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Rejection and fate of trace organic compounds (TrOCs) during membrane distillation

Kaushalya C. Wijekoon^a, Faisal I. Hai^a, Jinguo Kang^b, William E. Price^b,
Tzahi Y. Cath^c, Long D. Nghiem^{a,*}

^a Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

^b Strategic Water Infrastructure Laboratory, School of Chemistry, University of Wollongong, Wollongong, NSW 2522, Australia

^c Colorado School of Mines, Golden, CO 80401, USA

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ABSTRACT

In this study, we examined the feasibility of membrane distillation (MD) for removing trace organic compounds (TrOCs) during water and wastewater treatment. A set of 29 compounds was selected to represent major TrOC groups, including pharmaceuticals, steroid hormones, phytoestrogens, UV-filters, industrial chemicals, and pesticides that occur ubiquitously in municipal wastewater. Results reported here suggest that rejection and fate and transport of TrOCs during MD are governed by their volatility and, to a lesser extent, hydrophobicity. All TrOCs with $pK_H > 9$ (which can be classified as non-volatile) were well removed by MD. Among the 29 TrOCs investigated in this study, three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) possess moderate volatility ($pK_H < 9$) and therefore had the lowest rejection efficiencies of 54%, 73% and 66%, respectively. The results suggest that the rejection of TrOCs with $pK_H < 9$ may be governed by the interplay between their hydrophobicity and volatility. In addition, the fate and transport of the TrOCs during the MD process was also investigated. Hydrophilic TrOCs having negligible volatility were concentrated in the feed, while hydrophobic compounds with moderate volatility were substantially lost due to evaporation or adsorption. When MD treatment was integrated with a thermophilic membrane bioreactor (MBR), near complete removal (> 95%) of all 29 TrOCs investigated in this study was achieved despite their diverse physicochemical properties (i.e. hydrophobicity, persistency and volatility). The results suggest that MD could be a promising post-treatment to be used in conjunction with thermophilic MBR for TrOC removal.

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1. Introduction

Membrane distillation (MD) is a low temperature distillation process that involves the transport of water in the vapour phase from a feed solution through a microporous and hydrophobic membrane to the distillate (product) side. Direct contact membrane distillation (DCMD) is probably the most widely studied MD system configuration due to its simple operation [1,2]. In DCMD, the feed solution is maintained at a higher temperature than the distillate; thus, creating a vapour pressure difference between the feed and distillate. The membrane separates the liquid phase of the feed and distillate streams but allows water vapour to transport freely through its dry micro porous pores. In MD, the membrane material must be hydrophobic to prevent wetting of the pores by liquid feed or distillate under standard operating conditions. Because mass transfer can occur only in the gas phase, MD can offer

complete rejection of all non-volatile solutes such as inorganic salts and pathogenic micro-organisms. As a result, to date, much of the effort in MD research has focused on desalination applications [2–5].

Unlike pressure driven membrane processes, due to the absence of hydraulic pressure, MD is less susceptible to membrane fouling [3,6]. Even when a fouling layer does form on the membrane surface, it is expected to be less compacted and can be easily removed [3,7,8]. The low operating temperature of MD allows the utilisation of solar thermal or low grade heat as the energy source [1,2,9–13]. Given the advantages of high separation efficiency, low fouling propensity, and potentially low energy consumption (when low grade heat is readily available), MD can be used for a range of applications beyond those for brackish and seawater desalination. Several studies have explored the use of MD for food processing, such as whey protein recovery in dairy processing [8], polyphenolic antioxidants recovery from olive oil wastewater [14], and orange juice concentration [15], separation of fermentation broth [16] as well as treatment of wastewater from the textile [17] and petrochemical industries [10], and municipal water reuse [11,18].

* Corresponding author. Tel.: +61 24 221 4590.

E-mail address: longn@uow.edu.au (L.D. Nghiem).

Despite the growing interest in using MD for treatment of a range of wastewaters, there is still a lack of understanding of the rejection mechanisms of trace organic compounds (TrOCs) by MD. TrOCs have been frequently detected in raw sewage and biologically treated effluent at concentrations ranging from several ng/L to several $\mu\text{g/L}$ [19–23]. As a result, the removal of these TrOCs from secondary treated effluent by advanced treatment processes such as nanofiltration (NF), reverse osmosis (RO), oxidation and activated carbon adsorption has been extensively investigated in recent years [24–28]. Nevertheless, only a few studies have been conducted to elucidate the rejection of specific organic compounds by MD. Moreover, the available studies are mostly concerned with industrial chemicals such as benzene [29] and trichloroethylene [30] at an elevated feed concentration.

