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Abstract

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Removal of volatile organic compounds (VOCs) from groundwater by reverse osmosis and nanofiltration.

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ABSTRACT

A comprehensive study was conducted to examine the removal of volatile organic compounds (VOCs) which exist in groundwater at Southlands-Botany Bay (Sydney region). The ability of nanofiltration (NF) and reverse osmosis (RO) as advanced treatments was investigated using two commercially available NF or RO membranes. Laboratory-scale tests were used with cross-flow; tests were conducted with 16 ubiquitous compounds that represented the significant volatile organic compounds found in the contaminated groundwater.

The results reported in this study indicate that the removal efficiency of reverse osmosis (RO) was better than NF in rejecting the VOCs detected in groundwater. This study revealed that the performance of NF and RO membranes in rejecting hydrophilic volatile organic compounds was higher than that for hydrophobic compounds and the highest rejection achieved by NF and RO membranes amounted 98.4 % and 100 %, respectively. Hydrophilic compounds can be effectively rejected by NF/RO membranes using the size exclusion mechanism (steric hindrance), whereas hydrophobic compounds can be adsorbed into NF/RO membranes and then diffuse through the dense polymeric matrix, resulting in the lower removal for these compounds compared to hydrophilic compounds.

1. Introduction

The occurrence and fate of volatile organic compounds (VOCs) in surface and groundwater has been identified as a significant environmental health concern [1, 2]. It would be fair to say that there is full agreement between the scientific community and water authorities to minimise volatile organic compounds, however, the majority of these contaminants in the environment are still poorly understood, and are a topic of growing interest from both research and regulatory perspectives. Reclaimed wastewater, in particular, has some

significant benefits, including high reliability of supply, a known quality and frequently, a centralized source near urban demand centres.

In the last decade, nanofiltration (NF) and reverse osmosis (RO) have been proposed as attractive technologies for removal of organic trace contaminants including volatile organic compounds from the aquatic environment instead of conventional wastewater treatment [3-7]. It can be recognised that conventional treatment processes, such as chemical precipitation, ion exchange and electrochemical removal, are insufficient to remove and minimize organic contaminants to acceptable regulatory standards. Several previous studies have demonstrated the excellent capability of NF/RO to remove a wide range of volatile organic compounds including trihalomethanes, organochloric compounds, petroleum hydrocarbons and other low molecular weight compounds such as toluene and trichloroethylene [5, 8]. These studies have also revealed a substantial degree of complexity associated with the separation processes involved. As a result, various parameters such as membrane properties, solution chemistry and physicochemical properties of the volatile organic compounds can significantly affect the removal efficiency of these components by NF/RO membranes [5, 8]. Also Yangali-Quintanilla et al. [9] reported that the clean NF-90 membrane (virgin) rejected almost all of the hydrophobic neutral compounds (95- 98%) mainly because of size exclusion. High rejection was achieved after using the RO stage (>99% for macrolides, pharmaceuticals, cholesterol and disinfection byproducts, 95% for diclofenac, and >93% removal of sulphonamides [10]. The removal of triclosan by RO membranes was almost 100% since the molecular width of this compound was greater than the estimated mean effective membrane pore size [11]. Great rejection (90–100%) was achieved after using the RO (virgin XLE) to examine the removal of six pharmaceuticals and personal care products and size exclusion was the dominating mechanism [12].

A sieving mechanism, integrating molecular width and molecular length as the size parameters, and an interaction component with a logarithmic octanol-water partitioning coefficient ($\text{Log } K_{ow}$) gave the best expectation for the retention of volatile organic compounds by membranes. Solutes with larger widths, larger lengths and higher $\text{Log } K_{ow}$ will have higher retentions for most of the membranes used [8]. Thus the separation of volatile organic compounds by NF/RO processes is based predominantly on size exclusion [5]. In the case of charged trace organic compounds, electrostatic interactions between the charged solute and the negatively charged membrane surface can also play a key role [13,

14]. Additionally, it has been demonstrated that hydrophobic compounds can adsorb onto membrane surfaces and subsequently may diffuse through RO and especially NF membranes, resulting in lower rejections than would be expected based only on size exclusion mechanisms. In this case hydrophobicity is considered an important factor affecting rejection [15].

One of the objectives of this study was to examine the removal of volatile organic compounds by using a NF/RO filtration system. Experiments were conducted at laboratory-scale using commercially available NF/RO membranes, namely NF-90 and ESPA2. Sixteen volatile organic compounds with molecular weights between 78.11 g/mol (benzene) and 260.76 g/mol (hexachlorobutadiene) were used as model organic contaminants due to their widespread occurrence in groundwater. Removal efficiency by NF/RO filtration was linked to the physicochemical properties of these compounds to focus on the ability and effectiveness of this kind of treatment. Substantial characterisation work has been conducted to investigate the NF/RO membranes.

