1	Evaluation of Forward Osmosis as a Pretreatment Process for Multi Stage					
2	Flash Seawater Desalination					
3						
4						
5 6	Mshael S. Thabit ^a , Alaa H. Hawari ^{b,*} , Mhd. Hafez Ammar ^b , Syed Zaidi ^c , Guillermo Zaragoza ^d , Ali Altaee ^{e,*}					
7						
8						
9						
10						
11	^a Environmental Engineering Master Program (EEMP), Qatar University, P.O. Box					
12	2713, Doha, Qatar.					
13 14	^b Department of Civil and Architectural Engineering, Qatar University, P.O. Box 2713, Doha, Qatar.					
15	^c Centre for Advanced Materials, Qatar University, P.O. Box 2713, Doha, Qatar.					
16	^d CIEMAT-Plataforma Solar de Almería, Ctra. de Senés s/n, 04200 Tabernas, Almería,					
17	Spain.					
18	^e School of Civil and Environmental Engineering, University of Technology in Sydney,					
19	15 Broadway, Ultimo, NSW 2007, Australia.					
20						
21						
22						
23						
24						
25						
26						
27						
28						
28 29						
30	*Corresponding authors:					
30 31	Dr. Alaa H. Hawari; Tel.: +(974) 3393-1555; Fax: +(974) 4403-4172. E-mail address:					
32	a.hawari@qu.edu.qa,					
33						
	Dr. Ali Altaee; Tel.: +(614) 2060-6500, Email address: <u>Ali.altaee@uts.edu.au</u> ;					
34						
35						
36						
37						
38						
39						
40						
40 41						
42						
42 43						
45 44						
44 45						
40						

46 Abstract

47

The present study evaluates the feasibility of applying forward osmosis (FO) process for 48 the pretreatment of feed solution to a Multi Stage Flash (MSF) desalination plant. For the 49 first time, real brine reject and real seawater were used as the draw solution and the feed 50 solution, respectively in the FO process. The FO pretreatment is expected to dilute the 51 brine reject and reduce the concentration of divalent ions, which are responsible for scale 52 53 formation on the surface of heat exchanger in the MSF evaporator unit. The FO experiments were performed at different draw solution temperatures ranging between 25 54 55 - 40°C, different draw and feed solutions flowrates and different membrane orientations. A maximum average membrane flux of 22.3 L/m².h was reported at a draw solution 56 57 temperature of 40°C and 0.8 and 2.0 LPM flow rate of draw and feed solutions, 58 respectively. The experimental results also revealed the process sensitivity to the feed 59 solution temperature. It was found that the average membrane flux in the FO process operating at 0.8 and 2 LPM draw and feed solution flow rates, respectively was 16.9 60 L/m².h at 25°C brine temperature but increased to 22.3 L/m².h at 40°C brine temperature. 61 These membrane fluxes resulted in 3% and 8.5% dilution of the draw solution at 25°C 62 63 and 40°C temperatures, respectively. The average membrane flux in the FO mode was equal to that in the PRO mode at low flow rates but it was lower than that in the PRO 64 mode at high flow rates of the feed and draw solutions. The outcomes of the study are 65 very promising with regard to membrane flux and dilution of draw solution. 66

67

Keywords: Forward Osmosis (FO); Multi Stage flash (MSF); Pretreatment; Scaling;Membrane flux.