Given the concerns associated with human and environmental exposure to TrOCs, it is important to elucidate their fate and transport during MD, particularly in water reuse applications. Examples of these include the investigation by Cath et al. [18] and Cartinella et al. [31] to treat urine and hygiene wastewater by MD for water reuse in long term space missions and the novel membrane distillation bioreactor (MDBR) concept proposed by Phattaranawik et al. [11] and Goh et al. [32].

In this paper, we studied the rejection of a broad range of TrOCs by MD. The potential application of MD as a post-treatment for thermophilic MBR to enhance TrOC removal was also investigated. The transport and fate of TrOCs during MD treatment are discussed with respect to compound hydrophobicity and volatility (measured by the log D and the Henry's law constant, respectively). The results provide further insight with respect to TrOC rejection using MD, which is critical for further development of this technology for wastewater reclamation applications.

2. Materials and methods

2.1. Experimental system

The rejection of TrOCs by MD was evaluated using a hydrophobic microporous polytetrafluoroethylene (PTFE) membrane (GE, Minnetonka, MN) and a laboratory-scale DCMD system [33]. According to the manufacturer, the average pore size and porosity of the MD membrane were $0.22\ \mu\text{m}$ and 70%, respectively. The DCMD system (Fig. 1) comprised a membrane cell, a stainless steel feed tank, a glass distillate tank, two circulation pumps

(Micropump Inc., USA), a temperature controller (Coleparmer, USA), and a heating element (Process Technology, USA). The membrane cell was made of acrylic glass, and a flow channel was engraved in each of the two acrylic glass blocks that make up the feed and permeate semi-cells. The length, width, and height of the each channel were 145, 95, and 3 mm, respectively. The feed solution was circulated from a stainless steel reservoir to the membrane cell and then returned back to the feed reservoir. A temperature sensor was placed immediately before the feed inlet to the membrane cell. The heating element and the temperature sensor were connected to a temperature control unit that was used to regulate the temperature of the feed solution. Another temperature sensor was installed immediately at the outlet of the distillate semi-cell. The temperature of the distillate was regulated using a chiller (AquaCooler, Australia) equipped with a stainless steel heat exchanging coil immersed directly in the distillate reservoir. Excess water was allowed to overflow from the distillate reservoir into a glass container, placed and continuously weighed on an analytical balance (Mettler Toledo, Switzerland). All pipe-work used in the DCMD test unit was covered with insulation foam to minimise heat loss. The feed and distillate tanks were covered with aluminium foil to minimise evaporation loss during the experiment. At the end of each experiment, the solution volume was measured again and the total volume loss was found to be less than 6%.

One set of MD experiments was conducted using a synthetic feed solution containing approximately $5\ \mu\text{g/L}$ of each TrOC in Milli-Q water. In another set of experiments, effluent obtained from a thermophilic MBR system (Supplementary Data Fig. S1) was used as the feed solution to evaluate the feasibility of combining MD with MBR. The MBR and MD experiments were conducted separately. The MBR system consisted of a 5 L glass reactor immersed in a PID control water bath (Julabo, Germany), three peristaltic pumps (Masterflex L/S, USA) for feeding, recirculation and effluent extraction, and an external ceramic membrane module (NGK, Japan). The ceramic membrane had a nominal pore size of $1\ \mu\text{m}$ and effective area of $0.09\ \text{m}^2$. Further details of this MBR system are available elsewhere [34].

2.2. Experimental protocol

In all MD experiments, the feed and distillate temperatures were 40 and $20\ ^\circ\text{C}$, respectively, and the cross flow velocity of the

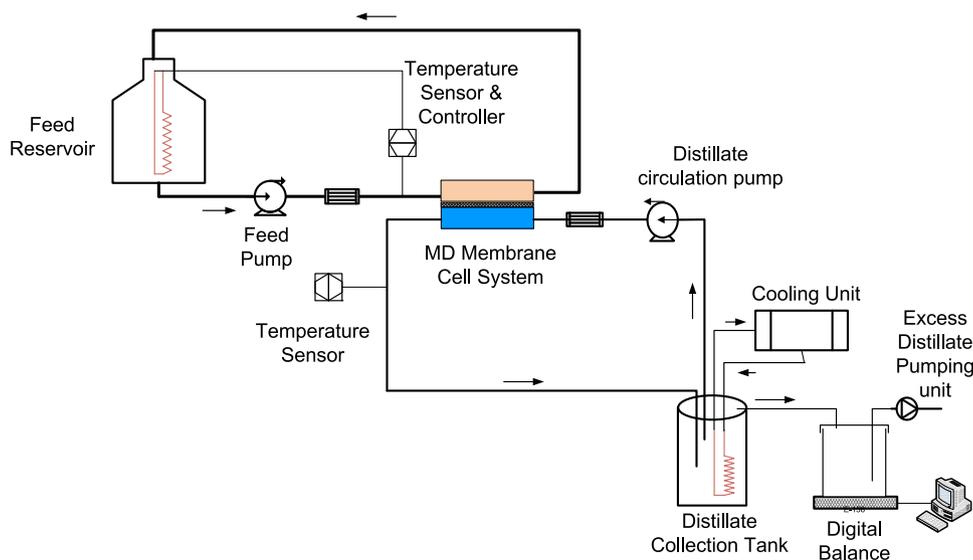


Fig. 1. Schematic diagram of the DCMD system.