1.1 Study area

In this study contaminated groundwater samples have been collected from Botany Bay. In the Botany area samples have been collected from two contaminated sites, namely EWB10D and EWB13D. Fig. 1 illustrates samples sites in the Sydney (Botany Bay) region.

Fig. 1: Image illustrates samples sites in the Sydney (Botany Bay) regions.

2. Materials and methods

2.1. Laboratory-scale NF/RO filtration system

A laboratory-scale, cross-flow membrane filtration system with a stainless steel cross-flow cell was constructed for this study (Fig. 2). The cell had an effective membrane area of 40 cm² (4 cm x 10 cm) and a channel height of 2 mm. The system was equipped with a Hydra-Cell pump (Wanner Engineering Inc., Minneapolis, MN). The temperature of the test solution was kept stable using a Neslab RTE 7 chiller/heater equipped with a stainless steel heat exchanger coil that was submerged directly into a stainless steel reservoir. The permeate flow was measured by a digital flow meter (Optiflow 1000, Agilent Technologies, Palo Alto, CA) connected to a personal computer, and the cross-flow rate was monitored using a rotameter.

Fig. 2: Schematic diagram of the laboratory-scale pressure driven membrane filtration system.

2.2. NF/RO membranes

A NF membrane (namely NF-90) and a RO membrane (namely ESPA2) were used in this project. NF-90 was obtained from Dow Film Tec (Minneapolis, MN, USA) whereas the ESPA2 was obtained from Nitto Denko (Oceanside, CA, USA). These membranes were received as flat sheet samples and stored dry. All membranes used in this study are made of a thin aromatic (or semiaromatic) polyamide active layer and thicker more porous supporting layer. Physicochemical characteristics of these membranes are illustrated in Table 1. Based on their estimated pore size, the NF-90 membrane could be classified as a tight nano-filtration membrane whereas ESPA2 can be assumed to have no obviously defined pore structure.

Table 1: Properties of the selected NF/RO membranes.

Membrane	Average pore Diameter ^a (nm)	Na ⁺ rejection ^b (%)	Molecular weight cut-off ^c (g/mol)	Contact angle ^d (°)	Surface Roughness ^d (nm)
NF-90	0.68	85.0	~200	42.5	63.9
ESPA2	Not applicable	96.5	~100	60.6	30.0

^a [15].

^b Feed solution contains 20 mM NaCl and 1 mM CaCl₂ (pH 8).

^c Provided by the manufacturers.

^d [16].

2.3. NF/RO membrane characterisation

The surface streaming potential of the membrane was measured using a SurPASS Electrokinetic Analyzer (Anton Paar GmbH, Graz, Austria) in a 1 mM KCl background solution. To calculate the zeta potential from the measured streaming potential the Fairbrother–Mastin method was used, which was performed at 500 mbar and at room temperature (25 ± 1 °C). The zeta potential of each membrane sample was measured four times, by repeatedly reversing the direction of electrolyte flow at each pH value. Apparatus error counted for less than 0.5 mV of the measurement at any given pH value. Analytical grade potassium hydroxide and hydrochloric acid were used to regulate the pH via automatic titration.

According to Alturki et al. [16] the contact angle can be measured with a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) by means of the standard sessile drop method. Milli-Q water is used as the reference solvent. The membranes are air dried before the measurement. No less than 5 droplets are applied onto duplicate membrane samples and contact angle is measured on both sides of the droplet.

The surface topography for NF/RO membranes was investigated by means of atomic force microscopy (AFM). On the other hand, the surface morphology and distribution of organic compounds deposited on the membrane surface were examined using field-emission scanning electron microscopy (SEM) on a JEOL JSM-7500FA - (BRUKER-QUANTAX 400), with additional semi-quantitative energy dispersive spectrometer (EDS) analysis.

2.4 Model organic contaminants

Sixteen compounds were used in this study to represent the major organic groups considered contaminants in groundwater samples – namely volatile organic compounds (e.g. dichloromethane, trichloroethylene, tetrachloroethylene, toluene and benzene). The analysis of these compounds was also based on their widespread occurrence in groundwater and their diverse physicochemical properties (e.g. hydrophobicity and molecular size). Key physicochemical properties of these organic contaminants are shown in (Table 2). The volatile organic compounds had molecular weights between 78.11 g/mol (benzene) and 167.85 g/mol (1,1,2,2-tetrachloroethane). The intrinsic hydrophobicity of these compounds varied significantly, as was reflected by the values of their octanol-water partitioning

coefficient (Log K_{ow}) or Log K_{ow} at specific pH (Log D). As can be seen in Table 2, the properties of the selected volatile organic compounds demonstrated that some compounds are hydrophilic (Log D >2.5) while others are hydrophobic (Log D <2.5) and ranged between 1.40 and 3.07 (log D at pH 7 and 8). However, most volatile organic compounds which were examined in this study are hydrophobic (Log D <2.5).