70

71

73 **1. Introduction**

74

Thermal desalination processes such as multi stage flash (MSF) and multi effect 75 distillation (MED) demonstrated a high performance in a harsh environment without the 76 requirements for seawater pretreatment. Conventionally, the top brine temperatures 77 78 (TBT- the operating temperature in thermal desalination plant) in the MSF (operating in brine recycle mode) and MED are 65°C and 112 °C, respectively. These temperatures 79 would achieve a recovery rate equal to 30% in both technologies [1-3]. However, these 80 processes experience a major drawback represented by scale formation and deposition on 81 the surface of heat transfer tubes. Scale formation reduces the heat transfer efficiency of 82 the heat exchangers and adversely impact the performance of the thermal plant [1-4]. 83 Alkaline scales, mainly CaCO₃, were reported in MED plants while non-alkaline scales, 84 such as MgSO₄ and CaSO₄, were the main scale formations in the MSF plants [3]. The 85 main strategies for scale minimization and removal in thermal plants are the use of 86 antiscalants and periodic cleaning. Technically, these strategies are not effective in 87 preventing scale deposition that builds up over time [2,5-8]. Alternatively, 88 89 unconventional processes such as pretreatment using Nanofiltration (NF) membrane was proposed for the removal of scale ions from the feed solution to thermal plants [9,10]. 90 91 Integrating NF with thermal desalination demonstrated a high efficiency in the removal of divalent ions, such as Ca²⁺, Mg²⁺ and SO4⁻², from seawater and allowed thermal plants 92 to operate at elevated top brine temperatures [11]. An experimental work by Hasan et al. 93 94 [10] demonstrated the advantage of NF pretreatment of seawater for the removal of scale ions and feasibility to increase the TBT of the MSF plant to 130°C. Operating at a TBT 95 equal to130°C increased the recovery rate in the MSF plant and produced a gained output 96 ratio (GOR) of 13. Despite the successful application of NF process for pretreatment of 97 seawater, economically the process was unfeasible due to the high-energy cost [12–14]. 98 The specific power consumption in the NF process was 1 kWh/m³ when operating at a 99 65% recovery rate which is considered relatively high for an economic desalination 100 101 process [15,16]. A previous study investigated the feasibility of FO pretreatment of feed solution to the 102

103 MSF plant [17]. Brine reject was used as the draw solution while seawater was the feed

solution. The study revealed the potential of the FO process to reduce the concentration

concentration of Ca^{2+} , Mg^{2+} and SO_4^{2-} ions was achieved by the FO process. Moreover, 106 the feasibility of the FO process combined to MSF plant is approved to reduce the 107 concentration of divalent ions in the feed solution at 130 °C [15]. The estimated water 108 flux for 45 g/L seawater salinity was in the range of 4 L/m^2 .h to 9.6 L/m^2 h depending on 109 the recovery rate of the FO process. For 45 g/L seawater salinity and 16% FO recovery 110 rate, the concentration of divalent ions in the draw solution decreased by 13% after the 111 FO treatment. The corresponding value for 32% FO recovery rate was 23.5% reduction in 112 the concentration of divalent ions [15]. Unlike the NF process, the driving force in the FO 113 process is the osmotic pressure gradient across the FO membrane instead of the hydraulic 114 pressure [17,18]. Therefore, the cost of such pretreatment process is expected to be lower 115 116 than that of the NF process. 117 Previous FO studies on the pretreatment of feed solution to the MSF plant were theoretical and there is no experimental data, yet to proof the concept. Experimental data, 118 therefore, are essential to demonstrate the feasibility of the FO-MSF system for seawater 119 desalination. In this study, we experimentally investigated the feasibility of FO process 120 121 for the treatment of the feed solution to the MSF plant. Real MSF brine reject and seawater, the draw and feed solution, respectively, were collected from a thermal 122 123 desalination plant in Doha City, Qatar. The study investigated the impact of different operating parameters on the performance of the FO process. Concentration of divalent 124 ions in the brine reject was measured before and after the FO process to determine the 125

of divalent ions in the brine reject [17]. At a 32% recovery rate, 62% reduction in the

dilution ratio.

127

126

105

2. Materials and Methods

- 128 2.1.

Draw and Feed solutions characteristics

129

In the FO process a brine reject (BR) collected from a MSF thermal desalination plant in 130

- Qatar was used as the draw solution (DS) while the feed solution (FS) was seawater 131
- collected from the west bay in Qatar. The characteristics and composition of the DS and 132

- the FS in terms of cation and anion concentrations, total dissolved solids (TDS),
- 134 conductivity, pH and turbidity are illustrated in Table 1.
- 135
- 136
- 137 Table 1: Characteristics of seawater and brine reject of MSF