feed and distillate circulation flow was 11.7 cm/s. The initial feed volume was 10 L. The experiment was concluded once the water recovery had reached 70%, at which stage the feed and distillate samples were collected for TrOC analysis. The duration of each MD experiment was approximately 24 h. At the beginning of each MD experiment, 3.35 L of Milli-Q water was used as the initial distillate. Thus, TrOC concentration in the distillate was corrected for dilution by taking into account the initial volume of Milli-Q water in the distillate.

The MBR system was operated under thermophilic conditions (40 °C) with an average dissolved oxygen (DO) concentration of 2.9 mg/L, hydraulic retention time of 24 h, and average mixed liquor pH of 7.7. Excess sludge was withdrawn every week to maintain the mixed liquor suspended solid (MLSS) concentration in the reactor at 5000 mg/L, resulting in a solids retention time (SRT) of 140 days. The system was fed with a synthetic wastewater containing 100 mg/L glucose, 100 mg/L peptone, 17.5 mg/L KH₂PO₄, 17.5 mg/L MgSO₄, 10 mg/L FeSO₄, 225 mg/L CH₃COONa and 35 mg/L urea [35].

Prior to the commencement of this study, the MBR system had been acclimatized at 40 °C and operated for more than 2 months to produce constant effluent quality (Supplementary Data Fig. S2). TrOCs were introduced to the MBR feed to obtain approximately 5 µg/L of each compound and the MBR system was operated continuously at similar operating conditions. Then, the effluent was collected and used as MD feed. In good agreement with the previous studies [24,36,37] no significant difference in the biological performances of the MBR was observed following the introduction of TrOC. Key operational parameters including MLSS, mixed liquor volatile suspended solid (MLVSS), DO, total organic carbon (TOC) and total nitrogen (TN) removal, and permeate turbidity were continuously monitored to ensure the biological stability of the MBR. The performance of the MBR system was stable throughout this study with respect to these parameters. TOC and TN removal were stable at 91% and 47%, respectively. The

turbidity of the MBR permeate was always below 0.9 NTU. The MLVSS/MLSS ratio of the sludge remained constant at approximately 0.76 throughout the experimental period. In addition, the MBR system was operated at a transmembrane pressure (TMP) below 90 kPa to maintain a constant permeate flux, and no abnormal variation in TMP was observed over the entire study (Supplementary Data Fig. S3).

TrOC removal or rejection (R) is defined as

$$R = 100 \times \left(1 - \frac{C_p}{C_f} \right) \quad (1)$$

where C_p and C_f are concentrations of the specific compound in the permeate and feed, respectively. The term 'rejection' was used for the MD process while the term 'removal' was used for MBR. Taking the combined treatment of MBR and MD into account, the term removal infers that TrOCs can also be biologically degraded. Losses of TrOCs during the MD process were calculated by considering the mass balance of each compound in the feed, concentrate and distillate as given in Eq. (2).

$$C_f \times V_f = (C_D \times V_D) + (C_C \times V_C) + \text{total loss} \quad (2)$$

In Eq. (2), C_f , C_D and C_C are concentrations in the feed, distillate and concentrate, respectively. Similarly, V_f , V_D and V_C are the volumes of the feed, distillate and concentrate, respectively.

2.3. Trace organic contaminants

A set of 29 TrOCs was selected to represent pharmaceuticals, steroid hormones, phytoestrogens, UV-filters (i.e., active ingredients of sunscreens), industrial chemicals, and pesticides ubiquitously found in municipal wastewater [19–23]. Analytical grade samples of these compounds were obtained from Sigma-Aldrich (Saint Louis, MO, USA). A combined stock solution of all the TrOCs was prepared in pure methanol and kept at –18 °C in the dark. Log D values of these compounds were obtained from the

Table 1
Physicochemical properties of the selected compounds (data from Scifinder Scholar).

