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Treatment of saline aqueous solutions using direct contact membrane distillation

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1 **TREATMENT OF SALINE AQUEOUS SOLUTIONS USING DIRECT CONTACT**
2 **MEMBRANE DISTILLATION**

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9 **ABSTRACT:** The treatment of highly saline aqueous solutions using direct contact membrane
10 distillation (DCMD) was evaluated in this study. Experiments were conducted using a flat
11 sheet polytetrafluoroethylene membrane with nominal pore size of 0.22 µm. Seawater,
12 reverse osmosis (RO) concentrate collected from a wastewater reclamation plant, and a
13 synthetic solution containing 2,000 mg/L of CaSO₄ were selected as the representative saline
14 solutions. A gradual decline in permeate flux was observed at the beginning of the
15 experiments when the seawater and RO concentrate solutions were treated using the DCMD
16 process, most likely due to initial organic fouling and scaling. In contrast, when the saturated
17 CaSO₄ solution was used as the feed, the permeate flux was stable for approximately 300
18 minutes of operation. However, when these solutions were concentrated beyond their
19 solubility limit, crystallization of the sparingly soluble salts occurred on the membrane
20 surface, leading to a complete loss of permeate flux at the end of the experiment. Contact
21 angle measurement of the fouled and scaled membranes revealed a significant reduction in
22 hydrophobicity. Membrane fouling and scaling were also confirmed by scanning electron
23 microscopy analysis. The results suggest that pretreatment to remove organic matter is
24 essential to prevent organic fouling. In addition, a major limiting factor for the treatment of
25 saline solutions using DCMD appears to be the solubility of sparingly soluble salts.

26 **Keywords:** Direct contact membrane distillation (DCMD), organic fouling, RO concentrate,
27 scaling, saline solution.

28 **1. Introduction**

29 Membrane distillation (MD) is a thermally driven desalination process that involves phase
30 conversion from liquid to vapor on one side of the membrane and condensation of vapor to
31 liquid on the other side [1]. The membrane facilitates the transport of water vapor through its
32 pores but does not participate in the actual separation process. Although the process of MD is
33 not new, it has only recently been recognized as a low cost, energy saving alternative to
34 conventional separation processes for the treatment of saline water and wastewater such as
35 thermal distillation and reverse osmosis [2-3]. MD has several advantages compared to
36 conventional thermal distillation and reverse osmosis processes [3-4]. Because water is
37 transported through the membrane only in a vapor phase, MD can offer complete rejection of
38 all non-volatile constituents in the feed solution; thus, almost 100% rejection of ions,
39 dissolved non-volatile organics, colloids, and pathogenic agents can be achieved via the MD
40 process. More importantly, due to the discontinuity of the liquid phase across the membrane,
41 the mass flux in an MD process is not subjected to an osmotic pressure gradient.
42 Consequently, the greatest potential of MD can be realized for the treatment of highly saline
43 solutions [5]. In fact, it has been experimentally demonstrated that the permeate flux of an
44 MD process is independent of the feed water salinity up to 76,000 mg/L total dissolved solids
45 (TDS), which is twice the salinity of a typical seawater [6]. MD also requires lower operating
46 pressures than reverse osmosis membrane separation processes. In a typical MD process,
47 since the applied pressure is negligible and the feed solution does not enter the membrane
48 pores, chemical interactions between membrane and process solutions are less intense [1]. In
49 addition, MD requires lower operating temperatures than conventional distillation, which can
50 facilitate the utilization of low grade heat [1, 7]. The unique ability of MD to utilize low
51 grade heat from industrial sources (which may otherwise be wasted) or solar thermal energy
52 provides an excellent platform for a greenhouse neutral desalination process [1].

