds, steroid hormones, industrial chemicals, pesticides and N-nitrosamines (Table 1). All chemicals were of analytical grade and were obtained from Sigma-Aldrich (Castle Hill, NSW, Australia). These TrOCs were categorised into four categories depending on their physiochemical properties: neutral hydrophilic (Log *D* < 2), neutral hydrophobic (Log *D* ≥ 2), and negatively and positively charged compounds (Table 1) [22, 23]. The Log *D* value is the logarithm of the apparent distribution coefficient (*D*) which represents hydrophobic properties at an ambient pH, accounting for ionisation. Charged compounds classified here were compounds that are dissociated by over 50% in pH 8 solution (Supplementary Material Table S1). Minimum projection area (Table 1) is two dimensional area of the conformer projected with the minimum plane of its circular disk. Minimum projection area can be calculated based on the Van der Waals radius and can be described as the area of

the surrounded circle in **Figure 2**. Among three parameters describing the size of molecules (i.e. molecular weight, molecular volume and minimum projection area), minimum projection area was expected to be most correlated with the retention of compounds, assuming the passage of solutes (e.g. free-volume hole) within the RO membrane has a circular shape. Minimum projection area has not been used in any previous literature for the investigation of the correlation between compound size and their rejections. An analyte stock solution of N-nitrosamines was prepared in methanol at 10 mg/L. All other TrOCs were included in a second analyte stock solution prepared in pure methanol at 10 mg/L of each compound. An internal standard stock solution of deuterated N-nitrosamines was prepared in pure methanol for isotope dilution during the analysis. Similarly, a second internal standard stock solution containing deuterated isotopes of all other TrOCs was also prepared in pure methanol. All deuterated compounds were from CDN isotopes (Pointe-Claire, Quebec, Canada). The analyte and internal standards stock solutions were kept at -18 °C in the dark and were used within 1 month of preparation. Analytical grade NaCl, CaCl₂ and NaHCO₃ were obtained from Ajax Finechem (Taren Point, NSW, Australia) and used as the background electrolytes during the filtration experiments.

[Table 1]

[Figure 2]

2.3. Experimental protocols

The experiment started with a stabilisation step where the filtration system was operated with Milli-Q water at 1000 kPa for three hours. The system water recovery and solution temperature were maintained at 25% and 20±0.1°C, respectively. Thereafter, the Milli-Q water in the feed was replaced with 13 L of a solution containing background electrolytes (20 mM NaCl, 1 mM CaCl₂ and 1 mM NaHCO₃). Unless otherwise stated, the standard pH of 8 was used. Feed pH was adjusted by dosing 1M HCl or 1M NaOH. The stock solution of N-nitrosamines was spiked into the feed reservoir to obtain 250 ng/L of each N-nitrosamine. The stock solution of the other compounds was also added to obtain 75 ng/L of each compound. The filtration system was then continuously operated at permeate flux of 3.1 L/m²h for 5 hours before the first **permeate and feed** samples were taken for analysis. **This was done in order to account for** any adsorption of chemicals to the membrane, which may occur predominantly during the initial period of filtration. Compound rejection was

147 calculated using $R [\%] = \left(1 - \frac{C_p}{C_f}\right) \times 100$, where C_p and C_f are measured concentrations of
148 the RO permeate and RO feed samples, respectively. The feed pressure and cross-flow
149 velocity during filtration were 950 kPa and 2.1-2.8 cm/s, respectively.

150 2.4. Analytical methods

151 N-nitrosamine concentrations were determined based on the analytical method previously
152 developed by McDonald et al. [24]. The analytical method includes solid phase extraction
153 (SPE) followed by gas chromatography and quantification using tandem mass
154 spectrometry and isotope dilution. Prior to SPE, the N-nitrosamine internal standard stock
155 solution was dosed into each sample (200 mL) to make up 50 ng/L of each internal
156 standard concentration. The SPE process was carried out using SupelcleanTM Coconut
157 Charcoal SPE cartridges (Supelco, St Louis, MO, USA). N-nitrosamines were quantified
158 using an Agilent 7890A gas chromatograph coupled with an Agilent 7000B triple
159 quadrupole mass spectrometer. The detection limits of N-nitrosamine concentrations using
160 this technique were 10 ng/L or lower.