FS DS		DS	Method		
	(SW)	(BR)			
Cl ⁻ (ppm)	22183.7	35377.9	APHA 4110 DETERMINATION OF ANIONS BY ION CHROMATOGRAPHY Equipment: Metrohm 850 Professional IC		
Br ⁻ (ppm)	74.93	118.79			
SO ₄ ²⁻ (ppm)	3153.6	5041.5			
Na ⁺ (ppm)	12952.6	20993.4	APHA 3120 METALS BY PLASMA EMISSION SPECTROSCOPY		
K ⁺ (ppm)	458.7	739.7			
Ca ²⁺ (ppm)	485.8	725.4	Equipment: iCAP 6500-ICP-OES CID		
Mg ²⁺ (ppm)	1535.0	2504.8	Spectrometer (Thermo Scientific)		
TDS (ppm)	43474	81492	APHA 2540 C. Total Dissolved Solids Dried at 180°C		
Conductivity	60750	93650	APHA 2510 B. Conductivity		
(µs/cm)					
рН	8.40	9.07	APHA 4500-H+ B. Electrometric Method		
Turbidity	1.45	0.35	APHA 2130 B. Nephelometric Method		
(NTU)					

139 **2.2. FO membrane**

140

In this study, a flat sheet Thin Film Composite (TFC) FO membrane made by HTI
(USA). According to the manufacturer the membrane can tolerate temperatures up to 40
°C and has a rejection rate for sodium chloride ions of 90%. The membrane was placed
inside the FO cell and washed for 30 minutes with distilled water for pre-conditioning

and removal of any impurities from the surface. A 1 mm Sepa CF high fouling spacer (8
x 3.5 cm) was always placed on the support side of the FO membrane.

147 148

2.3. FO Bench-scale unit

A CF042D-FO cell provided by Sterlitech was used in this study. The exterior 149 dimensions of the cell are 12.7 x 10 x 8.3 cm (5 x 4 x 3.25 in) with a membrane active 150 area of 42 cm^2 (6.5 in²). CF042D FO cell has a shape of a cube, made of acetal 151 copolymer and can withstand a maximum temperature and pressure of 82°C (180 °F) and 152 1000 psi (69 bar), respectively. The FO system has two stainless steel tanks of 9 L 153 capacity for the FS and DS supply provided by Sterlitech (USA). The flow rates of the FS 154 155 and the DS were measured using two panel mount flow meters F-550 from Blue-White industries Ltd. These flow meters have a maximum reading ability up to 4 LPM (1 GPM) 156 and a minimum of 0.4 LPM (0.1 GPM). The flows of the FS and the DS were set in a 157 countercurrent flow mode. The FS and the DS were circulated in the system using two 158 Mount Gear Pumps with Console Drive 115 V PEEK Gears/PTFE seals provided by 159 Sterlitech Company. The maximum motor rotation per minute for the pump is 5000 rpm 160 where the pump can achieve a maximum flow rate of 3200 mL/min (3.2 LPM). The 161 162 pressure of the FS and the DS were measured using pressure gauges type PEM series 163 provided by Winters Company in the range of 0 - 3 bar (0 - 45 psi). A MX-CA11B immersion circulator (PolyScience Co-USA) controlled the temperature of the DS during 164 the FO experiments. This controller measured the temperature of solutions which can 165 read up to 135 °C. The conductivity of the FS and the DS were measured by OAKTON 166 PCD650 multi meter. This device has the ability to measure the conductivity, salinity and 167 168 total dissolved solids (TDS) in the range of 0–500 mS, 0-800 ppt and 0–500 ppt, respectively. Ohaus RangerTM bench-scale balance connected to a computer to record the 169 change in the FS weight. Water flux was calculated by measuring the change in weight of 170 171 the FS over time divided by the membrane area multiplied by water density according to Equation (1): 172

173
$$J_w(LMH) = 1000x \frac{\Delta W}{A t \rho} = \frac{1000(W_f - W_i)}{A t \rho}$$
 Equation (1)

)

- 174 ΔW is the change in the FS weight (kg) before and after permeation time, A is the
- 175 membrane effective area (m²), t is the time (h) and ρ is water density (kg/m³). The initial
- volume of the DS and the FS were 6 L and the FS and the DS were recycled back to the
- same tanks. Figure 1 depicts a schematic diagram of the FO system used in this study.