53 The driving force of the process is supplied by the vapor pressure difference induced by
54 temperature difference between the liquid–vapor interfaces on the feed and distillate sides of
55 the membrane. MD can be employed in several different configurations [1]. Among them, the
56 direct contact membrane distillation (DCMD) configuration is best suited for applications
57 such as desalination or the concentration of aqueous solutions, in which water is the major
58 permeate component [8-9]. Indeed, DCMD requires the least equipment and is the simplest to
59 operate [8]. MD has potential applications in many areas of scientific and industrial interest,
60 yielding highly purified permeate and separating contaminants from liquid solutions. It has
61 been tested for the treatment of thermally sensitive industrial products such as concentrating
62 aqueous solution in fruit juices, the biotechnology industry, as well as for wastewater
63 treatment and water desalination [5, 10-18]. Since the process of membrane distillation is
64 independent of the solution osmotic pressure (or salinity), MD is particularly ideal for the
65 treatment of saline solution such as RO concentrate from inland water recycling or brackish
66 water desalination applications [4-5, 19].

67 While MD has been extensively studied over the last few years, it is noteworthy that the
68 process of membrane scaling and fouling has not yet been adequately investigated [16, 20].
69 Recent studies have revealed that the scaling phenomenon observed in MD can remarkably
70 differ from that of a typical pressure driven membrane filtration process. For example, while
71 CaCO_3 has been known to be a very potent scalant during a typical nanofiltration or reverse
72 osmosis process, it was not the case during membrane distillation [21]. In contrast, membrane
73 scaling in DCMD due to the precipitation of gypsum (CaSO_4) could be severe, leading to a
74 dramatic flux decline [21]. These salient aspects are in fact very important if MD will be used
75 for the treatment of highly saline wastewater containing sparingly soluble salts. Accordingly,
76 the objective of this study was to assess the membrane fouling and scaling phenomena during
77 the treatment of highly saline aqueous solutions using DCMD.

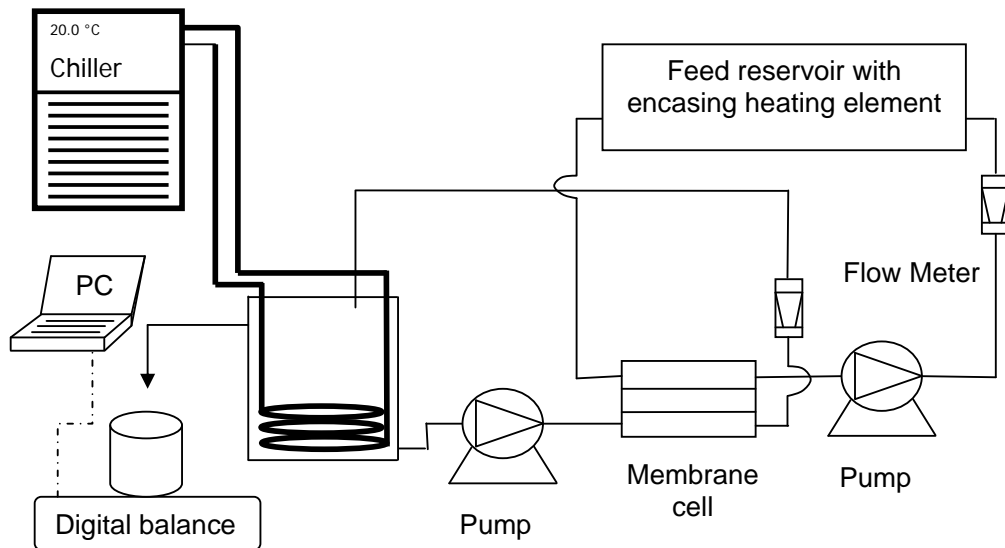
78 **2. Materials and Methods**

79 **2.1. DCMD test unit and experimental procedure**

80 DCMD experiments were conducted using a closed-loop bench-scale membrane test unit
81 (Figure 1). The membrane cell was made of acrylic plastic to minimize heat loss to the
82 surroundings. It was designed to hold a flat-sheet membrane under moderate pressure
83 gradients without any physical support. The flow channels were engraved in each of two
84 acrylic blocks that made up the feed and permeate semi-cells. Each channel was 0.3 cm deep,
85 9.5 cm wide, and 14.5 cm long; and the total active membrane area for mass transfer was 138
86 cm².

