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Membrane distillation for wastewater reverse osmosis concentrate treatment with water reuse potential

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Abstract

Membrane distillation (MD) was evaluated as a treatment option of wastewater reverse osmosis concentrate (WWROC) discharged from wastewater reclamation plants (WRPs). A direct contact MD (DCMD), at obtaining 85% water recovery of WWROC showed only 13-15% flux decline and produced good quality permeate (10-15 $\mu\text{S}/\text{cm}$, 99% ion rejection) at moderate feed temperature of 55 °C. Prevalent calcium carbonate (CaCO_3) deposition on the MD membrane occurred in treating WWROC at elevated concentrations. The combination of low salinity and loose CaCO_3 adhesion on the membrane did not significantly contribute to DCMD flux decline. Meanwhile, high organic content in WWROC (58-60 mg/L) resulted in a significant membrane hydrophobicity reduction (70% lower water contact angle than virgin membrane) attributed to low molecular weight organic adhesion onto the MD membrane. Granular activated carbon (GAC) pretreatment helped in reducing organic contents of WWROC by 46-50%, and adsorbed a range of hydrophobic and hydrophilic micropollutants. This ensured high quality water production by MD (micropollutants-free) and

enhanced its reuse potential. The MD concentrated WWROC was suitable for selective ion precipitation, promising a near zero liquid discharge in WRPs.

Keywords: Direct contact membrane distillation; micropollutants; organic fouling; pretreatment; reverse osmosis concentrate; wastewater reclamation.

1. Introduction

It is becoming a common practice for wastewater reclamation plants (WRPs) around the world to use reverse osmosis (RO) technology as a final polishing treatment [1,2]. Although RO is capable of maintaining a high grade water standard, a substantially large volume of wastewater RO concentrate (WWROC) is produced, generally comprising 20–25% of the feed stream volume [3,4]. WWROC contains elevated level of ions and salts present in the original wastewater including micropollutants that may be toxic or bio-accumulative [4]. As a result, stricter WWROC discharge regulations are being enforced in many countries [5]. For instance, two medium scale WRPs treating wastewater biologically in New South Wales in Australia (Homebush bay and St. Marys WRPs) are using RO technology as a final treatment process. On a daily basis, around 2000 kL of water is treated by RO in the Homebush bay WRPs, resulting in substantially large volumes of WWROC (300 kL/day) that contain inorganic ions and dissolved organic carbons (DOCs) as well as pharmaceuticals and personal care products (PPCPs) micropollutants [6,7]. A direct disposal of WWROC containing micropollutants into water bodies would pose eco-toxicological risk and threaten aquatic eco-system in the long-term, necessitating an appropriate treatment of WWROC prior to disposal.

This has led to significant attention on various approaches to sustainably manage WWROC discharge in WRPs. Conventional methods such as coagulation and granular activated carbon (GAC) as well as advanced technologies such as ozonation, electrochemical oxidation and photocatalysis are effective for treating WWROC contaminants, specifically in the reduction of DOCs as well as selective micropollutants [4]. Nonetheless, high operational costs and application in a large-scale

operation are the drawbacks of such processes [4,8]. Rather than treating WWROC followed by discharge, a more feasible approach for WRPs would be to obtain zero liquid discharge (ZLD) of WWROC. Suitable methods such as thermal evaporators, crystallizer, spray driers and brine concentrators have been evaluated [1]. However, large feed volume and size of evaporators can contribute to a significant increase in WRPs' operation cost and land usage. Essentially, pre-concentrating WWROC would be effective in downsizing the evaporator system and its related cost [9,10]. Furthermore, a method that enables to produce high quality water while concentrating WWROC would be a highly beneficial for water reuse purposes. One such suitable technology is membrane distillation (MD).

MD is a thermal integrated membrane process that operates by transporting water vapor through the pores of a hydrophobic membrane to the distillate (permeate) side. At moderate MD feed temperature settings (50-70 °C), the thermal requirement can be met by solar or heat waste integration [11]. The mass transfer mechanism of vapor in MD potentially offers complete rejection of ions. As WWROC generally contain low salinity and dissolved ions compared to seawater ROCs (SWROC) from seawater RO desalination plant, MD could achieve higher water recovery and ion rejection rate of WWROCs, producing a good quality permeate with possibly less scaling issues [12,13]. On the other hand, WWROC contains larger amount of DOCs, as well as trace micropollutants [1]. The presence of these elements in WWROC must be given due consideration in acquiring the feasibly highest water recovery rate under MD operation. Our previous MD studies established the phenomena of humic substance (HS) disaggregation to lower molecular weight (LMW) organics under thermal MD operation, depositing onto the membrane, resulting in reduced membrane hydrophobicity, as well as diffusion through the membrane pore [14,15]. A simple GAC filter pretreatment for DOC removal was recommended prior to DCMD operation to reduce organic fouling potential on MD membrane.

At the same time, as a system with high capacity to retain non-volatile compounds, MD would most likely exhibit superior micropollutants' rejection rate over other membrane processes such as micro filtration (MF) and nanofiltration (NF) which remove micropollutants via size hindrance/electrostatic interaction. For instance, Shanmuganathan et al. [7] reported that an effective rejection of micropollutants from WWROC was achieved only upon a combination of dual membrane of MF and NF with GAC adsorption. Comparatively, Wijekoon et al. [17] established the capability of MD to reject a wide range of micropollutants. It must however be acknowledged that MD rejection of the micropollutants is subjected to its volatility. At the same time, the impact of micropollutant adhesion on hydrophobic MD membrane must be evaluated.

In addition to reducing WWROC volume, recovering beneficial salts from WWROC can help to offset the treatment costs [1]. Zhang et al. [18] evaluated the viability of recovering valuable compounds from WWROC by applying electrodialysis (ED) and ion exchange membranes. However, these techniques led to scaling events, requiring mitigating measures such as acidification. As MD is capable of concentrating feed solutions, the prospect of precipitating selective salts and recovering valuable ions from MD concentrated WWROC should be evaluated.