161 All other TrOCs were determined using the method previously reported by Tadkaew et al.
162 [25]. The technique uses SPE followed by quantification by high performance liquid
163 chromatography (HPLC) – tandem mass spectrometry. Prior to SPE, 50 ng deuterated
164 internal standard of each TrOC was added to each 500 mL sample to account for any
165 variation in recovery during the sample preparation. Each sample was extracted to a 6 mL
166 Oasis HLB SPE cartridge (Waters, Milford, MA, USA). The concentration of TrOCs was
167 quantified using a HPLC system consisting of an Agilent 1200 series HPLC system (Palo
168 Alto, CA, USA) coupled with an API 4000 triple quadrupole mass spectrometer (Applied
169 Biosystems, Foster City, CA, USA). The detection limits of TrOC concentrations using
170 this analytical method were 20 ng/L or lower. Solution pH, electrical conductivity and
171 temperature were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo
172 Fisher Scientific, Waltham, MA, USA).

3. Results and discussion

3.1. Rejection of neutral TrOCs

A total of 11 neutral TrOCs investigated here are hydrophobic ($\log D \geq 2$), thus they can adsorb onto membranes during the initial stage of filtration, which might lead to overestimation of their rejections. As expected, the measured concentration of these TrOCs in the feed generally decreased as their hydrophobicity increased (Supplementary Material Figure S2). In general, compounds possessing Log D of over 2.5 exhibited very high adsorption (over 40% reduction in feed concentration). These results indicate that compound adsorption onto the CTA RO membrane can be strongly affected by their hydrophobicity. Concentrations of liuron and triclocarban in the feed solution were determined to be below their detection limits due to the adsorption effects, thus their rejections were excluded from further investigations conducted in this study. Permeate flux during 5 hours of filtration was stable and no evidence of membrane fouling was observed in this study.

In general, the rejection of neutral hydrophilic TrOCs by the CTA RO membrane increased with an increasing order of their molecular weight (Figure 3). The molecular weight cut-off, which refers to the molecular mass of a compound where the membrane have a rejection of greater than 90%, of the CTA RO membrane obtained from the rejection data of hydrophilic compounds (Figure 3a) was 220 Da. The results indicate that larger molecules are more likely to be well rejected by the CTA RO membranes. A similar trend was reported with PA RO membranes by Bellona et al [22]. Among the neutral hydrophilic TrOCs used in this investigation, the rejection of seven N-nitrosamines (MW 74-130 g/mol) was particularly low in the range from 25-78%. On the other hand, TrOCs possessing molecular weight over 190 g/mol exhibited high rejection values (over 90%) with simazine (82%) being the only exception. Similarly, the rejection of neutral hydrophobic compounds generally increased with an increasing order of their molecular weight (Figure 3). Hydrophobic compounds for which molecular weight was over 236 g/mol revealed rejections of over 95%. Notable exceptions include diuron (MW 233 g/mol) which revealed only 39% rejection, while the rejection of a similar molecular weight compound (carbamazepine, MW 236 g/mol) exhibited over 95% rejection (Figure 3). The results obtained here indicate that there can be compound properties other than

molecular weight that play an important role in determining compound rejection by a given membrane.

Further investigation was carried out by using the other physicochemical parameters of compounds (i.e. molecular volume and minimum projection area) (Figure 4). As a result, an improved correlation was observed between minimum projection area compared to molecular weight or volume of neutral TrOCs and their rejections (Figure 4). In particular, diuron, which has the lowest minimum projection area ($28.6 \text{ \AA}^2$) among the neutral hydrophobic TrOCs, also reasonably fit into the correlation (Figure 4c). Given that solutes diffuse within free-volume holes of RO membranes and solutes larger than the free-volume hole-size of RO membranes are unlikely to permeate through a membrane, it is reasonable that the rejection of solutes is governed by their minimum projection area. The results reported here suggest that the rejection of neutral TrOCs can be best predicted using their minimum projection area. Results from Figure 4 also show that the rejection of neutral hydrophobic TrOCs are lower than that of their neutral hydrophilic counterparts with the same molecular weight, volume or minimum projection area. A similar observation has been reported with PA RO membrane [26].