Compound	Chemical Formula	Molecular weight (g/mol)	Log D at pH 9	Water solubility at 25 °C (mg/L)	Vapour pressure (mmHg)	pK _H at pH 9
Enterolactone	C ₁₈ H ₁₈ O ₄	298.33	1.89	200	3.29 × 10 ⁻¹³	15.19
Primidone	C ₁₂ H ₁₄ N ₂ O ₂	218.25	0.83	1500	6.08 × 10 ⁻¹¹	13.93
Ketoprofen	C ₁₆ H ₁₄ O ₃	254.30	-0.84	554,000	3.32 × 10 ⁻⁸	13.70
Formononetin	C ₁₆ H ₁₂ O ₄	268.26	0.88	4800	8.17 × 10 ⁻¹⁰	13.22
Naproxen	C ₁₄ H ₁₄ O ₃	230.30	-0.73	435,000	3.01 × 10 ⁻⁷	12.68
Gemfibrozil	C ₁₅ H ₂₂ O ₃	250.30	0.67	263,000	6.13 × 10 ⁻⁷	12.11
Metronidazole	C ₆ H ₉ N ₃ O ₃	171.15	-0.14	29,000	2.67 × 10 ⁻⁷	11.68
Diclofenac	C ₁₄ H ₁₁ Cl ₂ NO ₂	296.15	0.83	20,000	1.59 × 10 ⁻⁷	11.51
Fenoprop	C ₉ H ₇ Cl ₃ O ₃	269.51	-0.29	230,000	2.13 × 10 ⁻⁶	11.48
Estriol	C ₁₈ H ₂₄ O ₃	288.40	2.5	32	1.34 × 10 ⁻⁹	10.80
Ibuprofen	C ₁₃ H ₁₈ O ₂	206.30	-0.19	928,000	1.39 × 10 ⁻⁴	10.39
Clofibric acid	C ₁₀ H ₁₁ ClO ₃	214.64	-1.32	100,000	1.03 × 10 ⁻⁴	9.54
17α-Ethinylestradiol	C ₂₀ H ₂₄ O ₂	296.48	4.08	3.9	3.74 × 10 ⁻⁹	9.43
Oxybenzone	C ₁₄ H ₁₂ O ₃	228.24	2.55	2700	5.26 × 10 ⁻⁶	9.23
Carbamazepine	C ₁₅ H ₁₂ N ₂ O	236.27	1.89	220	5.78 × 10 ⁻⁷	9.09
Estrone	C ₁₈ H ₂₂ O ₂	270.36	3.6	5.9	1.54 × 10 ⁻⁸	9.03
17β-Estradiol	C ₁₈ H ₂₄ O ₂	272.38	4.12	3	9.82 × 10 ⁻⁹	8.93
17β-Estradiol-17-acetate	C ₂₀ H ₂₆ O ₃	314.42	5.11	1.9	9.88 × 10 ⁻⁹	8.67
Bisphenol A	C ₁₅ H ₁₆ O ₂	228.29	3.62	73	5.34 × 10 ⁻⁷	8.66
Octocrylene	C ₂₄ H ₂₇ N	361.48	6.89	0.36	2.56 × 10 ⁻⁹	8.47
Ametryn	C ₉ H ₁₇ N ₅ S	227.33	2.97	140	1.72 × 10 ⁻⁶	8.43
Amitriptyline	C ₂₀ H ₂₃ N	277.40	4.01	83	1.50 × 10 ⁻⁶	8.18
Pentachlorophenol	C ₆ HCl ₅ O	266.38	1.99	4800	3.49 × 10 ⁻⁴	7.59
Atrazine	C ₈ H ₁₄ ClN ₃	215.68	2.64	69	1.27 × 10 ⁻⁵	7.28
Propoxur	C ₁₁ H ₁₅ NO ₃	209.24	1.54	800	1.53 × 10 ⁻³	6.28
Triclosan	C ₁₂ H ₇ Cl ₃ O ₂	289.54	4.12	19	3.26 × 10 ⁻⁵	6.18
Benzophenone	C ₁₃ H ₁₀ O	182.22	3.21	150	8.23 × 10 ⁻⁴	5.88
4-Tert-butylphenol	C ₁₀ H ₁₄ O	150.22	3.37	1000	0.0361	5.15
4-Tert-octylphenol	C ₁₄ H ₂₂ O	206.33	5.18	62	1.98 × 10 ⁻³	5.06

SciFinder Scholar database (<https://scifinder.cas.org/scifinder>) at pH 9 (Table 1). Vapour pressure, molecular weight (MW), and water solubility of each selected compound were also obtained from the SciFinder Scholar database to calculate the Henry's law constant as: H (atm m³/mol) = vapour pressure \times MW/water solubility. The pK_H value presented in Table 1 is defined as $pK_H = -\log_{10} H$. It is important to note that because the water solubility used to calculate the Henry's law constant was obtained at 25 °C, the actual pK_H values at 40 °C (which was used during the MD experiment) could deviate slightly from those values presented in Table 1.

The pHs of the synthetic feed solution were 8.5 and 8.6 at the beginning and the end of the MD experiment, respectively. The initial pH value of the MBR effluent was 7.8 and it increased to pH 9.1 at the end of the experiment. Accordingly, the $\log D$ and pK_H values of the TrOCs investigated in this study were obtained at pH 9 (Table 1).