Therefore, this study aims to evaluate the potential of MD to achieve high water recovery in treating ROCs from WRPs (WWROC), systematically reducing WWROC volume as well as supersaturating the concentrate for salt precipitation. Permeate quality, tendency of scaling and fouling development as well as the rejection rate of micropollutants were the main factors used in determining the feasibility of MD for water recovery from WWROCs. For this purpose, the performance of a direct contact membrane distillation (DCMD) in treating WWROC from Sydney Olympic Park Authority's (SOPA) WRP was tested. Further, GAC pretreated WWROC and synthetic WWROC solutions were also used, specifically to study the scaling and organic fouling pattern. Membrane characterization and detailed inorganic and organic analysis were carried out. Potential precipitation of salts from supersaturated WWROC solution was evaluated as an additional benefit to this approach.

2. Materials and methods

2.1 Direct contact membrane distillation (DCMD)

Direct contact membrane distillation (DCMD) is the most widely used configuration in MD due to its simplicity [19]. As such, a bench-scale DCMD was used in this study as shown in Fig. 1. The membrane cell was made of acrylic with depth, width, and length of 0.2 cm, 5.0 cm and 8.0 cm, respectively. A hydrophobic polytetrafluoroethylene (PTFE) flat sheet membrane (General Electric, US) was used with a 40 cm² effective membrane area for mass transfer. The membrane support layer is made of polypropylene. The porosity, average pore size and membrane thickness provided by the supplier were 70–80%, 0.2 μm, and 179 μm, respectively [15].

A moderate temperature of 55 °C was used as feed temperature (T_f). This is based on our previous study that showed organic fouling reduction at lower feed temperature [14]. Deionized (DI) water was used as the initial permeate solution, which was set at a permeate temperature (T_p) of 25 °C. The bulk temperatures were maintained at ± 3 °C for all experiments. The feed and permeate solutions (2 L each) were channelled into the membrane cell at a feed and permeate flow velocity (v_f and v_p) of 1.1 m/s in a counter current mode with a gear pump.

Fig. 1 Experimental setup of DCMD.

2.2 Feed solutions

2.2.1 Real/Untreated WWROC

The real/untreated WWROC was collected from Sydney Olympic Park Authority's (SOPA) WRP. The SOPA WRP treats the combined water of storm water and biologically treated sewage effluent. This WRP uses the following treatment operations consisting of biological treatment, and microfiltration for removal of particulate matter as well as pathogens, followed by RO for minimizing total dissolved salts and PPCPs. The RO is operated at a volumetric feed flow of 55 m³/h, achieving about 80% water recovery. Overall, SOPA WRP discharges around 300 kL of WWROC/day directly into a sewer system. The ionic composition of the untreated WWROC collected from SOPA WRP is listed in Table 1. The total dissolved solids (TDS), turbidity, and pH of the WWROC were 1.49 ± 0.12 g/L, 0.11 ± 0.02 NTU, and 8.01 ± 0.34 , respectively. Further, it contained a high amount of DOC in the range of 58-60 mg/L.

2.2.2. Synthetic inorganic WWROC

A synthetic inorganic WWROC was prepared from analytical grade salts to have the similar ion mass composition and TDS as the real/untreated WWROC from SOPA WRP (Table 1). The synthetic WWROC was used to study the inorganic scaling pattern without the presence of organics. This would enable to effectively establish the influence of organics in scaling formation and permeate flux decline.

2.2.3. Pretreated WWROC

The real/untreated WWROC was pre-treated by a batch adsorption using 5 g/L of GAC based on the results from a previous study [6]. Coal-based GAC (MDW4050CB, James Cumming & Sons Pty Ltd) was used and its particle size was in the range of 425 and 600 μm . The average pore diameter and surface area of GAC were 30 Å and 1000 m²/g, respectively. The pretreated WWROC feed solution was used to evaluate the scaling and fouling development in MD in comparison to the

real/untreated WWROC. The purpose of adsorption as pretreatment was to reduce the organic fouling on MD membrane by removing organic compounds.

Table 1 Ionic composition of real/untreated WWROC from SOPA WRP.

Ions	Concentration (mg/L)
Ca ²⁺	88.2
Mg ²⁺	72.0
Na ⁺	445.2
K ⁺	63.4
Sr ²⁺	0.7
Si as SiO ₂	1.9
SO ₄ ²⁻	198.1
Cl ⁻	605.3
PO ₄ ³⁻ as total P	2.8
F ⁻	2.7
NO ₃ ⁻ as N	7.8
Hardness as CaCO ₃	459.3

2.3. Analytical measurements

2.3.1. Water quality and ionic characterization

The pH and conductivity of feed and permeate solution were measured using HQ40d portable meter (Hach, USA). The initial and final dissolved ionic concentrations of feed and permeate solution were measured using inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500, Agilent, USA).

2.3.2. Organic characterization

The detailed organic fraction of the initial and final feed and permeate solution as well as the membrane foulant were determined as a DOC concentration using a liquid chromatography with organic carbon detection (LC-OCD) as described in our previous study [14]. To evaluate the foulant on the used MD membrane, small portions (6.25 cm^2) of the membrane (40 cm^2) were placed in beakers containing MQ water and acid solution (0.1 % citric acid). The beakers were sonicated to extract the organic residues on the MD membrane. This sonication was carried out in an ultrasonic bath (Powersonic 420, Thermoline Scientific, 300 W) for a short time (10 min) to prevent organic matter from denaturing and any biological modification [15]. The solutions were analyzed using LC-OCD.

2.3.3. Membrane characterization

2.3.3.1. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS)

The morphology of the membrane surface was examined using a scanning electron microscope (SEM, Zeiss Supra 55VP). It was coupled with a Bruker XFlash silicon drift detector energy-dispersive spectroscopy (EDS) to obtain the chemical composition information. Prior to SEM analysis, the membrane samples were dried in a desiccator and subsequently analyzed without any further treatment. SEM imaging was conducted at a voltage of 5 kV while a spot diameter of about 3 nm was used for the EDS analysis.