Table 2: Summary of relevant physiochemical properties of selected volatile organic compounds.

Compound	CAS no.	Formula	MW (g/mol)	Log K_{ow} ^a	Log D ^a at pH 7	Log D ^a at pH 8
Vinyl chloride (Chloroethene)	75-01-4	C ₂ H ₃ Cl	62.50	1.69	1.69	1.69
1,1-Dichloroethene	57-53-4	C ₂ H ₂ Cl ₂	96.94	2.05	2.05	2.05
DCM: Dichloromethane	75-09-2	CH ₂ Cl ₂	84.93	1.40	1.40	1.40
trans-1,2-Dichloroethene	156-59-2	C ₂ H ₂ Cl ₂	96.94	2.14	2.14	2.14
cis-1,2 Dichloroethene	156-59-2	C ₂ H ₂ Cl ₂	96.94	2.14	2.14	2.14
1,1-Dichloroethane	75-34-3	C ₂ H ₄ Cl ₂	98.96	1.76	1.76	1.76
Chloroform	67-66-3	CHCl ₃	119.38	1.94	1.94	1.94
1,1,1-Trichloroethane	71-55-6	C ₂ H ₃ Cl ₃	133.40	2.35	2.35	2.35
CTC: Tetrachloromethane (Carbon Tetrachloride).	56-23-5	CCl ₄	153.82	2.92	2.92	2.92
1,2-Dichloroethane	107-06-2	C ₂ H ₄ Cl ₂	98.96	1.65	1.65	1.65
Benzene	71-43-2	C ₆ H ₆	78.11	2.18	2.18	2.18
TCE: Trichloroethylene (Trichloroethene)	79-01-6	C ₂ HCl ₃	131.39	2.57	2.57	2.57
Toluene	108-88-3	C ₇ H ₈	92.14	2.72	2.72	2.72
1,1,2-Trichloroethane	79-00-5	C ₂ H ₃ Cl ₃	133.40	1.92	1.92	1.92
PCE: Tetrachloroethylene (Tetrachloroethene or Perchloroethene)	127-18-4	C ₂ Cl ₄	165.83	3.07	3.07	3.07
1,1,2,2-Tetrachloroethane	79-34-5	C ₂ H ₂ Cl ₄	167.85	2.33	2.33	2.33

^a Reference source: SciFinder Scholar, data calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14 for Solaris (1994–2007 ACD/Labs).

2.5. Volatile organic compounds analysis

All samples collected before and after using the NF/RO filtration system were analysed at ORICA Botany Environmental Laboratories. VOCs were analysed using a Shimadzu purge

and trap/Gas Chromatography/Mass Spectrometer Detector based on USEPA Methods 5030 and 8260. Method 5030 can be utilised for most volatile organic compounds that have boiling points below 200 °C and are insoluble or somewhat soluble in water. This method can include volatile water-soluble compounds; nevertheless, quantification limits (by GC or GC/MS) are roughly ten times higher due to poor purging efficiency [17]. On the other hand, Method 8260 is utilised to determine volatile organic compounds in a range of solid waste matrices. This method is appropriate to nearly all types of samples, irrespective of water content, containing numerous air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils and sediments [18]. This method has an inert gas bubbled through a portion of the aqueous sample at room temperature, and the volatile components are efficiently conveyed from the aqueous phase to the vapor phase. In the subsequent step, the vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is finished, the sorbent column is heated and back flushed with inert gas to desorb the components onto a gas chromatographic column [17].

2.6. Analysis of basic water parameters

The temperature, turbidity, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), salinity, density, (SG) and redox (water quality parameters) were measured using Water Quality Analyser-MODEL 516 during sampling (see Table 3 and Table 4). On the other hand, the temperature, conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity meter in all experiments. The measurements were applied at 0 time, one hour and at 8 hours for each experiment.

Table 3: Water quality parameters for samples which were collected from EWB10D at Southlands-Botany Bay ^a.

Depth (m)	Turbidity (ntu)	Dissolved Oxygen (mg/l)	Electrical conductivity (µS/cm)	Total Dissolved Solids (g/l)	PH	Temperature (°C)	Senility (ppt)	Density (g/cm ³)	SG (t/m ³)	Redox (mV)
6.7	19.5	3.78	4270	3.73	4.6	22.03	2.28	999	1.000	- 107

^a All data were obtained using Water Quality Analyser (MODEL 516).