[Figure 3]

[Figure 4]

3.2. Rejection of charged TrOCs

Unlike neutral TrOCs, adsorption of charged TrOCs onto the CTA RO membrane was not observed, with the exception of triclosan (Supplementary Material Figure S3). Triclosan is a hydrophobic-ionogenic compound [27]. Therefore, despite possessing a negative charge, it is still highly hydrophobic ($\text{Log } D = 4.57$). As expected, triclosan concentration in the feed solution decreased to an undetectable level (i.e. $<5 \text{ ng/L}$) at the end of the filtration experiment, thus the rejection of triclosan was not calculated or reported.

The rejections of charged TrOCs selected here were commonly very high (over 90%) with the exception of paracetamol (Figure 5). Paracetamol (MW 151 g/mol) is the smallest molecular weight compound among the charged TrOCs selected in this investigation. No notable difference in rejection between positively and negatively charged TrOCs was observed (Figure 6). The results reported here indicate that the rejection of charged

compounds is high (i.e. over 90%) when the minimum projection area of the tested compounds are over 35 Å² (Figure 6), which is similar to the neutral TrOCs (i.e. 40 Å²) as observed in Figure 4. Although these charged TrOCs selected here has relatively higher molecular weight than the neutral TrOCs, this finding is noteworthy because the electrostatic repulsion which effective to charged TrOCs is expected to significantly enhance their rejection, as previously observed from the PA RO membranes [28]. The zeta potential of the CTA RO membrane used in this study could not be measured because of its very thin hollow fibre configuration. However, the zeta potential of flat sheet CTA membrane obtained from a previous study suggests that the CTA surface (i.e. zeta potential of -5 mV at pH 8) [21] has a significantly lower surface charge density than a PA surface (i.e. zeta potential of -25 to -10 mV at pH 8) [29, 30]. As a result, the role of electrostatic interaction in removing charged TrOCs by the CTA RO membrane is expected to be less significant compared to PA RO membranes.

[Figure 5]

[Figure 6]

3.3. Rejection of N-nitrosamines and inorganics by CTA and PA membranes

The rejection of N-nitrosamines by the CTA membrane was compared with that by a PA membrane that was previously reported in a pilot-scale study [31]. N-nitrosamines are the smallest compounds of all the neutral TrOCs selected in this study (Table 1), and thus their rejections by the CTA membrane were low (25-78%). The rejection of N-nitrosamines by the CTA RO membrane (i.e. HKC3023V, Toyobo) generally increased in the increasing order of their minimum projection area, but the two largest N-nitrosamines (i.e. NDPA and NDBA) exhibited low rejections (53% and 28%, respectively) (Figure 7a). In contrast, the effects of size exclusion for a given PA RO membrane (TFC-HR, Koch Membrane systems) can be identified by a good correlation between the minimum projection area of N-nitrosamines and their rejections (Figure 7a). The results indicate that the rejection of N-nitrosamines by the CTA RO membrane may be affected by molecular properties other than the minimum projection area.

Among compound physicochemical properties, Log *D* of N-nitrosamines exhibited a good correlation with the rejection of high molecular weight N-nitrosamines (i.e. NPYR, NDEA, NPIP, NMOR, NDPA and NDBA) (Figure 7b). Dipole moment of these compounds was

not correlated with their rejections (**data not shown**). High Log *D* N-nitrosamines (e.g. NDPA and NDBA) may adsorb more progressively onto the CTA RO membrane surface and the adsorbed N-nitrosamines may subsequently diffuse through the CTA RO membrane without being retained on the membrane surface, leading to a low rejection. Although a complete explanation of their mechanism cannot be provided from the data obtained in this study, it is clear that the rejection of high molecular weight N-nitrosamines (NPYR, NDEA, NPIP, NMOR, NDPA and NDBA) by the CTA RO membrane can be governed by two solute properties (i.e. minimum projection area and hydrophobicity).