2.3.3.2. Water Contact angle

Water contact angle measurement on MD membrane was used to determine i) the hydrophobic reduction of the membrane upon MD operation (used MD membranes) and ii) the hydrophobicity recovery after membrane cleaning (washed MD membranes). Small portions of the used membranes (6.3 cm^2 of 40.0 cm^2) were placed in a beaker containing Milli-Q (MQ) water and acid solution (0.1% citric acid). The beakers were stirred at 120 rpm for 5 h and thereafter, the MQ and acid washed membrane coupons were air-dried prior to analysis. The water contact angle measurement was carried out by sessile drop method using a goniometer (Theta Lite) with 1.8–2.0 mL of MQ water droplet on the dried membrane surface. Measurements were repeated 5 times and the average reading was reported.

2.3.3.3. Zeta potential

Zeta potential was measured to compare the membrane surface charges of the virgin, used and cleaned MD membrane. The measurement was carried out with a Nano surface zetasizer cell cuvette dipped in a negatively charged standard solution containing trace particles (Nano ZS Zen3600, Malvern, UK). This instrument detected the membrane surface zeta potential by a set method of measuring the electrophoretic mobility of the solution trace particles at varying distances from the planar membrane surface in the cuvette. The magnitude of the particle electrophoresis and the electro-osmosis generated by the wall zeta potential was used to automatically derive the zeta potential at the wall surface. All measurements were carried out in triplicates with a R^2 of 0.95 to 0.99.

2.3.4. Fouling reversibility

Membrane fouling reversibility and effectiveness of membrane washing were evaluated by carrying out repeated cycles of MD operation followed by membrane cleaning using the same membrane.

2.3.5. Micropollutants

The micropollutants' concentrations were detected by high performance liquid chromatography (HPLC) with tandem mass spectrometry detector. Initial and final feed, and permeate solutions of untreated and pretreated WWROC before and after MD operation were analysed. In order to measure the micropollutants, firstly, a solid phase extraction procedure was used to extract 5 mL of samples using 500 mg hydrophilic/lipophilic balance cartridges (Waters, Milford, MA, USA). Subsequently, the samples were separated using an Agilent (Palo Alto, CA, USA) 1200 series HPLC system equipped with a 150 x 4.6 mm², 5 µm particle size, LunaC18(2) column (Phenomenex, Torrance, CA, USA). Mass spectrometry was executed using an API4000 triple quadrupole mass spectrometer (Applied Biosystems, Foster City, CA, USA) equipped with a turbo-V ion source employed in both positive and negative electro-spray modes. All calibrations had a correlation coefficient of 0.99 and above.

A variety of micropollutants (PPCPs) classes were detected in the WWROC solution. The PPCPs were categorized based on class type with their detailed physical/chemical properties (Table 2).

The molecular weight (MW) and charge, Log D value and vapor pressure of the detected PPCPs were obtained from commercial software Advanced Chemistry Development (ACD/I-Lab) [20]. The charge and LogD values are reported at pH 8.0 based on the pH of WWROC (as described in Section 2.2.1). The volatility was represented by pK_H, which is defined as $-\log_{10}K_H$, with K_H being Henry's law constant at 25°C, obtained from Chemspider [21]. A lower pK_H indicates a higher volatility of the compound [17]. It is important to note that the pK_H values at 55 °C (which was used as feed temperature in the MD experiment) could differ slightly from the values presented in Table 2.

Table 2 Micropollutants' characteristics and their concentrations in the real/untreated WWROC feed solution.

Chemical name	Molecular Weight (g)	Charge (pH 8.0)	Log D (pH 8.0)	Vapor pressure mmHg at 55 °C	pK _H	Concentration in untreated WWROC (ng/L)
Household products & industrial chemicals						
Benzotriazole	119.1	0	1.54	7.78x10 ⁻⁴	9.19	4560
Benzophenone	214.2	0	2.98	1.54x10 ⁻²	5.68	963
Propylparaben	180.2	0	2.75	1.77x10 ⁻²	6.86	54
Triclocarban	315.6	0	5.06	1.83x10 ⁻³	8.64	25
Triclosan	289.5	0	5.15	1.03x10 ⁻³	6.42	35
n-Nonylphenol	220.3	0	5.95	2.33x10 ⁻³	5.18	28
Oxybenzone	228.2	0	3.86	2.21x10 ⁻⁴	7.54	136
Antibiotics/ prescription drugs						
Sulfamethoxazole	253.3	-	-1.23	2.83x10 ⁻⁷	10.96	768
Carbamazepine	236.3	0	2.23	3.36x10 ⁻⁵	8.81	723
Salicylic acid	138.1	-	-1.62	1.36x10 ⁻²	8.82	254
Diclofenac	296.2	-	1.06	1.59x10 ⁻⁷	8.28	74
Caffeine	194.2	0	0.11	3.72x10 ⁻⁷	12.15	54
Omeprazole	345.4	0	2.37	0	13.19	25
Primidone	218.3	0	0.55	1.66x10 ⁻⁸	13.79	<20
Meprobamate	218.3	0	1.02	7.52x10 ⁻⁶	7.59	<20
Fire retardant						
TCEP ^a	285.1	0	1.14 ^b	n.a	6.76	507
Hormone						
Bisphenol A	228.3	0	3.45	3.24x10 ⁻⁵	9.40	203
Pesticide/Herbicide						
Diuron	233.1	0	2.70	1.66x10 ⁻⁴	8.02	249
Atrazine	215.7	0	2.53	4.51x10 ⁻⁴	7.42	50
Simazine	201.7	0	2.20	2.20x10 ⁻⁸	8.38	<20

Physio-chemical information was obtained from [20] and [21]; ^aTECP is tri(2-chloroethyl)- phosphate; ^bLogD was measured at pH 7.4 n.a- non available

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3. Results and discussion

This study aims to i) evaluate the potential of MD for high water recovery from WWROC, which reduces the volume of WWROC discharged and supersaturates the concentrate for salt precipitation, ii) operate MD in a sustainable manner (by reducing fouling with moderate feed temperature operation), and (iii) produce safe water (micropollutant-free) with suitable pretreatment. For these purposes, three different WWROC feed solutions (real/untreated, pretreated and synthetic) were used. The details of these feed solutions are described in Section 2.2.