87 Feed solution was circulated from a stainless steel feed reservoir through the feed membrane
88 semi-cell and back to the reservoir. A heating element encased inside a stainless steel tube
89 was placed directly into the feed reservoir. A temperature sensor was placed immediately
90 before the inlet of the feed solution to the membrane cell. The heating element and the
91 temperature sensor were connected to a temperature control unit to regulate the temperature
92 of the feed solution. MilliQ water was used as the initial condensing fluid. The distillate was
93 circulated from a 2 L Perspex reservoir through the distillate membrane semi-cell and back to
94 the reservoir. The distillate reservoir allowed overflow of excess permeating water into a
95 collecting container. The overflowing distillate was continuously weighed on an electronic
96 balance (PB32002-S, Mettler Toledo Inc., Hightstown, NJ). Another temperature sensor was
97 installed immediately at the outlet of the distillate semi-cell. The temperature of the distillate
98 was regulated using two cooling units (Neslab RTE 7, Thermo Fisher Scientific, Waltham,
99 MA, USA) equipped with a stainless steel heat-exchanging coil, which was submerged in the
100 distillate reservoir. Two pumps (Model 120/IEC71-B14, Micropump Inc., Vancouver, WA,
101 USA) were used to circulate feed and distillate from their respective reservoirs through the
102 membrane cell and back to the reservoirs (at up to 4 L/min and 70 °C). Flow rates of the feed

103 and distillate were monitored using two rotameters and were kept constant and similar at all
104 times. All the pipes used in the DCMD test unit were covered with insulation foam to
105 minimise heat loss.



106
107

108 **Figure 1:** Schematic diagram of the CDMD system.

109 A feed volume of 10 L was used in all experiments in this study. Temperature of the distillate
110 was kept constant at 20 °C. When evaluating the performance of the DCMD system using tap
111 water, permeate flux was measured for at least 2 hours at each feed temperature. A new
112 membrane sample was used for each experiment in this study. At the completion of each
113 experiment, the membrane was removed from the cell, air dried, and kept in a desiccator until
114 surface analysis.

115 **2.2. Microporous membrane**

116 A hydrophobic, microporous membranes were acquired from (GE Osmonics, Minnetonka,
117 MN) for this investigation. This is a composite membrane having a thin
118 polytetrafluoroethylene (PTFE) active layer on top of a polypropylene (PP) support sublayer.
119 The pore size and porosity of the membrane are 0.22 μm and 70%, respectively. The
120 membrane thickness is 175 μm , of which the active layer is 5-10 μm .

121 **2.3. Chemical reagents and test solutions**

122 Three different saline solutions were used in this investigation. An RO concentrate solution
123 was obtained from the Wollongong Water Recycling plant (Wollongong, Australia).
124 Seawater was obtained from Wollongong beach which opens out to the Tasman Sea. Both the
125 RO concentrate solution and seawater were used directly in the DCMD without any
126 pretreatment. Analytical grade CaSO₄ obtained from Sigma-Aldrich (Castle Hill, Australia)
127 was dissolved into MilliQ water to make up a saturated solution (2,000 mg/L) of CaSO₄. The
128 compositions of the three test solutions are presented in Table 1. These three solutions
129 represent three different scenarios involving the treatment of saline solution. The RO
130 concentrate solution has a relatively low salinity with TDS of just over 4,000 mg/L but has
131 significant organic matter content (Table 1). In contrast, the presence of organic matter in
132 both the seawater and the synthetic CaSO₄ solution used in this study was negligible.
133 Although TDS concentration of the synthetic gypsum solution is relatively low, the solution
134 was at saturation with respect to CaSO₄.

135 **Table 1:** Characteristics of the test solutions used in this study.