Table 4: Water quality parameters for samples which were collected from EWB13D at Southlands-Botany Bay ^a.

Depth (m)	Turbidity (ntu)	Dissolved Oxygen (mg/l)	Electrical conductivity (μS/cm)	Total Dissolved Solids (g/l)	PH	Temperature (°C)	Senility (ppt)	Density (g/cm ³)	SG (t/m ³)	Redox (mV)
4.49	19.5	3.78	1553	1.37	4.4	22	0.60	997	0.998	- 193

^a All data were obtained using Water Quality Analyser (MODEL 516).

2.7. NF/RO filtration protocol

Prior to each pressure driven filtration experiment, the membrane was compacted using Milli-Q water (8 L) for approximately 1 hour until a stable baseline flux was obtained. The compacting pressures were 12 and 18 bars for the NF and RO membranes, respectively. The Milli-Q water used for membrane compaction was replaced with 8 L of a solution containing contaminated groundwater. The cross-flow velocity flux was adjusted to 30.4 cm/s. The system was completely sealed and the feed reservoir temperature was kept constant at 4 ± 0.1 °C throughout the experiment using chiller device to avoid evaporation of these compounds. Permeate and feed samples of 40 mL (two duplicates) were collected after 1 hour and at 8 hours of filtration to analyse volatile organic compounds. All samples collected from both feed and permeate were sent immediately to ORICA Botany Environmental Laboratories for analysis. The rejection rate is defined by the equation:

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

where C_p and C_f are the permeate and the feed concentrations, respectively.

3. Results and discussion

3.1. SEM-EDS and AFM analysis

The AFM images of the ESPA2 and NF-90 membranes are described in Fig. 3 and 4, reveal different extents and occurrences of surface roughness. Surface topography of ESPA2, as seen in Fig. 3, shows a typical nodular (hills and valleys) morphology. This characteristic includes most RO membranes as reported in other studies ([19, 20]. The same applies to the NF-90 membranes used in this study (Fig. 4) with the hill to hill distance being much smaller, which associates completely with the much lower thickness of the active layer (15–40 nm for NF compared to 200–300 nm for RO). This morphology seems to be affected by means of the underlying supporting layer, and could be viewed as a fingerprint of the thin-film composite (TFC) polyamide (PA) membrane ([20]. Since these “valleys” are likely to be of irregular shape, such as the surface topography of the NF-90 membrane (Fig. 4), a lodged particle may not fully “plug” the “pore-like” valley; however it may considerably restrict flow through the opening. Thus, the valleys quickly become “clogged,” resulting in remarkable loss of permeate flux. In the case of the ESPA2 membrane (Fig. 3), the “valleys” are likely to have a slightly more regular shape and there will be less “valley clogging.” Even though the same number of particles are placed on the membrane, they would likely be more equally spaced leading to less overall flux decline (or fouling; [19].

Fig. 3: Surface topography image of ESPA2 membrane.

Fig. 4: Surface topography image of NF-90 membrane.

Comparison among the surface of virgin and fouled membrane samples is demonstrated in Fig. 5 and 6. SEM images clearly display the remarkable differences between the surface morphologies of the two membrane samples. While the foulant layer on the fouled membrane surfaces consisted of particulate matter embedded in an apparently amorphous matrix (Fig. 5B, 5C, 6B and 6C), the virgin membrane appeared clean with a quite smooth surface (Fig. 5A and 6A). Due to the roughness of NF and RO membranes, the colloids are located mainly in the valleys on the surface after filtration; i.e. “valley clogging” has taken place ([19, 21]. Nevertheless, the colloids are distributed over the entire membrane surface and formed a dense and uniform cake layer on the membrane surface due to hydrophobic interactions between the foulants and membrane surfaces ([22, 23].

Fig. 5: SEM images of the (A) virgin ESPA2 membrane, (B) ESPA2 membrane surface fouled by EWB10D and (C) ESPA2 membrane surface fouled by EWB13D at Southlands-Botany Bay.

Fig. 6: SEM images of the (A) virgin NF-90 membrane, (B) NF-90 membrane surface fouled by EWB10D and (C) NF-90 membrane surface by fouled EWB13D at Southlands-Botany Bay.

Distribution of elements deposited on the membrane surface which formed the fouling layer was obtained from SEM with additional semi-quantitative energy dispersive spectrometer (EDS) analysis. It was noticed that carbon, oxygen and sulphur were detected in all samples including the virgin membrane because they were parts of the membrane polymeric composition. Noteworthy, platinum existed in all samples, including the virgin membrane as a result of membrane coating. Specifically, a sulphur peak was observed with wastewater samples which were collected from both EWB10D and EWB13D at Southlands-Botany Bay indicating the participation of sulphate scale in fouling (see Fig. 7B, 7C, 8B and 8C). Small aluminium peaks were noticed on fouled ESPA2 and NF-90 membrane surfaces (Fig. 7C, 8B and 8C) and silicon as well (Fig. 8B) indicating their high scaling tendency even when present in a small amounts. Furthermore, a small level of sodium was found in the alginate fouling layer (Fig. 7B and 8B) as well as chlorine (Fig. 8B). The reasons for the deposition of foulants (Si, Al, Na and Cl) on the membranes are caused by the increase in membrane selectivity due to biofouling ([24].