3.1. WWROC treatment by MD

3.1.1. Flux decline

An initial MD permeate flux of around 16 kg/(m²-h) was achieved with the WWROC solutions (untreated, synthetic and pretreated) (Fig. 2a). As the WWROC was concentrated by a 7 times volume concentration factor (VCF) to obtain 85% water recovery, a gradual flux decline (13-25%) was observed. The untreated WWROC showed a slightly higher flux decline (20-25%), compared to the pretreated WWROC (13-16%), which could be attributed to the high organic content in the saturated untreated WWROC. Low salinity (2-3 g/L) of WWROC was an advantage in achieving high water recovery with minimal impact on the MD flux performance compared to rapid and sharp flux decline with SWROC. The high salinity concentration of SWROC decreases the water vapor partial pressure due to the decrease in the solution activity coefficient, resulting in more prevalent flux decline [22]. On the other hand, compared to SWROC, WWROC contains higher organics. Thus, the organic fouling development must be evaluated.

3.1.2. Permeate quality

A high quality permeate was maintained up to 85% of water recovery. A final permeate conductivity of 10-15 µS/cm was maintained for all WWROC feed solutions, achieving 99% ion rejection.

Fig. 2. Untreated, pretreated and synthetic WWROC (a) permeate flux as a function of feed volume concentration factor (VCF), and (b) membrane SEM images (c) membrane EDX element analysis ($T_f = 55\text{ }^{\circ}\text{C}$, $T_p = 25\text{ }^{\circ}\text{C}$, $v_{f,p} = 1.1\text{ m/s}$).

3.2. Membrane analysis

3.2.1. SEM-EDX

The presences of significant amount of crystals were evident on the MD membrane with synthetic and pretreated WWROC, even at low SEM magnification (1,000x) (Fig. 2b). On the other hand, MD membrane with the untreated WWROC appears to show only small amount of crystal scatterings at low magnification. This could be due to the presence of high DOC contents in the untreated WWROC. It has been established that DOCs such as humics, act as a binding agent for inorganics such as Ca, inhibiting the crystal growth but forming large colloid like scale deposition [14,23].

At high SEM magnification (15,000x), the presence of rhombohedron and hexagon shaped crystals, likened to CaCO_3 [24] were observed on the MD membrane with untreated and pretreated WWROC (Fig. 2b). Comparatively, different crystal formation shape was observed on the MD membrane with synthetic WWROC (which only contained inorganic ions) with clear occurrence of aragonite and vaterite type CaCO_3 . Previous studies have shown the tendency of aragonite and vaterite CaCO_3 crystal formation (described as ‘morning star CaCO_3 ’), due to the presence of inorganics such as magnesium and sulphate, which suppress crystal transformation to calcite CaCO_3 [24-26]. The presence of organics appears to break these star shaped CaCO_3 crystals into small rhombohedron colloids [27]. This was especially evident with the flattened crystals on the membrane with untreated WWROC that appeared to show almost no presence of crystal formation at low SEM magnification. The EDX analysis showed that Ca was the main deposit on the membrane with small peaks of Mg, Cl, Na and P. However no peaks of S and K were observed, confirming these two elements were not involved in the scaling (Fig. 2c). Hence the presence of Mg was most likely the contributing factor to the star shaped CaCO_3 crystals in WWROC.

It must be highlighted that the loose deposition of inorganics on the MD membrane with the synthetic and pretreated WWROC did not cause significant flux decline. Similarly, other MD studies also reported insignificant flux decline by CaCO_3 compared to sharp flux decline by CaSO_4 . This

was due to bulk precipitation of CaCO_3 and beneficial acidification of the solution and membrane by CO_2 formation under thermal condition [28,29]. Comparatively, in the case of untreated WWROC, as the feed concentration increased with the DCMD operation, a formation of brownish colloid like substances of humics with inorganics was observed. This resulted in a thick fouling layer on the membrane, which could have contributed to the slightly higher flux decline (Fig. 2a).

3.2.2. Contact angle and zeta potential

The water contact angle measurement showed that the hydrophobicity of the used MD membrane with untreated WWROC could not be restored to its original condition (virgin membrane: $139.4 \pm 1.5^\circ$) with MQ water washing ($18.9 \pm 0.7^\circ$) and acid washing ($26.8 \pm 2.3^\circ$) (Fig. 3a). On the other hand, the hydrophobicity of the MD membrane used with pretreated WWROC was mostly restored ($123.6 \pm 2.3^\circ$) with chemical cleaning (0.1% citric acid). The significant hydrophobicity loss of MD membrane with untreated WWROC could be due to the combined adhesion of hydrophilic organics and inorganic CaCO_3 on the membrane. Invariably, the synthetic WWROC (which contain no organic related matters), showed restored hydrophobicity upon membrane washing with MQ water ($109.8 \pm 1.7^\circ$) and acid ($125.1 \pm 1.7^\circ$). This was similar to the MD membrane with pretreated WWROC.

The zeta potential of virgin and used MD membranes (untreated, pretreated and synthetic WWROC) was measured to evaluate the changes on the membrane surface charge (Fig. 3b). The fouling layer reduced the negative charge of the virgin membrane (-41.1 ± 0.7 mV). Upon membrane washing, the initial charge was able to be restored. The MD membrane with synthetic WWROC showed the lowest surface charge at -16.1 ± 0.9 mV compared to the untreated WWROC (-20.4 ± 1.3 mV) and pretreated WWROC (-20.8 ± 0.8 mV). This could be related to the positively charged CaCO_3 deposition on the synthetic WWROC [30]. Nevertheless, the membranes with pretreated and synthetic WWROC showed higher membrane surface charge restoration capacity compared to the case of untreated WWROC.

Fig. 3. MD membrane (virgin, used and washed -MQ and acid) (a) water contact angle and (b) surface zeta potential.