| Parameter | RO Concentrate | Seawater | Synthetic solution |
|--|----------------|-----------------|--------------------|
| pH (-) | 8.1 | 8.2 – 8.66 | 6.0 |
| Total Organic Carbon (mg/L) | 33 | <3 | <1 |
| Total Alkalinity as CaCO ₃ (mg/L) | 690 | 117 – 129 | <10 |
| Electrical Conductivity (mS/cm) | 6.7 | 43.6 – 49.0 | 2.5 |
| Calcium (mg/L) | 150 | 350 – 510 | 588 |
| Magnesium (mg/L) | 140 | 1,100 – 1,500 | |
| Sodium (mg/L) | 1,200 | 9,920 – 12,000 | |
| Potassium (mg/L) | 97 | 350 – 600 | |
| Silicon (mg/L) | 26 | 0.1 – 0.3 | |
| Bicarbonate (mg/L) | 580 | 106 – 132 | |
| Chloride (mg/L) | 1,800 | 18,000 – 22,000 | |
| Sulfate (mg/L) | 380 | 2,300 – 3,584 | 1,412 |
| Total dissolved solid (mg/L) | 4,347 | 32,903 – 39,272 | 2,000 |

136 **2.4. Analytical techniques**

137 Conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity meter
138 (Thermo Fisher Scientific, Waltham, MA, USA). The conductivity probe was immersed
139 directly into the permeate container to allow for continuous monitoring of the permeate

140 conductivity. The morphology and the composition of the fouling layer deposited onto the
141 membrane surface were examined by scanning electron microscopy (SEM) using a JEOL
142 JSM-6460A instrument (Tokyo, Japan), with additional semi-quantitative energy dispersive
143 spectrometer (EDS) analysis. Prior to SEM analysis, the membrane samples were air-dried
144 and subsequently coated with an ultrathin layer of carbon. Extreme care was taken when
145 preparing the fouled and scaled membrane samples to ensure that the fouling and scaling
146 layer remained intact. Contact angle measurements of the membrane surfaces were performed
147 with a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ) using the standard
148 sessile drop method. Milli-Q water was used as the reference solvent. The membrane samples
149 were air dried prior to the measurement. At least 5 droplets were applied onto duplicate
150 membrane samples.

151 **3. Results and Discussion**

152 **3.1. DCMD of a diluted solution**

153 The driving force in DCMD is a vapor pressure difference across the membrane, which is
154 usually induced by a temperature difference between the feed and distillate sides of the
155 membrane. In general, it can be assumed that the kinetic effects at the vapor-liquid interface
156 are negligible. This assumption is valid at steady state condition, when the vapor and liquid
157 are at equilibrium corresponding to the membrane surface and the pressure within the
158 membrane pores [1]. The vapour pressure (P^0) within the membrane pores can be determined
159 by the Antoine equation:

$$160 \quad P^0 = \exp \left[A - \frac{B}{C + T} \right] \quad (1)$$

161 where P^0 is in Pa and T is the temperature in K. For pure water, the constants A, B, and C are
162 23.1964, 3816.44, and -46.13 , respectively [22]. For non-ideal binary solutions, the

163 membrane pore vapor pressure can be corrected by taking into account the molar fraction of
164 the solute and the solvent (water).

165 In the DCMD process, heat transfer and mass transfer occur simultaneously. The total heat
166 transferred across the membrane is given by [8]:

$$167 \quad Q = \left[\frac{1}{h_f} + \frac{1}{h_m + N\Delta H_v / \Delta T_m} + \frac{1}{h_p} \right]^{-1} \times \Delta T_m \quad (2)$$

168 where h_f , h_m , and h_p are the heat transfer coefficient of the feed, membrane, and permeate,
169 respectively. N and ΔH_v are the molar flux and the heat of vaporisation, respectively. ΔT_m is
170 the temperature difference between the feed and distillate sides of the membrane. The total
171 mass transferred across the membrane can be simply expressed as the product of the mass
172 transfer coefficient and the driving force:

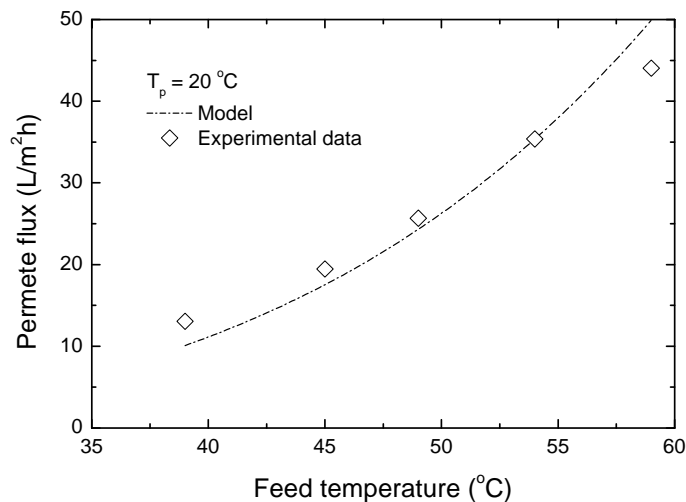
$$173 \quad N = k_f \Delta P^0 \quad (3)$$