2.4. Analytical methods

2.4.1. Basic water quality parameters

TOC and TN were analysed using a Shimadzu TOC/TN-V_{CSH} analyser (Shimadzu, Kyoto, Japan). TOC analysis was conducted in non-purgeable organic carbon mode. Electrical conductivity and pH of the feed and distillate were monitored using an Orion 4 Star Plus portable pH/conductivity meter (Thermo Scientific, Waltham, MA).

2.4.2. TrOC analysis

TrOC concentrations were determined using an analytical method previously reported by Hai et al. [38]. This method consisted of a solid phase extraction procedure followed by gas chromatography separation and quantitative determination using a mass spectrometry detector with electron ionisation. Feed and distillate samples (500 mL each) were extracted using 6 mL 200 mg Oasis HLB cartridge (Waters, Milford, MA, USA). First, the cartridges were preconditioned with 7 mL dichloromethane and methanol mixture (1:1 v/v), 7 mL methanol, and 7 mL reagent water (Milli-Q water). The samples were acidified to pH 2–3 and loaded onto the cartridges at a flow rate of 1–5 mL/min. The cartridges were then rinsed with 20 mL Milli-Q water and dried in a stream of nitrogen for 30 min. The extracted TrOCs were eluted from the cartridge using 7 mL of methanol followed by dichloromethane and methanol mixture (1:1 v/v) at a flow rate of 1–5 mL/min. The eluents were subsequently evaporated using a water bath (40 °C) under a gentle stream of nitrogen. The extracts were dissolved with 200 μ L methanol which contained 5 μ g bisphenol A-d₁₆ and transferred into 1.5 mL vials, and then further evaporated under a gentle stream of nitrogen. Finally, the extracts were derivatized by adding 100 μ L of N,O-bis(trimethylsilyl)trifluoroacetamide (1% trimethylchlorosilane) and pyridine (dried with KOH solid), then heated on a heating block (60–70 °C) for 30 min. The derivatives were cooled to room temperature and analysed using a Shimadzu QP5000 GC–MS (Shimadzu, Kyoto, Japan) equipped with a AOC20i autosampler and a Phenomenex Zebtron ZB-5 (5% diphenyl–95% dimethylpolysiloxane) capillary column (30 m \times 0.25 mm ID, d_f = 0.25 μ m). The detection limit of the selected compounds was in the range of 1–20 ng/L [38].

3. Results and discussion

3.1. Basic performance of the MD process

The MD experiments were analysed considering the distillate flux, water recovery, pH and conductivity variation

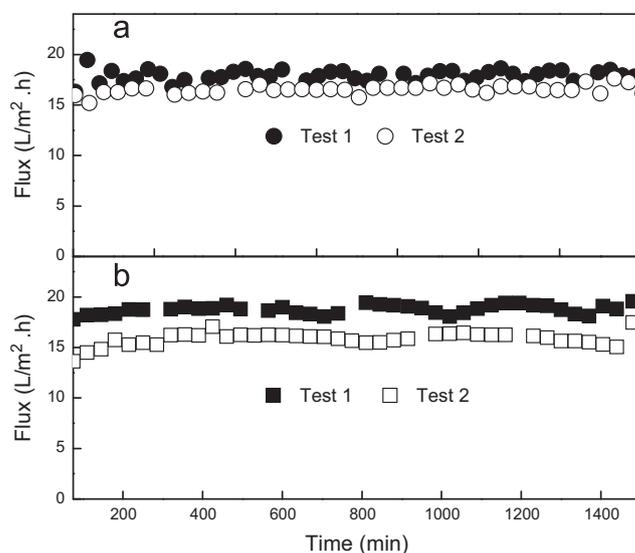


Fig. 2. Permeate flux variation of MD and MBR–MD experiments: MD was carried out at feed and distillate temperatures of 40 and 20 °C, respectively; and feed and distillate circulation flow rate of 2 L/min (corresponding to 11.7 cm/s). (a) MD experiment and (b) MBR–MD experiment.

(Supplementary Data Table S1). The distillate flux was continuously monitored to assess the stability (Fig. 2). There was no notable difference in the performance of the MD process with respect to the water flux and conductivity rejection when either the synthetic solution or MBR effluent was used as the feed. Both experiments achieved satisfactory water recovery at 70%. The average TOC and TN concentrations of the MBR effluent were 15 ± 6 and 17 ± 4 mg/L, respectively. However, this high residual organic content in the MBR effluent did not exert any negative impact on the MD process. TOC and TN concentrations of the distillate were consistently less than 1 mg/L. When either the synthetic solution or the MBR effluent was used as the feed to the MD process, the water flux was stable at approximately 17.5 L/m² h and no flux decline was observed during the entire experimental period (Fig. 2). The conductivity of the distillate was consistently below 10 μ S/cm regardless of the salinity level in the feed (Supplementary Data Table S1).