3.3. Scaling with WWROC

The initial pH of WWROC feed solutions (untreated, pretreated and synthetic) were in the range of 7.8 and 8.0, while the pH of the final concentrated solutions increased slightly between 8.5 and 9.0. The inorganic ion concentrations of the initial and final untreated and pretreated WWROC solutions are presented in Table 3. The major ions present in the WWROC solution were Na^+ , Ca^{2+} , Mg^{2+} , K^+ , SO_4^{2-} and Cl^- . The ion mass balance between the initial and final WWROC solution concentration showed that amongst the major ions, a significant mass reduction of Ca^{2+} (89 - 91%) and CO_3^{2-} (54 - 62%) occurred in the final WWROC solution. Additionally, a lower mass reduction of Mg^{2+} (33 - 44%), Na^+ and K^+ (20 - 30%), Cl^- and SO_4^{2-} (<12%) was observed. The ion mass reduction was associated to precipitation of crystal formation during the MD operation. Based on the mass reduction shown in Table 3, CaCO_3 was most likely the dominant scalant under this operating condition. Further, the saturation index value was calculated to predict the propensity of scale formation due to the feed solution characteristics. In this context, the Langelier Saturation Index (LSI) was used as it a common saturation index for determining the potential of CaCO_3 scale formation [31,32]. A solution showing LSI value above zero is considered to be supersaturated, resulting in CaCO_3 formation, while a LSI value below zero would indicate that the solution is undersaturated for CaCO_3 formation. The calculated LSI value was 0.8 for the initial WWROC solution, while it was 1.7 and 2.0 for the final untreated and pretreated WWROC. The LSI value (0.8) of the initial WWROC feed solution indicated that in its natural condition, the feed solution displays tendencies to form CaCO_3 crystals. Upon MD concentration, the high LSI values (1.7-2.0) indicated the further enhanced supersaturated condition for CaCO_3 formation for both the untreated and pretreated WWROC. This was in line with the observation deduced from the WWROC membrane SEM-EDX analysis that detected CaCO_3 crystal formation (Fig. 2b and c).

Table 3 Composition of main ions in untreated and pretreated WWROC (initial and final feed solution) upon DCMD operation.

	WWROC concentration (mg/L)			WWROC mass (mg)		
	Initial feed solution		Final feed solution	Initial feed solution		Final feed solution
	untreated & pretreated	untreated	pretreated	untreated & pretreated	untreated	Pretreated
Ca ²⁺	88.1	80.2	70.1	175.3	18.4	16.1
Mg ²⁺	72.2	320.1	380.3	131.3	73.6	87.4
Na ⁺	445.3	2760.1	2970.0	890.1	634.8	683.1
K ⁺	63.1	375.0	420.2	126.2	86.3	96.6
Sr ²⁺	0.7	2.0	1.7	1.4	0.6	0.4
Si as SiO ₂	1.9	11.2	12.3	3.7	2.6	2.8
SO ₄ ²⁻	198.1	1530.3	1650.2	396.2	351.9	425.5
Cl ⁻	605.3	4350.1	5150.4	1210.1	1000.5	1184.5
PO ₄ ³⁻ as total P	2.82	0.9	0.8	4.6	0.2	0.9
F ⁻	2.65	8.1	10.2	5.31	1.8	2.3
NO ₃ ⁻ as N	7.8	51.2	52.6	15.5	14.8	12.2
Hardness as CaCO ₃	459.2	1520.4	1850.1	918.3	349.6	425.5
LSI (pH _s)*	0.8 (7.2)	1.7 (7.0)	2.0 (7.0)			

*The LSI was calculated using initial and final feed solution TDS and pH values at 25°C, pH_s is saturation pH

3.4. Organic fouling with WWROC

The presence of organics appears to contribute to a slightly higher flux decline as well as to a significant loss of membrane hydrophobicity. To evaluate the fouling pattern in DCMD due to the presence of organics in WWROC, a detailed organic analysis was carried out using LC-OCD.

3.4.1. Feed and permeate organic characteristics

The initial feed solution of untreated WWROC contained 58.9 mg/L of DOC comprising mainly of HS (17.73 mg/L) and LMW organics including building blocks (36.68 mg/L) (Fig. 4a and Table 4). The pretreatment with 5 g/L of GAC was able to remove biopolymer (BP) and HS, which are relatively high molecular weight (HMW) organic compounds, by around 90%, resulting in a lower initial DOC of 31.97 mg/L containing mainly of LMW organics in the pretreated WWROC (Fig. 4b and Table 4). In a batch adsorption study with GAC, Shanmuganathan et al. [6] reported an 80% DOC removal from WWROC. The effectiveness of GAC for removal of HMW organic substances, such as BP and HS through adsorption has also been well established in other studies [33-35].

The DOC content in the initial and final permeate solutions remained low (Fig. 4 and Table 4), indicating that organics did not penetrate into the membrane pores. However, the DOC concentration of the final feed solution was 40-50% lower than the expected value for 7 times concentration (VCF 7) of the initial DOC feed solution. For instance, for the untreated WWROC, based on the initial feed solution DOC concentration (58.87 mg/L), the expected final feed concentration (upon 7 times of concentration) would be around 412.02 mg/L, however the detected value was only 205.53 mg/L (Table 4). As DOC was not detected in the permeate side, the reduced final feed DOC concentration could presumably be attributed to its binding with inorganic scalants in the bulk feed solution forming colloids and adhesion onto the membrane as organic foulant.

Fig. 4. Feed and permeate solution LC-OCD chromatogram of (a) untreated WWROC and (b) pretreated WWROC (BP- Biopolymers, HS- Humic substances, BB- Building blocks).

Table 4 Organic composition of untreated and pretreated WWROC (initial and final feed and permeate solution).

	Total DOC	Hydrophobic DOC	Hydrophilic DOC	BP*	HS*	BB*	LMW organics
Untreated WWROC (mg/L)							
Initial permeate	0.38	n.q.	0.38	0.01	<0.01	n.q.	0.39
Final permeate	0.55	0.08	0.45	0.02	0.03	0.023	0.39
Initial feed	58.87	n.q.	58.87	4.45	17.73	8.30	28.38
Final feed	205.35	3.11	202.23	12.68	89.75	47.01	52.79
Membrane organic content - 1.76 mg/cm ²							
Pretreated WWROC (mg/L)							
Initial permeate	0.48	n.q.	0.48	0.047	0.11	0.05	0.22
Final permeate	0.53	0.14	0.39	0.044	0.04	0.04	0.27
Initial feed	31.97	n.q.	31.97	2.11	1.96	1.08	26.83
Final feed	131.65	n.q.	131.65	20.34	47.43	n.q.	64.20
Membrane organic content – 0.84 mg/cm ²							

*BP- Biopolymers, HS- Humic substances, and BB- Building blocks

3.4.2. Organic foulant deposition on membrane

The foulant deposited on the membrane was extracted with MQ water as well as chemical agent (citric acid). The results showed that the membrane foulant predominantly contained of LMW organics (Fig. 5). Only a small portion of foulant on the membrane with untreated WWROC was able to be extracted with MQ water washing, necessitating chemical washing to remove the remaining foulant. Comparatively, a majority of foulant depositions on the pretreated WWROC membrane could be extracted with MQ washing. Further, a higher deposition of organics was present on the MD membrane with untreated WWROC (1.76 mg/cm^2) of membrane compared to the pretreated WWROC (0.84 mg/cm^2) (Table 4). The organic mass on the membrane per membrane area (40 cm^2) was calculated based on the mass difference between the initial and final feed and permeate solution organic content.