In addition to the overall rejection trend, the difference in rejection between these two membranes is also of great interest. In general, rejections by the PA RO membrane were higher than those by the CTA RO membrane (**Figure 7a**). This is somewhat reasonable, considering that the experiments using the PA and CTA RO membranes were conducted under distinctly different permeate fluxes (10 and 3.1 L/m²h, respectively). Permeate flux has been reported to considerably affect the rejection of small N-nitrosamines by PA RO membranes. For example, a previous laboratory-scale study which used a PA RO membrane (ESPA2, Hydranautics) revealed that NDMA rejection increased from 14 to 38 % with increasing permeate flux from 5 to 10 L/m²h [30]. This increase in rejection for increased permeate flux can occur for any solutes, since solute flux does not increase as much as solution (i.e. water) flux [32]. In addition, the CTA RO membrane is very likely to be somewhat more “loose” than typical PA RO membranes. For example, the free-volume hole-radius of a CTA RO membrane analysed by positron annihilation techniques was reported to be 0.3 nm [33], while that of PA RO membranes was 0.20-0.29 nm [34-36], indicating that the performance of PA RO membrane for neutral compound removal would be expected to be greater than that of a CTA RO membrane.

[Figure 7]

4. Conclusions

The rejection behaviours of TrOCs by the hollow fibre CTA RO membrane used in this study were similar to those previously reported for PA RO membranes. In general, the rejection of neutral TrOCs by the CTA RO membrane was strongly affected by their molecular size. Among several physicochemical properties investigated here, the best correlation was obtained between minimum projection area of TrOCs and their rejections. The rejection of charged TrOCs by the CTA RO membrane was over 90% with

paracetamol which has a molecular weight of only 151 g/mol being the only exception. There was no apparent difference in rejection between positively and negatively charged TrOCs. The role of electrostatic interaction in removing charged TrOCs by the CTA RO membrane appeared to be less significant compared to PA RO membranes previously reported in literature. Further investigation revealed that the rejection of N-nitrosamines by the CTA RO membrane was strongly affected by their hydrophobicity and molecular size, while that by a PA RO membrane was correlated with molecular size only. The results obtained here indicate that the separation performance of the CTA RO membrane for TrOC removal is comparable with that of PA RO membrane. To evaluate its separation performance during a long-term operation, further investigations will be required focusing on the impact of fouling and chlorination on TrOC rejection. Modelling of TrOC rejection by the CTA RO membrane is also essential as part of future work to predict their rejections during full-scale system operation.

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6. References

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423 447.

Table 1: Physicochemical characteristics of the selected TrOCs.

Compound	Molecular weight [g/mol]	Log D^a [-]	pK _a (pK _b) ^a [-]	Minimum projection area ^a [Å ²]
Neutral hydrophilic				
N-nitrosodimethylamine (NDMA)	74.1	0.04	(3.5)	19.5
N-nitrosomethylethylamine (NMEA)	88.1	0.40	(3.4)	22.1
N-nitrosopyrrolidine (NPYR)	100.1	0.44	(3.3)	25.0
N-nitrosodiethylamine (NDEA)	102.1	0.75	(3.3)	25.4
N-nitrosopiperidine (NPIR)	114.1	0.89	(3.3)	27.2
N-nitrosomorpholine (NMOR)	116.1	-0.18	(3.1)	25.2
N-nitrosodipropylamine (NDPA)	130.1	1.80	(3.3)	28.3
Caffeine	194.2	-0.55	(0.9)	30.0
Simazine	201.7	1.78	(3.2)	35.8
Atrazine	215.7	1.32	9.6	40.0
Primidone	218.3	1.12	11.5	42.7
Meprobamate	218.3	0.93	15.2	45.8
Triamterene	253.3	1.11	(3.1)	35.2
Trimethoprim	290.3	1.28	(7.2)	51.1
Neutral hydrophobic				
N-nitrosodi-n-butylamine (NDBA)	158.1	2.69	(3.3)	28.8
N,N-Diethyl-meta-toluamide (DEET)	191.3	2.50	(0.1)	40.1
Bisphenol A	228.3	4.04	9.8; 10.4	44.0
Diuron	233.1	2.53	13.2	28.6
Carbamazepine	236.3	2.77	16.0	38.8
Linuron	249.1	2.68	12.0	30.8
Diazepam	284.7	3.08	(2.9)	47.3
Triclocarban	315.6	4.93	11.4	50.1
Clozapine	326.3	3.40	(7.4)	55.5
Omeprazole	345.4	2.43	(4.8); 9.3	43.5
Hydroxyzine	374.9	3.24	(2.1, 7.8)	64.7
Negatively charged				
Paracetamol	151.2	0.91	7.1	23.7
Ibuprofen	206.3	0.97	4.9	35.4
Naproxen	230.3	-0.16	4.2	34.8
Gemfibrozil	250.3	1.33	4.4	43.4
Dilantin	252.3	0.91	6.5	47.8
Sulfamethoxazole	253.3	0.39	7.7	45.2
Ketoprofen	254.3	0.48	3.9	43.0
Triclosan	289.5	4.57	7.7	40.0
Diclofenac	296.1	1.16	4.0	43.3
Enalapril	376.5	-0.91	3.7; (5.2)	59.8
Simvastatin hydroxy acid	436.6	0.63	4.2	68.1
Zwitterion				
Tris(2-carboxyethyl)phosphine (TCEP)	250.2	-10.4	3.2; (9.0)	51.1
Positively charged				
Atenolol	266.3	-1.18	(9.7)	36.9
Amitriptyline	277.4	3.02	(9.8)	58.8
Fluoxetine	309.3	2.46	(9.8)	44.3
Verapamil	454.6	3.44	(9.7)	81.2