174 The mass transfer coefficient k_f is a function of the temperature, pressure, and membrane
175 properties. In addition, ΔP^0 can be dependent on the temperature and the actual composition
176 at the membrane surface, which may differ from that of the bulk solution. As a result, the heat
177 flux and the mass flux are interdependent. The coupling mass-heat transfer problem can be
178 solved via numerical iteration. An analytical solution to the mass and heat flux equations can
179 also be obtained based on several simplifying assumptions. In particular, it is assumed that
180 the pressure on each side of the membrane is the same as the saturation of pure water at the
181 temperature at the membrane surface. One can also assume that the heat transfer coefficients
182 on each side of the membrane are equal. This assumption allows for substitution of
183 membrane properties (P_m^0 , T_m , and ΔT_m) with their bulk counterparts (P^0 , T , and ΔT).

184 According to Lawson and Lloyd [1, 8], Equation 3 can then be written as a function of the
185 temperature drop across the membrane:

186
$$N = K \frac{dP^0}{dT} \Delta T = K \frac{P^0 \Delta H_v}{RT^2} \Delta T \quad (4)$$

187 To evaluate the performance of the DCMD system, experiments were conducted with tap
 188 water at a distillate temperature of 20 °C and different feed temperatures in the range between
 189 40 °C to 60 °C. The overall mass transfer coefficient can be determined by fitting the flux
 190 data to the model (equations 1 and 4) using an optimisation procedure (Solver, Microsoft
 191 Excel). Overall, the model and the experimental data are in good agreement (Figure 2).
 192 Accordingly, the overall mass transfer coefficient was determined to be 0.0223 (mol/Pa.m².s).
 193 Because the mass flux is proportional to the temperature gradient across the membrane,
 194 permeate flux increased dramatically as the feed temperature increased (Figure 2). It is
 195 noteworthy that the performance of the DCMD modelled here is under an ideal condition and
 196 with pure water. In a realistic situation when DCMD is used for the treatment of highly saline
 197 solutions the membrane surface properties may gradually change overtime making this
 198 simplified mathematical model invalid. The process of DCMD of highly saline solutions is
 199 further discussed in the next section.



200
 201 **Figure 2:** Modelled and experimental permeate flux as a function of feed temperature
 202 (Permeate temperature (T_p)=20 °C, V_f=60 L/h, V_p=60 L/h, tap water with pH ~ 7).