It is well established that organic compounds are a mix of hydrophilic and hydrophobic compounds [14,36]. For instance, Ghernaout [37] presented the various organic compounds categories, where LMW organics were shown to exhibit hydrophilic tendencies. Hence, the high deposition of hydrophilic LMW organics on the untreated WWROC membrane most likely attributed to the significant reduction of membrane hydrophobicity, as reflected by the low water contact angle ($15.6 \pm 0.5^\circ$) compared to the virgin MD membrane ($139.4 \pm 1.5^\circ$) (Fig. 3a).

Fig. 5. LC-OCD chromatogram representing membrane foulant composition of (a) untreated WWROC and (b) pretreated WWROC (BP- Biopolymers, HS- Humic substances, and BB- Building blocks).

3.5. Membrane cleaning

Membrane fouling reversibility of the pretreated and untreated WWROC was evaluated by repeated cycles of MD operation with membrane cleaning using the same membrane (Fig. 6). Stable permeate flux pattern and permeate quality (in terms of conductivity of 10-15 $\mu\text{S}/\text{cm}$) were maintained for three subsequent operation cycles of pretreated WWROC with simple MQ washing. On the other hand, the untreated WWROC showed a reducing permeate flux pattern with an increasing permeate conductivity, indicating partial wetting occurrence after two cycles. The results verified that pretreatment and membrane washing were essential for mitigating fouling and wetting occurrence in treating WWROC using the MD.

Fig. 6 Permeate flux and conductivity for repeated cycles (I to III) of MD operation with MQ membrane washing ($\square$ untreated WWROC $\blacktriangle$ pretreated WWROC).

3.6. Rejection of WWROC micropollutants

Twenty (20) micropollutants with different classifications were detected in the untreated WWROC solution, mainly in the category of household products and industrial chemicals (Table 2). It is worth highlighting that most of the micropollutants in the WWROC solution from WRP were lower than 5 $\mu\text{g}/\text{L}$. The five micropollutants detected with high concentrations in the untreated WWROC solution were benzotriazole (4560-5000 ng/L), benzophenone (960-970 ng/L), sulfamethoxazole (768-770

ng/L), carbamazepine (720-740 ng/L) and tri(2-chloroethyl)- phosphate (TCEP) (507-510 ng/L) (Table 2). The micropollutants with low concentrations <20 ng/L (primidone, meprobamate and simazine) are not included in the rejection evaluation to avoid analysis detection errors at such low concentration levels.

DCMD treatment showed considerably good micropollutants' rejection (96-99%). The micropollutants content in the permeate solution was well below the detection value (5 ng/L) with the exception of moderately low rejection (50-88%) of several compounds, namely propylparaben (50%), salicylic acid (86%), benzophenone (62%), triclosan (83%), bisphenol A (84%) and atrazine (88%). A number of factors could be associated to the lower rejection of these compounds based on their physico-chemical characteristics, especially the hydrophobic/hydrophilic ($\log D > 3$ for hydrophobic) and the volatility (lower $pK_H \approx$ higher volatility). For instance, propylparaben, benzophenone, atrazine and triclosan, which possessed the lowest pK_H values (pK_H less than 7, higher volatility) showed lower rejection rates in comparison to the other compounds. In MD operation, the thermal vapor pressure mass transfer driving force has been related to the lower rejection tendencies of micropollutants that are volatile [38]. It is noteworthy to highlight that a high quality of final DCMD permeate with above 96% rejection rate of majority of the micropollutants compounds was achieved with the GAC pretreated WWROC feed solution (Fig. 7).

It must be acknowledged that these rejection efficiencies are highly subjective to the varied concentration of the micropollutants present in the WWROC solution. As such, to observe the fate and transportation of the micropollutants in MD operation, a mass distribution percentage based on individual micropollutants mass content of the initial and final MD feed solution (mass concentrate) as well as the permeate was tabulated (Fig. 8). This was especially important to identify the micropollutants that did not accumulate in the feed solution, categorized as losses. Losses of micropollutants in the MD operation could be attributed to their tendency to either evaporate or adsorb onto the membrane [17]. The results exhibited the prevalent losses of micropollutants as the

Log D increased (higher hydrophobicity) with the exception of triclosan. If these hydrophobic compounds' losses were due to adsorption onto the hydrophobic MD membrane, in the long term, the presence of these micropollutants could be expected to affect the MD membrane hydrophobicity. At the same time, losses observed in neutrally charged carbamazepine, benzotriazole and omeprazole (in spite of their hydrophilic nature) could be related to surface charge attraction onto the highly negative MD membrane surface charge (Fig. 3b). Further, the high loss and low rejection (86%) observed with salicylic acid could be related to its high vapour pressure of 1.36×10^{-2} under MD thermal operation at 55 °C compared to the other hydrophilic compounds with much lower vapour pressure (10^{-4} to 10^{-8}).

In this regard, the role of GAC pretreatment was especially advantageous in view of its affinity to adsorb hydrophobic micropollutants. Previous studies have established that GAC being hydrophobic has a preference for the adsorption of hydrophobic compounds [6,39]. At the same time, GAC also moderately removed hydrophilic compounds, which could be related to reduction by polar interaction, surface complexation and hydrogen bonding [39,40]. The GAC pretreated WWROC was able to achieve rejection of most micropollutants, resulting in high quality final DCMD permeate (Fig. 7).

Fig. 7 Rejection rate of micropollutants in untreated and pretreated WWROC solution based on average value of two samples.