Fig. 7: EDS data of the virgin ESPA2 membrane (A), ESPA2 membrane fouled by EWB10D (B) and ESPA2 membrane fouled by EWB13D (C) at Southlands-Botany Bay.

Fig. 8: EDS data of the virgin NF-90 membrane (A), NF-90 membrane fouled by EWB10D (B) and NF-90 membrane fouled by EWB13D (C) at Southlands-Botany Bay.

3.2. Removal of volatile organic compounds by the NF/RO system

To investigate the ability of the NF/RO membranes to remove volatile organic compounds from contaminated groundwater, several experiments were conducted for samples collected from EWB10D and EWB13D at Southlands-Botany Bay.

3.2.1. EWB10D at Southlands-Botany Bay

An overall comparison of NF-90 and ESPA2 membrane performances in terms of removal efficiency is presented in Table 5 and Fig. 9. The results in Table 5 and Fig. 9 exhibited that the performance of the NF-90 and ESPA2 membranes after one hour was better than after 8 hours. Moreover, it was observed that the ESPA2 membrane has a higher ability than the NF-90 membrane for rejecting volatile organic compounds. Additionally, it was notable that the performance of the NF-90 and ESPA2 membranes in rejecting hydrophilic compounds [(Log $D > 2.5$), carbon tetrachloride, trichloroethylene and tetrachloroethylene] was higher than that for its hydrophobic compounds rejection [(Log $D < 2.5$), other volatile organic compounds which are demonstrated in Table 2]. As stated by Nghiem et al. [15] the removal of some hydrophobic compounds can be actually lower than that expected based only on a steric hindrance transport model. It can be elucidated that hydrophobic compounds can adsorb to NF/RO membranes and then diffuse through the dense polymeric matrix, resulting in significant transport of these compounds across the ultra-thin active skin layer. On the other hand, because hydrophilic compounds do not adsorb to the membrane polymeric matrix, hydrophilic volatile organic compounds can be effectively rejected by NF/RO membranes using steric hindrance or size exclusion mechanisms. These results also support the findings which are reported in other previous studies [5].

It is noteworthy that the highest rejection achieved by NF-90 and ESPA2 for tetrachloroethylene reached 98.4 % for NF-90 and 100 % for ESPA2 while the lowest rejection achieved by NF-90 and ESPA2 was for dichloromethane and amounted to 27.6 % and 43.4 %, respectively. According to Wells [25] tetrachloroethylene has the highest Log D of the model foulants (3.07) and therefore it is considered to be a hydrophilic compound and it can be effectively rejected by NF/RO membranes using steric hindrance or size exclusion mechanisms, whereas dichloromethane has the lowest Log D of the model foulants (1.40) and it is classified hydrophobic compound and it can adsorb to NF/RO membranes and then

diffuse through the dense polymeric matrix, resulting in the lower removal for this compound compared to tetrachloroethylene [15].

Complete rejection of carbon tetrachloride, trichloroethylene, tetrachloroethylene and 1,1,2,2-tetrachloroethane by ESPA2 could be attributed to the sieving (or size exclusion) as result of the molecular weights of these compounds, (which are 153.82 g/mol, 131.39 g/mol, 165.83 g/mol and 167.85 g/mol respectively) higher than the molecular weight cut-off (MWCO) for NF-90 and ESPA (~100 Da). In other words, the sieving of large molecules (carbon tetrachloride, trichloroethylene, tetrachloroethylene and 1,1,2,2-tetrachloroethane) occurs because of the small size of the membrane pores and this phenomenon is named a steric hindrance effect that operates principally for neutral solutes [5, 26].

Table 5: Overall removal efficiency of the volatile organic compounds which were detected in EWB10D at Southlands-Botany Bay.