3.2. Rejection and fate of TrOCs during MD

3.2.1. TrOC rejection

Most of the 29 TrOCs investigated were effectively removed by MD (Fig. 3). However, it is important to note that only a moderate rejection efficiency was observed for several compounds. In particular, 4-tert-octylphenol showed the lowest rejection (54%). In MD, mass transfer occurs only in the gas (vapour) phase. Thus, the transport of TrOCs from the feed to the distillate solution depends on their volatility. Not surprisingly, all TrOCs with pK_H value higher than 9 (low volatility) were well removed by the MD process. Oxybenzone is the only exception. Compared to other TrOCs, the relatively lower rejection (81%) of oxybenzone in relation to its pK_H value as plotted in Fig. 3 could be attributed to the strong dependence of its pK_H value on pH. pK_H values at pH 9 have been plotted in Fig. 3. However, it is noteworthy that the pK_H value of oxybenzone changes from 9.23 to 8.39 when the solution pH decreases from 9 to 8 (Supplementary Data Table S2). Because in this study the feed solution pH was 8.5 and 8.6 at the beginning and the end of the MD experiment, respectively, the interpolated pK_H (8.6) value of oxybenzone is actually below 9. The three TrOCs with the lowest rejection (i.e., 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) also have the highest

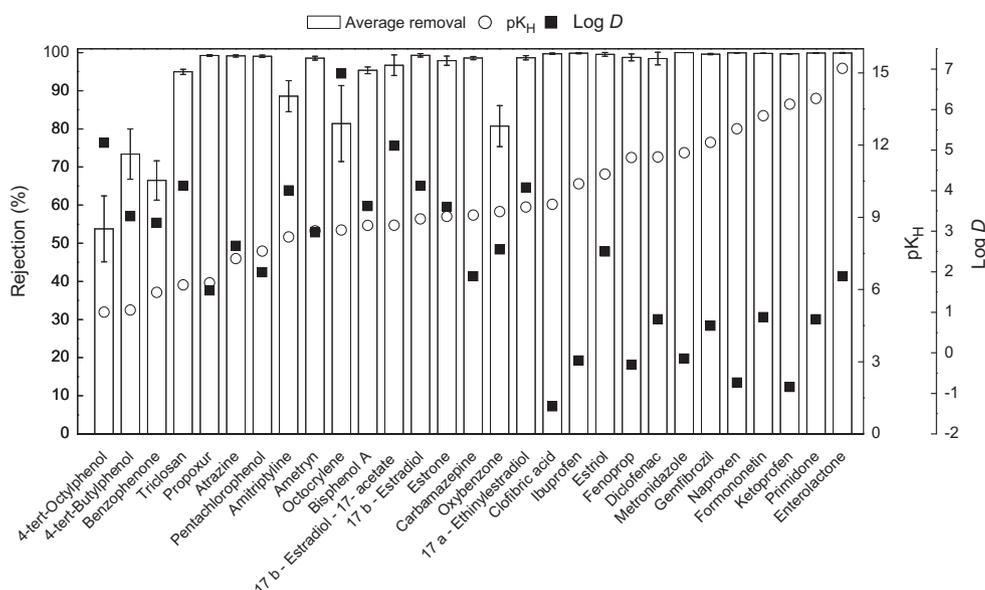


Fig. 3. Rejection of the 29 TrOCs by DCMD and their $\log D$ and pK_H values. $\log D$ and pK_H illustrate the values at the pH 9. Error bars represent the standard deviation from four replicate measurements. Synthetic solution containing approximately 5 $\mu\text{g/L}$ of each TrOC in Milli-Q water was used as the feed. The MD was carried out at feed and distillate temperatures of 40 and 20 $^{\circ}\text{C}$, respectively. The feed and distillate circulation flow rate was 2 L/min (corresponding to 11.7 cm/s).