Fig. 8 Micropollutants in untreated and pretreated WWROC solution based on mass distribution percentage (mass in feed concentrate and permeate, and losses due to evaporation or adsorption)

based on average value of two samples (1st bar =untreated WWROC, and 2nd bar= pretreated WWROC).

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3.6. Salt precipitation for nutrient removal

The final saturated pretreated WWROC solution upon DCMD contained mainly of Na^+ , Mg^{2+} and K^+ cations and CO_3^{2-} , Cl^- , F^- , SO_4^{2-} and PO_4^{3-} as well as NO_3^- anions at pH of 9.4 (Table 3). A precipitation was carried out with a synthetic solution containing the same ions as the final saturated WWROC. The pH of the synthetic solution was increased to 10.3 using NaOH, followed by stirring the solution at 23.0 ± 2.0 °C for 12 h. At this setting, the precipitation of low solubility salts occurred, specifically $\text{Mg}(\text{OH})_2$ ($K_{\text{sp}} = 1.2 \times 10^{-11}$) and $\text{Mg}_3(\text{PO}_4)_2$ ($K_{\text{sp}} = 1.0 \times 10^{-24}$) (Table 5). Most of Ca^{2+} was converted into calcium carbonate (CaCO_3) during the DCMD operation, while the remaining Ca^{2+} precipitated under this batch precipitation condition. The WWROC solution after precipitating contained only trace amounts of F^- and PO_4^{3-} .

Meanwhile only a small amount of Na^+ and SO_4^{2-} , was related with precipitate formation under this condition. This was attributed to the high solubility of these ions. Similarly, minimal changes were observed for K^+ and N (representing NO_3^-) as well as Cl^- ions. Therefore, the MD followed by precipitation was useful in reducing specific contents of the WWROC solution such as F^- , Ca^{2+} , Mg^{2+} as well as PO_4^{3-} . Further investigation must be carried out to evaluate selective fractioning and recovering of economically useful salts such as K^+ , Ca^{2+} and PO_4^{3-} .

Table 5 Changes in ion contents (as mass in g) of synthetic WWROC after MD concentration followed by precipitation.

Mass (g)	Ca^{2+}	Mg^{2+}	PO_4^{3-}	F^-	K^+	Na^+	Cl^-	SO_4^{2-}	NO_3^-
Final WWROC solution	17.2	82.3	0.2	2.3	91.5	658.7	1011.4	379.1	13.4
(synthetic) after MD									
Final WWROC solution									
(synthetic) after MD and precipitation	<0.1	0.7	<0.1	0.4	89.8	503.4	895.7	264.5	11.9

4. Significance

4.1. MD as a treatment option for WWROC

MD was able to treat WWROC to produce substantially high quality distillate with an only small decrease in permeate flux. This was due to the minimal effect of polarization at low NaCl content in the WWROC (only 3 g NaCl/L) compared to SWROC, enabling to achieve a high water recovery of 85%. At high water recovery, the WWROC volume was significantly reduced, ultimately leading to a highly saturated WWROC, which was a favourable condition for precipitation and crystallization of salts with low solubility limits such as Ca^{2+} , Sr^{2+} , Mg^{2+} and F^- . The precipitation of salts was beneficial to reduce the inorganic content in WWROC brine. Moreover, these salts can be further selectively recovered by adsorbents and polymeric resins.

Stringent legal requirements have resulted in the significant increase in WWROC disposal cost in WRPs [4]. Therefore, the option of zero liquid discharge is much sought after. One of the common approaches to achieve zero liquid discharge and recover salts is by evaporation and crystallization steps. The economic efficiency of this approach is highly dependent on the concentration of the feed solution. For instance, for substantial results, Mohammadesmaeili et al. [41] proposed the approach of softening the initial WWROC by lime – soda treatment and a subsequent treatment with a second stage RO treatment to achieve a higher feed concentration, suitable for evaporation and crystallization. Similarly, other studies have indicated the need for a supersaturated feed solution for an economically viable evaporation and crystallization method [1,9]. In this regard, the capacity for MD to achieve highly saturated WWROC (85% water recovery, 7 times the original concentration), effectively meets the zero liquid discharge option and salt recovery potential from WWROC. Hickenbottom et al. [42] established the advantages of using DCMD for treating saline lake water, as it not only produced high quality distillate but also accelerated the natural evaporation process by approximately 170 times at a significantly smaller footprint (24 m²) compared to 4,047 m² of evaporation ponds.

4.1.1 MD thermal requirement

As a thermal membrane process, MD would likely appear to be an energy-intensive option. However, at present, design modifications such as multi effect stages with heat recovery and better insulations have considerably improved the thermal efficiency of MD operation [11,43]. Further, when MD is operated at moderate feed temperature ranges below 60 °C, the capacity to tap into alternative thermal application such as solar technology and industry waste heat is attractive. For instance, Banat and Jwaied [43] reported on the capacity of a large pilot scale MD coupled with solar to obtain up to 0.5 kL/day water production. Recently, Schwantes et al. [42] demonstrated the potential of operating three pilot-scale parallel multi MD-modules for seawater desalination with diesel waste heat and solar collector at design capacities of 3.5- 5.0 kL/day. Nevertheless, it must be acknowledged that most of these pilot-scale MD studies demonstrated operation rates of less than 5 kL/day. This may not meet the requirements of large WWROC streams with capacities of up to 300 kL/day. As such, more upscaling and module design efficiency must be carried out for practical MD implementation in large WRPs.

4.2. Scaling formation

Scaling formation due to sparingly soluble salts is by far one of the main limiting factor for ROC treatment, particularly when MD is operated at high recovery rates. As a thermally driven membrane operation, scaling is intensified in MD by the inverse solubility of CaSO_4 (gypsum) and CaCO_3 with temperature increment [23]. Scaling development of WWROC is primarily different compared to SWROC. The high contents of HCO_3^- in the WWROC, resulted in the precipitation of CaCO_3 unlike the predominant CaSO_4 formation with SWROC [12, 13]. The precipitation of CaCO_3 did not play a significant role in influencing the permeate flux pattern attributed to its loose deposition onto the membrane surface as observed in this present study. On the other hand, in SWROC, the formation of

needle-like CaSO_4 in the presence of high NaCl have been related to significant permeate flux decline, pore blocking and membrane wetting [12,28]. Moreover, a number of studies related the presence of high NaCl in SWROC to membrane wetting tendencies [45,46]. Hence, the inorganic composition in WWROC (high HCO_3^- and low NaCl) was advantageous in achieving highly concentrated WWROC by MD operation with no membrane wetting.