	NF90						ESPA2					
Compound Name	F1	P1	F8	P8	R @ 1hr (%)	R @ 8hrs (%)	F1	P1	F8	P8	R @ 1hr (%)	R @ 8hrs (%)
Vinyl Chloride	0.30	0.093	0.045	0.018	69.0	60.0	0.35	0.008	0.085	0.015	97.7	82.4
1,1-Dichloroethene	0.05	0.007	0.009	0.003	86.0	66.7	0.049	0.001	0.017	0.001	98.0	94.1
Dichloromethane	0.10	0.053	0.029	0.021	47.0	27.6	0.16	0.019	0.053	0.03	88.1	43.4
trans-1,2-Dichloroethene	0.20	0.04	0.043	0.018	80.0	58.1	0.28	0.002	0.083	0.010	99.3	88.0
1,1-Dichloroethane	0.050	0.009	0.011	0.003	82.0	72.7	0.056	0.001	0.023	0.001	98.2	95.7
cis-1,2-Dichloroethene	2.3	0.46	0.68	0.4	80.0	41.2	2.7	0.066	1.1	0.35	97.6	68.2
Chloroform	4.6	0.8	1.4	0.73	82.6	47.9	5.0	0.072	2.2	0.24	98.6	89.1
1,1,1-Trichloroethane	0.002	0.001	0.0017	0.001	50.0	41.2	0.002	0.001	0.0018	0.001	50.0	44.4
Carbon tetrachloride	6.0	0.22	1.1	0.05	96.3	95.5	8.0	0.001	2.7	0.001	100.0	100.0
1,2-Dichloroethane	3.3	0.94	1.5	1.2	71.5	20.0	3.4	0.81	2.0	0.59	76.2	70.5
Benzene	0.010	0.001	0.003	0.001	90.0	66.7	0.014	0.001	0.006	0.001	92.9	83.3
Trichloroethylene	4.4	0.12	0.98	0.34	97.3	65.3	5.3	0.002	1.9	0.032	100.0	98.3
1,1,2-Trichloroethane	1.4	0.28	0.77	0.22	80.0	71.4	1.6	0.032	0.97	0.075	98.0	92.3
Tetrachloroethylene	5.5	0.086	1.0	0.12	98.4	88.0	6.9	0.002	2.2	0.003	100.0	99.9
Chlorobenzene	0.009	0.001	0.002	0.001	88.9	50.0	0.009	0.001	0.004	0.001	88.9	75.0
1,1,2,2-Tetrachloroethane	3.4	0.32	2.1	0.24	90.6	88.6	3.3	0.038	2.6	0.058	98.8	97.8

Fig. 9: Overall removal efficiency of the volatile organic compounds which were detected in the contaminated groundwater EWB10D. The NF/RO membrane filtration experiment was conducted at an initial permeate flux of 41 L/m²h and temperature of 4 °C, with a cross-flow velocity of 30.4 cm/s. Samples were collected after 1 and 8 hours of filtration.

3.2.2. EWB13D at Southlands-Botany Bay

The removal efficiency for both NF-90 and ESPA2 are reported in Table 6 and Fig. 10. Only 11 volatile organic compounds were detected at this site, whereas in EWB10D site, 16 volatile organic compounds were detected. The findings shown in Table 6 and Fig. 10 confirm the results concluded above for EWB10D (part 3.2.1); however there are some differences between them based on the difference in concentrations of model foulants at this site compared to the previous site (EWB10D). In fact, the concentration of VOCs in EWB13D was much higher than in EWB10D as shown in Table 6 and hence the deposition rate of contaminants (colloids and particles which existed in the groundwater) on membrane layer was higher. This explains why the rejection of VOCs in EWB13D (Table 6) was lower than EWB10D (Table 5). This interpretation can be confirmed with AFM images of NF-90 and ESPA2 (Fig. 3 and Fig. 4), shows a typical nodular (hills and valleys) morphology and this contributes significantly to the accumulation of contaminants over the entire membrane surface. Table 6 and Fig. 10 display that the performance of the NF-90 and ESPA2 membranes after one hour was better than after 8 hours. Furthermore, it was observed that the ESPA2 membrane has a higher ability than the NF-90 membrane for rejecting volatile organic compounds. Moreover, it was noteworthy that the performance of the NF-90 and ESPA2 membranes in rejecting hydrophilic compounds [(Log D >2.5), trichloroethylene and

tetrachloroethylene] was higher than that of its hydrophobic compounds rejection [(Log D <2.5), other VOCs which are shown in Table 4]. The reason for this phenomenon has been explained above in part 3.2.1 for the reasons given by Nghiem et al. [15].

It is remarkable that the highest rejection achieved by NF-90 and ESPA2 for tetrachloroethylene and has reached 95.7 % for NF-90 and 96.2 % for ESPA2 while the lowest rejection achieved by NF-90 and ESPA2 was for 1,1-dichloroethane and has amounted of 41.2 % and 44.4 %, respectively. According to Wells [25] the Log D of tetrachloroethylene is 3.07 and therefore it is considered to be a hydrophilic compound and it can be successfully rejected by NF/RO membranes using steric hindrance or size exclusion mechanisms, whereas the Log D of 1,1-dichloroethane is 2.05 and thus it is classified as a hydrophobic compound and it can adsorb onto NF/RO membranes and then diffuse through the dense polymeric matrix, resulting in the lower removal for this compound compared to tetrachloroethylene (cf. [15]).