^a Chemaxon (<http://www.chemicalize.org/>).

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Figure 1: (a) Schematic structure of the HKC3023V membrane module and (b) schematic diagram of the cross flow RO filtration system.

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

Figure 3: Rejection of neutral (a) hydrophilic and (b) hydrophobic TrOCs (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed pressure 1.05 MPa, permeate flux 3.1 L/m²h, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1°C). The molecular weight (g/mol) is shown in the parentheses. Values reported here are the average and ranges of duplicate samples.

Figure 4: Rejection of neutral TrOCs as a function of (a) their molecular weight, (b) molecular volume, and (c) minimal projection area. Experimental conditions are described in Figure 3. Values reported here are the average and ranges of duplicate samples.

Figure 5: Rejection of charged TrOCs (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed pressure 1.05 MPa, permeate flux 3.1 L/m²h, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1°C). The molecular weight (g/mol) is shown in the parentheses. Values reported here are the average and ranges of duplicate samples.

Figure 6: Rejection of charged TrOCs as a function of their minimum projection area. Experimental conditions are described in Figure 5. Values reported here are the average and ranges of duplicate samples.

Figure 7: N-nitrosamine rejection by the CTA (HKC3023V) and PA (TFC-HR) RO membranes as a function of their (a) minimum projection area and (b) Log *D* (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed pH 8.0 ± 0.1, feed temperature 20.0 ± 0.1 °C). Values reported here are the average and ranges of duplicate samples. The rejection data by the CTA membrane was obtained with permeate flux 3.1 L/m²h and recovery 25%. The rejection data by the PA membrane was reported by Fujioka et al. [30] (three of 4-inch membrane elements, permeate flux 10 L/m²h and recovery 25%) where NDBA rejection data is not available.

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453 **Figure 1**

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457 **Figure 3**

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459 **Figure 4**

Figure 5

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463 **Figure 6**

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465 **Figure 7**

Rejection of trace organic chemicals by a hollow fibre cellulose triacetate reverse osmosis membrane

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SUPPLEMENTARY MATERIAL

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1 **Table S1:** Physicochemical properties of the selected TrOCs.