In this regard, the SEM image revealed that both the pretreated and synthetic WWROC contained significant deposition of CaCO_3 crystal formation. However, with synthetic WWROC (which only contained inorganic ions) MD membrane, showed the presence of large aragonite and vaterite type CaCO_3 (star shaped CaCO_3), attributed to the presence of Mg^{2+} that suppressed the formation of calcite CaCO_3 [24,26]. Comparatively, the pretreated WWROC membrane contained small crystals due to the presence of small quality of organics that act as scale inhibitors [27]. In a way, compared to the synthetic WWROC (inorganics only), the presence of organics appears to be beneficial in retarding the CaCO_3 induction time and formation on the membrane. This is reflected in the slightly lower LSI value of the concentrated untreated WWROC (LSI of 1.7) compared to the pretreated WWROC (LSI of 2.0), suggesting a lower tendency for CaCO_3 scaling in the presence of organics. Nonetheless, the CaCO_3 deposition in pretreated and synthetic WWROC did not result in a significant permeate flux decline or wetting phenomenon, while the deposition of brownish dense colloid like substances due to the presence humics with inorganics significantly reduced the membrane hydrophobicity, indicating membrane wetting susceptibility. Moreover, the CaCO_3 inhibition in the presence of organics (untreated WWROC) will be potentially disadvantageous for the precipitation and production of large salt crystals.

4.3. Necessity of GAC pretreatment for WWROC

The DOC content in WWROC (35 - 60 mg/L) is considerably higher in comparison to SWROC (2 - 3 mg/L). The elevated DOC concentration in the WWROC by the MD operation resulted in a

prevalent hydrophilic LMW organic deposition on the membrane during the MD operation. This in turn, contributed to significant membrane hydrophobicity reduction by up to 70%. The MD membrane hydrophobicity was not able to be restored to its original condition even upon chemical cleaning, indicating the irreversibility of the organic formation on MD membrane. Nevertheless, the presence of DOC did not significantly contribute to permeate flux decline, and the permeate quality remained unchanged, which raises the question on the significant impact of organic formation by WWROC in MD operation. In MD, the reduction of hydrophobicity of membrane leads to membrane wetting [16,45]. For instance, Goh et al. [16] used MD for WWROC treatment and observed significant hydrophobicity reduction of membrane from 126.3° to 32.9° which is a similar phenomenon in the present study. However, the reduction of permeate quality (increased permeate organic contents) associated with membrane wetting was only observed after 9 to 11 days of MD operation. In line with this, a repeated cycle of MD operation with membrane cleaning was carried out with untreated and pretreated WWROC. An increase of permeate flux decline and permeate conductivity was observed after two cycles with the untreated WWROC while stable condition was maintained with the pretreated WWROC cycles. This indicated that the reduction of membrane hydrophobicity due to DOC in WWROC might lead to membrane wetting in a long term operation. This will detrimentally affect the membrane life span as well as product water quality. Hence, GAC pretreatment to reduce the organic contents in WWROC is highly essential prior to MD operation. In this study, a simple GAC sorption effectively reduced the organic content by 46%, resulting in considerably less effect on the membrane hydrophobicity reduction, which was restored by chemical cleaning.

4.4. Mechanism of micropollutants rejection by MD

The mechanism of MD rejection of micropollutants in WWROC is highly dependent on their characteristics such as volatility, surface charge and hydrophobicity. MD rejection was especially

challenged with volatile and hydrophobic micropollutants. Furthermore, a pattern of feed concentration reduction (losses) was observed with micropollutants that were hydrophobic, neutrally charged with high vapour pressure. The losses could indicate adhesion of the micropollutant onto the negatively charged hydrophobic MD membrane. The long-term impact of micropollutants' adhesion on the MD membrane must be evaluated in detail. GAC was found to be an effective pretreatment in effectively adsorbing hydrophobic micropollutants (reducing adhesion onto the MD membrane) as well as hydrophilic micropollutants, obtaining high removal of most micropollutants.

5. Conclusion

The interest towards zero liquid discharge in WRPs led to this study in evaluating the suitability of MD technology for treating WWROC. The results showed that:

- DCMD was able to achieve 85% water recovery of WWROC with only a 13-15% flux decline, producing good quality permeate (10-15 $\mu\text{S}/\text{cm}$, 99% ion rejection).
- At elevated concentration of WWROC, the tendency for CaCO_3 deposition on the membrane was evident based on the inorganic chemical analysis as well as SEM-EDX. The loose adhesion of CaCO_3 in low salinity WWROC, did not contribute to significant permeate flux decline and membrane wetting.
- The presence of high amount of organics in WWROC resulted in significant membrane hydrophobicity loss. This was attributed to the adhesion of hydrophilic LMW organics present in WWROC (based on the detailed LC-OCD organic characterization).
- Membrane hydrophobicity was able to be restored with pretreated WWROC, indicating a simple GAC pretreatment was essential to reduce the organic content in WWROC prior to MD operation. The GAC was also beneficial in adsorbing most of the micropollutants from WWROC. Hence, the GAC-MD process ensured the production of high quality water with the potential of meeting the requirements for reclaimed water reuse.
- At 85% water recovery, the MD concentrated WWROC was suitable for precipitation of ions such as PO_4^{3-} , Ca^{2+} and Mg^{2+} , obtaining an almost zero liquid discharge in a compact small footprint compared to conventional evaporation method.

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Highlights

- MD is used for wastewater reverse osmosis concentrate (WWROC) treatment.
- A direct contact MD (DCMD) achieves up to 85% water recovery with WWROC.
- CaCO_3 scaling due to WWROC does not cause prevalent issues in DCMD.
- Granular activated carbon (GAC) pretreatment mitigates organic fouling.
- GAC-MD process ensures high quality (micropollutants-free) water production.

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