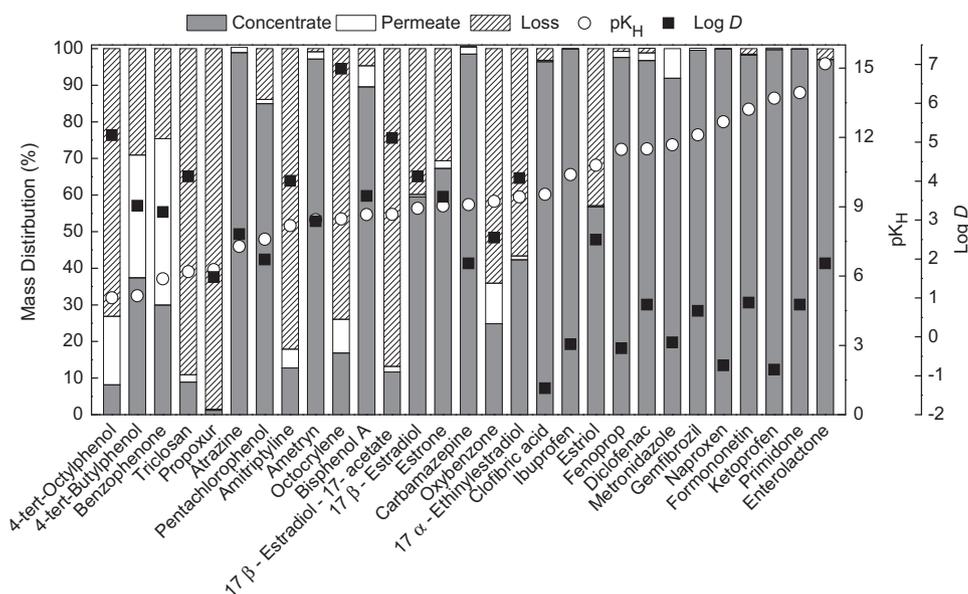


Fig. 4. The fate of the 29 TrOCs in the DCMD process with their $\log D$ and pK_H values. $\log D$ and pK_H illustrate the values at the pH 9. Synthetic solution containing approximately 5 $\mu\text{g/L}$ of each TrOC in Milli-Q water was used as the feed. The fate of each compound was analysed by mass balance considering the total input, mass in concentrate and permeate, and loss due to evaporation or adsorption. Calculation of the fate of TrOCs during the MD process was based on the average value of four measurements (duplicate samples from two replicate experiments).

volatility (or lowest pK_H values) amongst the 29 TrOCs studied. Low rejection of volatile organic compounds such as benzene [29] and trichloroethylene [30] by MD have been previously reported in the literature. However, in this study, there was no obvious correlation between rejection efficiencies and pK_H values for TrOCs possessing a pK_H value of less than 9. The data presented in Fig. 3 suggest that in addition to volatility, other physicochemical properties such as hydrophobicity (which can be obtained from $\log D$) may also influence the transport of TrOCs during MD. In fact, octocrylene, which has the fourth lowest rejection value of 81%, is also the most hydrophobic compound of the 29 TrOCs. In addition, in this study most of the TrOCs with pK_H of less than 9 were also hydrophobic (i.e., $\log D > 3$), and their rejection efficiency varied widely from as low as 54% (i.e., 4-tert-octylphenol) to near

complete rejection. Significant adsorption of hydrophobic organics to the MD membrane has been previously reported by Zuo and Wang [39]. The results reported in Fig. 3 suggest that the rejection of TrOCs may be governed by the interplay between their volatility and hydrophobicity.

3.2.2. Fate of TrOCs during the MD process

The fate of TrOCs during the MD experiments is presented in Fig. 4. Considering each experiment as a closed system, any loss of TrOCs could be attributed to either evaporation or adsorption to the membrane. The former is governed by the volatility and the latter is governed by the hydrophobicity. Both of these physicochemical properties could be important in determining the fate of

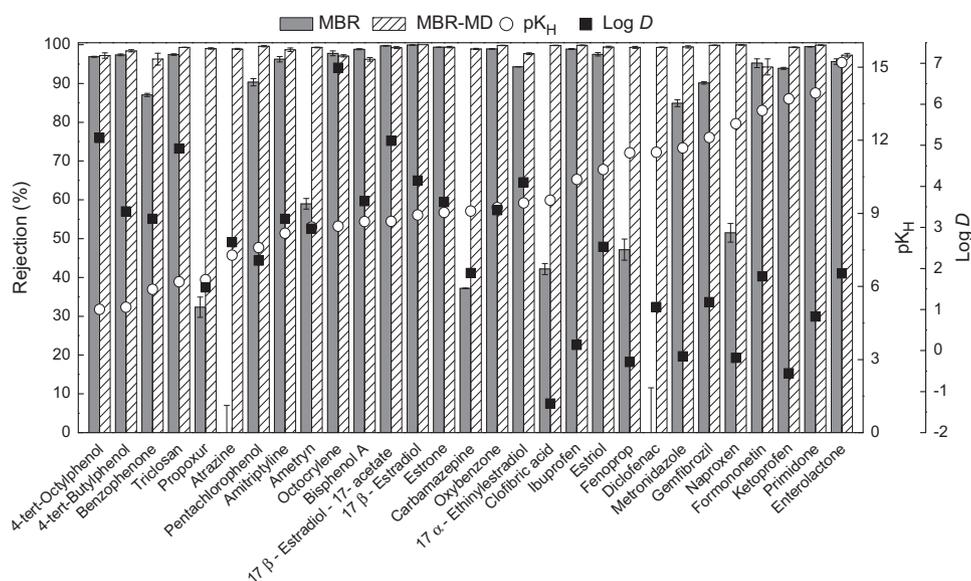


Fig. 5. Removal of TrOCs by the thermophilic MBR and by the MBR–MD as well as their log D and pK_H values. Log D and pK_H illustrate the values at the pH 9. MBR permeate was used as the feed for MD. Error bars represent the standard deviation from two replicate experiments.