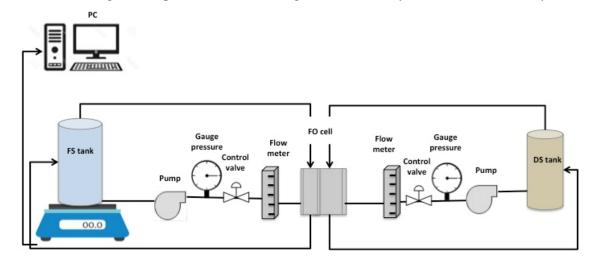




Figure 1. A schematic diagram of the FO system used in this study

2.4. Experimental procedure

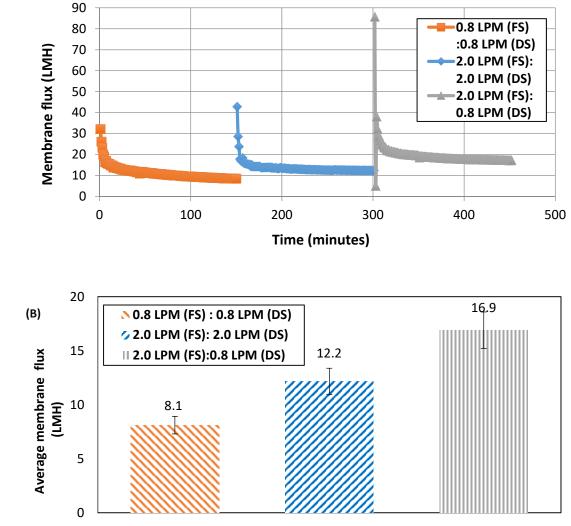
The experiments were designed to operate for 150 minutes. Firstly, the impact of 181 changing the circulation flow rate of the FS and the DS was studied. Three different flow 182 rates were studied, 0.8:0.8 LPM, 2.0:2.0 LPM, 0.8:2.0 LPM for the draw solution and the 183 feed solution, respectively. Secondly, the influence of increasing the temperature of the 184 DS from 25 °C to 40 °C by a 5 °C increment was studied. Finally, the impact of the 185 membrane orientation was studied where firstlty the membrane active layer (AL) faced 186 the DS (AL-DS), PRO mode and then the membrane AL faced the FS (AL-FS), FO 187 188 mode. After each run and before the next run the system was washed with distilled water for 30 minutes. 189

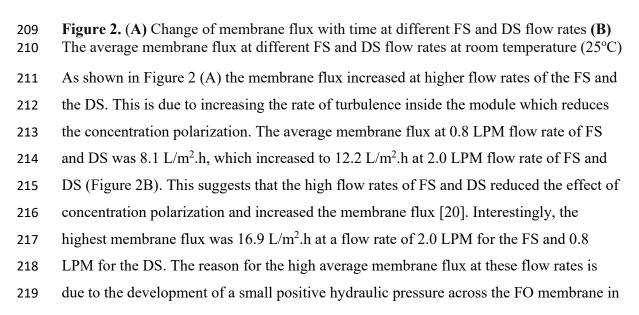
3. Results and discussion

- 191 3.1. Impact of Feed Solution (FS) and Draw Solution (DS) flow rates
- 192 3.1.1 Membrane flux

193 The impact of increasing the FS flow rate and the DS flow rate on the membrane flux was evaluated at room temperature (i.e. 25°C). The experiments were conducted at a flow 194 rate of 0.8 LPM for the FS and the DS then the flow rates were elevated to 2 LPM for 195 both the FS and the DS. Finally, the membrane flux was evaluated at a FS and DS flow 196 rate of 2.0 and 0.8 LPM, respectively. Each experiment lasted for 150 minutes and the 197 membrane active layer was facing the DS (i.e. PRO mode). Figure 2 (A) shows the 198 change of membrane flux with time at the different flow rates of the FS and the DS. 199 Figure 2 (A) shows the three consecutive runs where the membrane was washed for 30 200 minutes with distilled water between each run. Figure 2 (B) illustrates the average 201 membrane flux in the FO process at the different flow rates of the FS and the DS. In 202 general, membrane flux decreased over time due to the dilution and concentration of 203 204 draw and feed solution, respectively, that resulted in reducing the osmotic pressure 205 driving force across the FO membrane (Figure 2(A)). 206

(A)