Table 6: Overall removal efficiency of the volatile organic compounds which were detected in EWB13D at Southlands-Botany Bay.

	NF90						ESPA2					
Compound Name	F1	P1	F8	P8	R @ 1hr (%)	R @ 8hrs (%)	F1	P1	F8	P8	R @ 1hr (%)	R @ 8hrs (%)
Vinyl Chloride	1.9	0.5	0.2	0.1	73.7	50.0	0.8	0.2	0.3	0.1	75.0	66.7
1,1-Dichloroethane	0.2	0.1	0.17	0.1	50.0	41.2	0.22	0.1	0.18	0.1	54.5	44.4
cis-1,2-Dichloroethene	1.1	0.3	0.3	0.1	72.7	66.7	0.8	0.2	0.4	0.1	75.0	75.0
Chloroform	2.2	0.7	0.2	0.1	68.2	50.0	1.2	0.3	0.8	0.2	75.0	75.0
Carbon tetrachloride	0.7	0.1	0.25	0.1	85.7	60.0	0.8	0.1	0.26	0.1	87.5	61.5
1,2-Dichloroethane	210	40	95	42	81.0	55.6	150	27	110	24	82.0	78.2
Benzene	0.2	0.1	0.1	0.055	50.0	45.0	0.2	0.05	0.1	0.05	75.0	50.0
Trichloroethylene	2.2	0.1	1.8	0.1	95.5	94.4	2.3	0.1	1.6	0.2	95.7	87.5
1,1,2-Trichloroethane	0.8	0.1	0.4	0.1	87.5	75.0	0.6	0.1	0.5	0.1	83.3	80.0
Tetrachloroethylene	2.3	0.1	2	0.1	95.7	95.0	2.1	0.08	2	0.1	96.2	95.0
1,1,2,2-Tetrachloroethane	1.0	0.1	0.7	0.1	90.0	85.7	1.1	0.1	0.7	0.1	90.9	85.7

Fig. 10: Overall removal efficiency of the selected volatile organic compounds which were detected in the contaminated groundwater EWB13D. The NF/RO membrane filtration experiment was conducted at an initial permeate flux of 41 L/m²h and temperature of 4 °C, with a cross-flow velocity of 30.4 cm/s. Samples were collected after 1 and 8 hours of filtration.

3.3. Performance of the NF/RO membranes

To examine performance of the NF/RO membranes regarding rejecting volatile organic compounds, it is essential to study the membrane permeate flux as a function of filtration time for samples that were collected from different sites (EW10D and EW13D at Southlands-Botany Bay).

3.3.1. EWB10D at Southlands-Botany Bay

Fig. 11 shows the evolution of the membrane permeate flux as a function of filtration time. Significant permeate flux decline could be observed with the NF-90 membrane exhibiting a permeate flux decline of 34.2 % over 8 hours. In contrast, indiscernible flux decline could be observed with the ESPA2 membrane that only exhibited a permeate flux decline of 1.7 % over 8 hours (Fig. 11); this can be attributed to membrane surface roughness. Indeed, there is a correlation between fouling tendency and the membrane surface roughness and this totally agrees with previous studies (e.g. [19, 23, 27]). As presented (Table 1) the NF-90 has a significant surface roughness of 63.9 nm whereas the ESPA2 has a slightly smoother membrane surface with a corresponding surface roughness (30.0 nm). The rougher surface of

NF-90 membrane induces a higher adsorption of VOCs and consequently covering and clogging the membrane mainly in the valleys on the surface after filtration; i.e. “valley clogging” has taken place. In particular, hydrophobic VOCs were readily adsorbed onto the fouled membrane and diffuse to the permeate side (see part 3.1). In fact, the ESPA2 did not show any measurable flux decline over roughly 8 hours of filtration time. On the other hand, there was a noticeable permeate flux decline by the NF-90 membrane and this is consistent with several previous studies (e.g. [16]). Clogging of membrane pores by organic molecules principally accounts for the flux decline observed in the fouled membranes. A reasonable explanation is that the membrane pores became narrower due to organic molecules being adsorbed onto the membrane polymer, especially chlorinated hydrocarbons in the contaminated water samples. Consequently, the smaller pore sizes of contaminated membranes would theoretically permit only molecules smaller than them to pass [5]. This would suggest that the membrane should become more effective at rejecting large contaminants as it becomes contaminated however this negatively affected the flux performance for the membrane.