TrOCs during MD (Fig. 4). Results reported in this study reveal that the hydrophilic TrOCs with low volatility ($pK_H > 9$) can accumulate in the feed. On the other hand, significant losses through either evaporation or adsorption could be observed for moderately volatile (i.e. pK_H value < 9) and hydrophobic (i.e. $\log D > 3$) compounds. As a result, moderately volatile and hydrophobic compounds such as triclosan, propoxur, amitriptyline, octocrylene and 17β -estradiol- 17 -acetate did not accumulate in the feed. Indeed, concentrations of all three compounds (i.e. 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) with the lowest pK_H in the concentrate at the end of the experiment were lower than the initial values (Supplementary Data, Table S3). In addition, the rejections of these compounds by MD were also the lowest amongst the 29 TrOCs investigated here (Fig. 4).

3.3. MBR–MD system

MD can be operated with feed temperature compatible with that of thermophilic MBR. These two processes can be combined with each other to obtain enhanced TrOC removal. TrOC concentrations in the feed and after each of these treatment steps are shown in Supplementary Data Table S4. MBR treatment effectively removed most of the 29 TrOCs investigated in this study. High removal of these compounds during MBR treatment has also been reported elsewhere [25,36,37,40]. However, several compounds including propoxur, atrazine, ametryn, clofibric acid, diclofenac, carbamazepine, naproxen and fenprop were found to be persistent to MBR treatment, and their residual concentrations in the MBR effluent were relatively high. Low removal efficiencies of these compounds have also been reported in several previous studies [36,41,42]. It is noted that the removal efficiency of these compounds under thermophilic conditions in this study were comparatively lower than that observed in our previous study under mesophilic conditions [37]. The low removal of most of the persistent compounds can be attributed to the disturbed metabolic activity generally associated with the biological treatment at elevated temperatures [38]. Nevertheless, as illustrated in Fig. 5, all TrOCs including those that were resistant to MBR treatment were effectively removed by the MD process. In this study, complete or near complete ($> 95\%$) removal efficiency of all 29 TrOCs was achieved by the combined MBR–MD treatment.

TrOC removal by MD as a post-treatment step following an MBR has not been reported in the literature. On the other hand, the use of other post-treatment processes such as NF and RO desalination subsequent to MBR has been previously demonstrated [24,25,43,44]. Tam et al. [43] reported near complete removal of estrogens and disinfection by-products (trihalomethanes and halo-acetic acids) by a pilot MBR/RO system. Alturki et al. [24] also demonstrated the benefits of coupling MBR treatment and NF/RO desalination for removing 40 TrOCs with a diverse range of physicochemical properties. Results reported in the current study suggest that an MBR–MD hybrid system could be as effective as an MBR–NF/RO system for removing TrOCs. In addition, high removal of TrOCs by a combination of MBR and MD treatment can be achieved regardless of the diversity of their volatility, persistency, and hydrophobicity.

The results shed light on the prospect of integrating MD with MBR for TrOC removal (e.g., MBR coupled MD (multi pass) system and MD bioreactor), and the salinity affected complexities on removal performance would be vital to investigate. However, it was not within the scope of the current study. Overall, the high water flux, excellent distillate quality and the near complete removal of TrOCs reported here suggest that MBR–MD system could be used to ensure safe water reuse.

4. Conclusion

In this study, we have investigated the rejection of 29 trace organic compounds (TrOCs) and their fate in a membrane distillation (MD) system. Results reported here suggest that rejection and fate and transport of TrOC during MD would be mainly governed by the volatility and partially governed by the hydrophobicity of the compound. All TrOCs with $pK_H > 9$ (which can be classified as non-volatile) were highly removed by MD. However, three compounds (i.e., 4-tert-octylphenol, 4-tert-butylphenol and benzophenone) with $pK_H < 9$ and thus classified as partially volatile showed relatively low rejection efficiencies (i.e., 54%, 73% and 66%, respectively). The results also suggest that the rejection of TrOCs with $pK_H < 9$ may be governed by the interplay between their hydrophobicity and volatility. In addition, the reported results show that hydrophilic TrOCs having negligible volatility were concentrated in the feed, while hydrophobic compounds with moderate volatility were substantially lost due to evaporation or adsorption to

membrane. Membrane bioreactor followed by MD treatment resulted in near complete (> 95%) removal of all 29 TrOCs despite their diverse physicochemical properties (i.e., hydrophobicity, persistency and volatility).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2013.12.002>.

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