203 **3.2. DCMD of saline solutions**

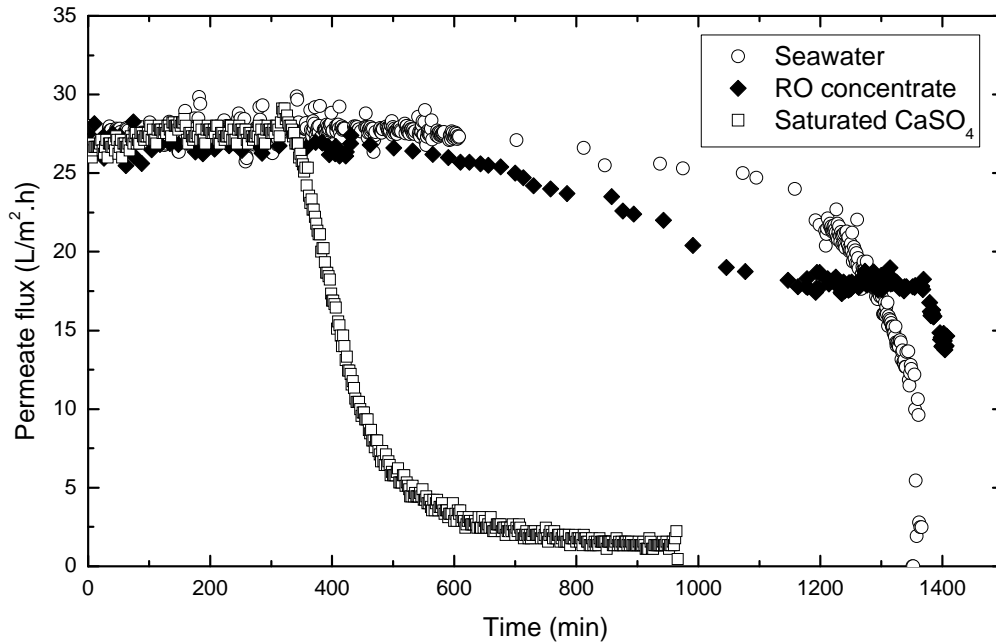
204 The membrane permeate fluxes obtained with the three saline solutions investigated in this
205 study are shown in Figure 3. The initial permeate flux is similar despite the significant
206 difference in composition of the three feed solutions (Table 1 and Figure 3). In fact, this
207 initial permeate flux is also similar to the permeate flux obtained with tap water at the same
208 feed temperature (50 °C). Results reported here reconfirm that up to the salinity of seawater,
209 the influence of the feed solution salinity on the initial permeate flux is negligible [6].

210 Significant decline of permeate flux was observed with time, potentially suggesting dramatic
211 alteration of membrane surface characteristics due to membrane fouling and/or scaling. The
212 permeate flux during the desalination process of seawater declined slowly over the first 1200
213 minutes, then sharply dropped to zero over a short period of time. The gradual permeate flux
214 declined could possibly be attributed to the formation of salt crystals on the membrane
215 surface. It is also plausible that the rate of crystallisation would increase as the feed water
216 solution became more concentrated (higher concentration of sparingly soluble salts) and the
217 number of seed crystals had reached the threshold for rapid growth.

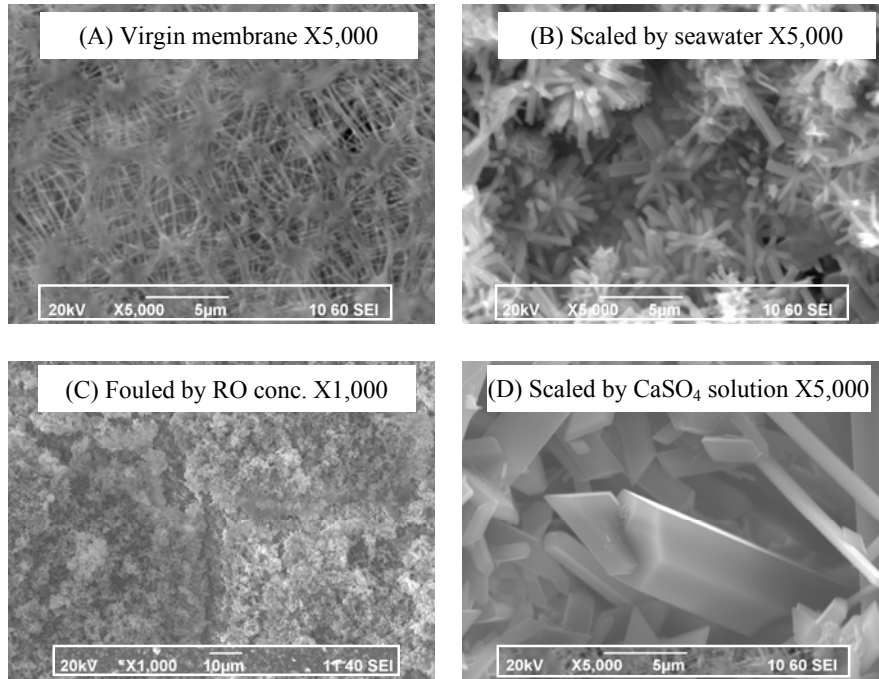
218 During the first 1,200 minutes of DCMD desalination of RO concentrate, a notable
219 permeate flux was also observed. The rate of flux decline was higher than that observed with
220 seawater feed solution. The RO concentrate used in this experiment had a high total organic
221 carbon content. In contrast, the organic content in seawater was negligible. Higher flux
222 decline during first phase of DCMD could therefore be attributed to the gradual adsorption of
223 organic foulants onto the membrane surface. Once RO concentrate in the feed reservoir
224 became over saturated, a dramatic flux decline was also observed, similar to that of the
225 desalination process of seawater.