Concentration polarization could play a significant role in reducing the rejection of VOCs and eventually affecting performance of membrane. It can explain that, the high rejection of certain VOCs lead to increase of VOCs at the membrane surface. Additionally, the existence of contaminants (colloidal particles) in the groundwater resulted in deposition of these contaminants over the entire membrane surface and formed a dense and uniform cake layer on the membrane surface due to hydrophobic interactions between the foulants and membrane surfaces. Thus, it can be concluded that both these situations will lead to concentration polarization effect affect critically the membrane performance.

Fig. 11: Permeate flux of the NF-90 and ESPA2 as a function of filtration time. Experiments were conducted at an initial permeate flux of 41 L/m²h and temperature of 4 °C, with a cross-flow velocity of 30.4 cm/s. Samples were collected after 1 and 8 hours of filtration. Samples were collected from EWB10D-Botany Bay.

3.3.2 EWB13D at Southlands-Botany Bay

Fig. 6 displays the evolution of the membrane permeate flux as a function of filtration time. The same pattern was observed in performance of the NF/RO membranes when they were used to examine the rejection of volatile organic compounds for samples were collected from EWB13D. As seen in Fig. 12, a noteworthy permeate flux decline was observed with the NF-90 membrane due to fouling and it exhibited a permeate flux decline of 49.2 % over 8 hours. In contrast, a slight flux decline could be observed with the ESPA2 membrane and it displayed a permeate flux decline of only 15.5 % over 8 hours which can be attributed to the surface roughness of the membrane. Obviously as reported in many studies, there is a strong relationship between fouling tendency and the membrane surface roughness (e.g. [19, 23, 27]). The NF-90 membrane has a significant surface roughness 63.9 nm whereas the ESPA2 membrane has slight smoother membrane surface with the corresponding surface roughness 30.0 nm as shown in Table 1. Therefore the ESPA2 membrane exhibited a slight flux decline over 8 hours of filtration time. The rougher surface of NF-90 membrane encourages a higher adsorption of VOCs and thus covering and clogging the membrane principally in the valleys on the surface after filtration; i.e. “valley clogging” has taken place. Especially, hydrophobic VOCs were readily adsorbed onto the fouled membrane and diffuse to the permeate side (see part 3.1). Another explanation for flux decline using the NF-90 membrane is due to physicochemical properties of the membrane, particularly pore size. Membranes having a larger pore size (e.g. NF-90) could be more affected with fouling compared to membranes

having smaller pore size (e.g. ESPA2 which is classified as nonporous [28]. This study revealed that permeate flux decline due to membrane fouling would be more severe with membranes having a larger pore size.

Concentration polarization could play a crucial role in decreasing the rejection of VOCs and eventually affecting performance of membrane. It can elucidate that, the high rejection of certain VOCs result in increase of VOCs at the membrane surface. Furthermore, the existence of contaminants (colloidal particles) in the groundwater lead to deposition of these contaminants over the entire membrane surface and formed a dense and uniform cake layer on the membrane surface as a result of hydrophobic interactions between the foulants and membrane surfaces. Accordingly, it can be concluded that both these scenarios will lead to concentration polarization effect affect critically the membrane performance.

Fig. 12: Permeate flux of the NF-90/ESPA2 membranes as a function of filtration time. Experiments were conducted at an initial permeate flux of 41 L/m²h and temperature of 4 °C, with a cross-flow velocity of 30.4 cm/s. Samples were collected after 1 and 8 hours of filtration. Samples were collected from EWB13D-Botany Bay.

4. Conclusion

Results reported in this study indicate that NF/RO membrane filtration can achieve enhanced removal efficiency over the wide range of volatile organic compounds which were detected in groundwater collected from EW10D and EW13D, respectively. Findings of this study revealed that the performance of the NF-90 and ESPA2 membranes after one hour was better than after 8 hours when using these membranes for the removal of volatile organic compounds at the two sites (EW10D and EW13D). Furthermore, this study revealed that the

performance of NF and RO membranes in rejecting hydrophilic volatile organic compounds was higher than that for hydrophobic compounds and the highest rejection achieved by NF and RO membranes amounted 98.4 % and 100 %, respectively. Hydrophilic compounds can be effectively rejected by NF/RO membranes using the size exclusion mechanism (steric hindrance), whereas hydrophobic compounds can be adsorbed into NF/RO membranes and then diffuse through the dense polymeric matrix, resulting in the lower removal for these compounds compared to hydrophilic compounds. Also findings of this study indicate that membrane fouling significantly affects the rejection of volatile organic compounds by NF-90 membranes, however is less significant for thin film composite ESPA2 membrane. Flux decline through the NF-90 and ESPA2 membranes in this study could be attributed to physicochemical properties of the membranes in particular surface roughness and pore size.

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