Compound	Formula	Distribution of charged species at pH 8 ^a [%]	Molecular volume ^b [nm ³ /mol]	Dipole moment ^c [Debye]
Neutral hydrophilic				
N-nitrosodimethylamine	C ₂ H ₆ N ₂ O	0	75	3.71
N-nitrosomethylethylamine	C ₂ H ₈ N ₂ O	0	91	3.71
N-nitrosopyrrolidine	C ₄ H ₈ N ₂ O	0	81	3.74
N-nitrosodiethylamine	C ₄ H ₁₀ N ₂ O	0	108	3.72
N-nitrosopiperidine	C ₅ H ₁₀ N ₂ O	0	97	3.73
N-nitrosomorpholine	C ₄ H ₈ N ₂ O ₂	0	87	2.68
N-nitrosodipropylamine	C ₆ H ₁₄ N ₂ O	0	140	3.77
Caffeine	C ₈ H ₁₀ N ₄ O ₂	0	133	2.24
Simazine	C ₇ H ₁₂ ClN ₅	0	153	2.29
Atrazine	C ₈ H ₁₄ ClN ₅	33	163	4.03
Primidone	C ₁₂ H ₁₄ N ₂ O ₂	0	192	3.69
Meprobamate	C ₉ H ₁₈ N ₂ O ₄	0	192	2.82
Triamterene	C ₁₂ H ₁₁ N ₇	0	169	1.33
Trimethoprim	C ₁₄ H ₁₈ N ₄ O ₃	12	232	4.34
Neutral hydrophobic				
N-nitrosodi-n-butylamine	C ₈ H ₁₈ N ₂ O	0	172	3.82
N,N-Diethyl-meta-toluamide	C ₁₂ H ₁₇ NO	0	194	3.14
Bisphenol A	C ₁₅ H ₁₆ O ₂	2	200	1.85
Diuron	C ₉ H ₁₀ Cl ₂ N ₂ O	0	170	4.32
Carbamazepine	C ₁₅ H ₁₂ N ₂ O	0	187	3.52
Linuron	C ₉ H ₁₀ Cl ₂ N ₂ O ₂	0	177	4.52
Diazepam	C ₁₆ H ₁₃ ClN ₂ O	0	226	1.88
Triclocarban	C ₁₃ H ₉ Cl ₃ N ₂ O	0	206	4.41
Clozapine	C ₁₈ H ₁₉ ClN ₄	18	248	1.62
Omeprazole	C ₁₇ H ₁₉ N ₃ O ₃ S	2	252	4.53
Hydroxyzine	C ₂₁ H ₂₇ ClN ₂ O ₂	40	317	0.91
Negative Charge				
Paracetamol	C ₈ H ₉ NO ₂	89	131	0.48
Ibuprofen	C ₁₃ H ₁₈ O ₂	100	200	1.68
Naproxen	C ₁₄ H ₁₄ O ₃	100	192	1.38
Gemfibrozil	C ₁₅ H ₂₂ O ₃	100	240	0.65
Dilantin	C ₁₅ H ₁₂ N ₂ O ₂	97	201	2.18
Sulfamethoxazole	C ₁₀ H ₁₁ N ₃ O ₃ S	69	173	4.71
Ketoprofen	C ₁₆ H ₁₄ O ₃	100	212	3.27
Triclosan	C ₁₂ H ₇ Cl ₃ O ₂	68	194	2.95
Diclofenac	C ₁₄ H ₁₁ Cl ₂ NO ₂	100	207	1.67
Enalapril	C ₂₀ H ₂₈ N ₂ O ₅	100	313	4.59
Simvastatin hydroxy acid	C ₂₅ H ₄₀ O ₆	100	384	5.24
Zwitterion				
tris(2-carboxyethyl)phosphine	C ₉ H ₁₅ O ₆ P	100	n.a.	2.31
Positive Charge				
Atenolol	C ₁₄ H ₂₂ N ₂ O ₃	98	237	4.92
Amitriptyline	C ₂₀ H ₂₃ N	98	258	0.52
Fluoxetine	C ₁₇ H ₁₈ F ₃ NO	98	267	1.31
Verapamil	C ₂₇ H ₃₈ N ₂ O ₄	98	429	7.04

2 ^a Chemaxon (<http://www.chemicalize.org/>).3 ^b Chemspider (<http://www.chemspider.com/>), data calculated using Advanced Chemistry
4 Development (ACD/Labs).5 ^c Millsian 2.1 Software (Millsian UNC).

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7 **Figure S2:** Reduction of feed concentration of neutral TrOCs as a function of $\text{Log } D$ after 5
8 hours filtration (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed pressure 1.05 MPa,
9 permeate flux 3.1 L/m²h, feed pH 8.0 ± 0.1 , feed temperature $20.0 \pm 0.1^\circ\text{C}$). HL and HP
10 represents hydrophilic and hydrophobic compounds, respectively.

11

12 **Figure S3:** Reduction of feed concentration of charged TrOCs as a function of Log D after 5
 13 hours filtration (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed pressure 1.05 MPa,
 14 permeate flux 3.1 L/m²h, feed pH 8.0 ± 0.1 , feed temperature $20.0 \pm 0.1^\circ\text{C}$).