226 A very different permeate flux profile was observed when the saturated CaSO₄ solution was
227 used as the feed. The permeate flux of the saturated CaSO₄ solution was stable for

228 approximately 300 minutes, followed by a sudden drop to almost zero. This stable permeate
229 flux could be explained as an induction period for crystallisation of gypsum that has been
230 widely reported in the literature [23-25].

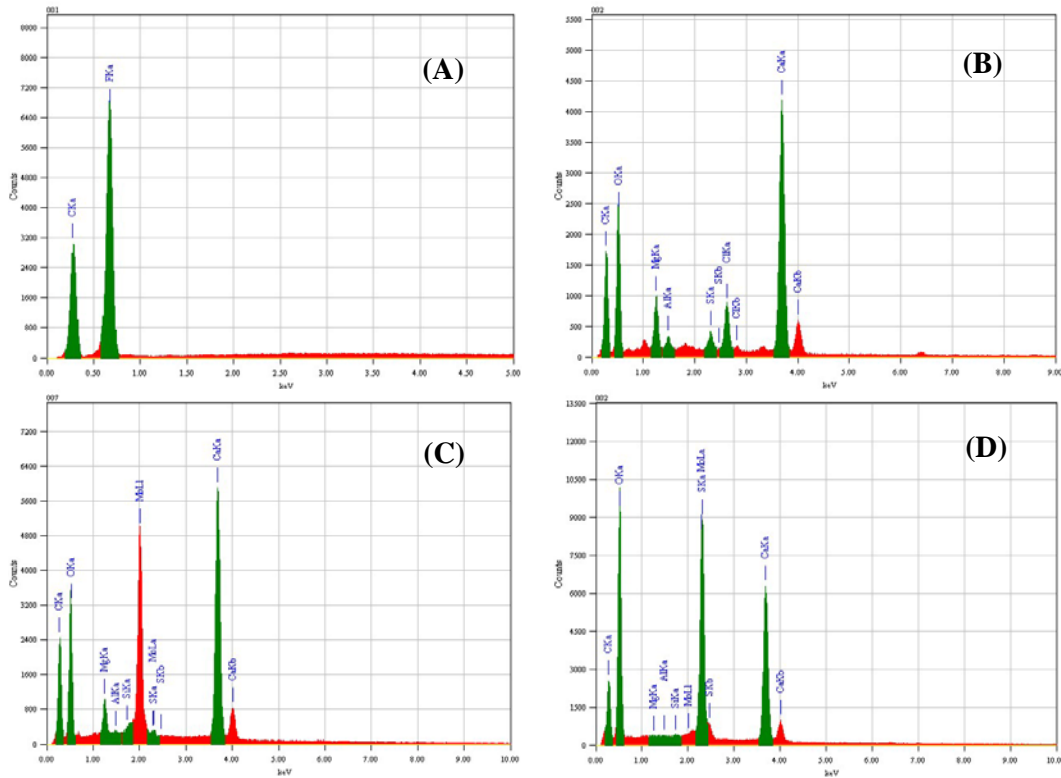


231
232 **Figure 3:** Permeate flux of different saline solutions as a function of time ((Permeate
233 temperature (T_p)=20 °C, V_f =60 L/h, V_p =60 L/h, feed volume = 10 L).
234 SEM micrographs of a virgin membrane side by side with the membrane surfaces after
235 processing the three saline solutions are illustrated in Figure 4. In good agreement with the
236 discussion above, at the completion of the DCMD experiment using seawater, small crystal
237 structures had completely covered the membrane surface (Figure 4B). Similarly, a fluffy
238 amorphous fouling layer can be observed on the membrane surface after the DCMD of RO
239 concentrate (Figure 4C). The formation of the small crystals or the amorphous fouling layer
240 could be attributed to heterogeneous composition of the seawater or RO concentrate
241 solutions. In contrast, the CaSO₄ solution used in this investigation had almost no impurities.
242 As a result, large CaSO₄ crystals can be seen deposited on the membrane surface at the
243 completion of the DCMD experiment using CaSO₄ solution (Figure 4D).



244 **Figure 4:** SEM images of the membrane surface under clean and pre-fouled/scaled
 245 conditions: (A) virgin membrane, (B) after treating seawater, (C) after treating RO
 246 concentrate, and (D) after treating a saturated CaSO₄ solution.

247 The discussion above is consistent with the results obtained from qualitative elementary
 248 analysis of the scaling/fouling layers using SEM-EDS. Because the microporous membrane
 249 used in this investigation has a PTFE active layer, fluoride and carbon are the only two
 250 elements detectable on the membrane surface of a virgin sample (Figure 5A). After the
 251 DCMD with each of the three saline solutions, major elements responsible for the
 252 scaling/fouling of the membrane surface can be clearly identified in Figures 5B, 5C, and 5D.
 253 The presence of calcium is particularly notable in all three cases. In fact, calcium salts are
 254 sparingly soluble and calcium is ubiquitous in natural water including seawater and RO
 255 concentrate. In addition to calcium, several other metals such as magnesium, aluminium, and
 256 molybdenum can also be seen on the membrane surface after processing either seawater or
 257 RO concentrate. Once again, it is not surprising that calcium is the only metallic element
 258 observed in Figure 5D, which shows the EDS spectrum of the scaling deposit of CaSO₄ on
 259 the membrane surface.



260 **Figure 5:** EDS spectra of the membrane surface under clean and pre-fouled/scaled
 261 conditions: (A) virgin membrane, (B) after treating seawater, (C) after treating RO
 262 concentrate, and (D) after treating a saturated CaSO₄ solution.

263 The deposition of a scaling or fouling layer on the membrane surface does not only restrict
 264 the active surface area available for mass transport but also render the membrane surface
 265 hydrophilic. The latter can result the wetting of the membrane pores leading to the intrusion
 266 of liquid water to the membrane pores, which in turn hinders the mass transfer of water
 267 vapour across the membrane. Contact angle measurement conclusively confirms a
 268 transformation of the membrane surface characteristic from being hydrophobicity prior to the
 269 experiment to very hydrophilic after being used in the DCMD experiment involving any of
 270 the three saline solutions (Table 2).

271 **Table 2:** Contact angle values of the membrane samples before and after experiments with
 272 the three saline solutions.

| Sample | Contact angle (°) |
|---|-------------------|
| Virgin membrane | 137.7 |
| After treating seawater | 8.9 |
| After treating RO concentrate | 23.9 |
| After treating saturated CaSO ₄ solution | 8.9 |

273 **4. Conclusion**

274 Results reported here underscore the importance of membrane scaling and fouling control
275 during DCMD. Scaling and organic fouling were observed with the treatment of seawater and
276 RO concentrate, respectively, resulting in an initial gradual permeate flux decline. In contrast,
277 when the saturated CaSO₄ solution was used as the feed, the permeate flux was stable for
278 approximately 300 minutes of operation. However, as the concentration factor of these
279 solutions increased beyond their solubility limit, crystallization of the sparingly soluble salts
280 occurred on the membrane surface, leading to a complete loss of permeate flux at the end of
281 the experiment. Contact angle measurement of the membrane surface revealed a complete
282 loss of hydrophobicity when membrane fouling or scaling occurred. Membrane fouling and
283 scaling were also confirmed by scanning electron microscopy analysis. Results obtained from
284 SEM-EDS analysis of the membrane surface after being used for the desalination of the three
285 saline solutions revealed the ubiquitous presence of calcium in the fouling/scaling layer.
286 Results reported here suggest that pretreatment to remove organic matter and particularly
287 calcium could be essential to prevent membrane fouling and scaling.

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