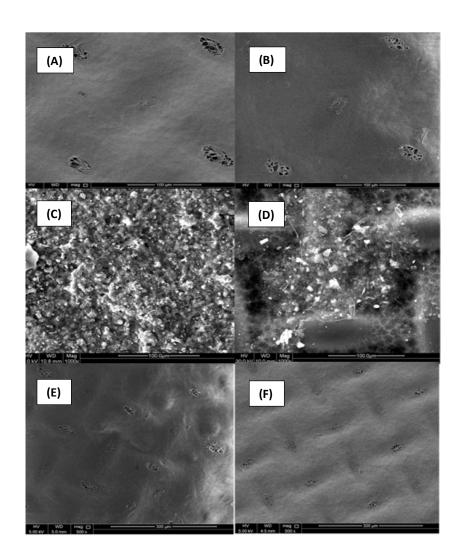




the same direction of the draw solution. A value of 0.15 bar hydraulic pressure was 220 measured on the feed solution side. This hydraulic pressure was created by the higher 221 222 flow rate of the FS, 2.0 LPM, compared to FS, 0.8 LPM, inducing an additional permeation flow across the membrane. Increasing the flow rate of the FS and the DS 223 from 0.8 LPM: 0.8 LPM to 2.0 LPM: 2.0 LPM resulted in 33.6% increase in the average 224 membrane flux while over 52% increase in the average membrane flux was achieved at 225 2.0:0.8 LPM flow rate of the FS and the DS, respectively. It is apparent that operating the 226 FO system at higher flow rates does not necessarily result in the most desirable 227 228 membrane flux despite its advantage in reducing the effect of concentration polarization. Operating the FO system at different feeds flow rates with the flow rate of the FS being 229 higher than that of the DS would result in a better membrane flux in the FO process. 230 231 The drop in the membrane flux over time can be attributed to either the reduction in the 232 osmotic pressure driving force due to the dilution and concentration of the draw and the 233 feed solution as mentioned earlier or it could be due to the fouling of the membrane. Figure 3 shows the Scanning Electron Microscope (SEM) images for the active and 234 support layer of the FO membrane before and after the FO experiments. Figure 3 (A) and 235 236 Figure 3 (B) show the clean (i.e. before use) active layer and support layer of the membrane, respectively. Figure 3 (C) and Figure 3 (D) show the membrane active layer 237 238 and support layer, respectively, after the experimental run and before washing the membrane with distilled water. Figure 3 (E) and Figure 3 (F) show the membrane active 239 layer and support layer, respectively, after washing the membrane with distilled water for 240 241 30 minutes. It is clear from Figure 3 (C) and Figure 3(D) that salts accumulated on both sides of the membrane forming a fouling layer on the membrane surface. However, it 242 should be noted that the same membrane was used for three consecutive runs. The 243 membrane was washed after every experiment for 30 minutes with distilled water. In fact, 244 all tests were repeated three times and the membrane flux results were very close in all 245 runs after membrane washing. This indicates that the fouling materials were washed out 246 during the washing process. Figure 3 (E) and Figure 3 (F) show the membrane active 247 layer and support layer were clean after washing with distilled water for 30 minutes. 248 249 Generally, fouling of the FO membrane seems to be reversible by membrane cleaning

250 with distilled water. This finding is in an agreement with previous work carried out by

- 251 Modern Water in Oman [9]
- 252



253

Figure 3. Fouling on the FO membrane surface after permeation during PRO mode (A) clean active layer, (B) clean support layer, (C) active layer after use, (D) support layer after use, (E) active layer after washing with distilled water for 30 minutes, (F) support layer after washing with distilled water for 30 minutes.

254

- 255 3.1.2 Recovery rate
- Figure 4 shows the achieved recovery rates at the studied flow rates after 150 minutes.
- 257 The recovery rate percentage is calculated using Equation (2) [39]:

259 %R =
$$\frac{\frac{\Delta V_p}{\Delta t}}{\frac{\Delta V_F}{\Delta V_F}}$$
100 Equation (2)

260 ΔV_p and ΔV_F are the change in volume of permeate and feed solution (L), respectively, 261 and Δt is time of the experiment (h). Equation 2 can be described in terms of V_p and V_F 262 since Δt is equal for both permeate and feed solution:

263

264 %R =
$$\frac{V_p}{V_F} \times 100\%$$
 Equation (3)

265 V_p is the permeate volume at the end of each run and V_F is the initial volume of the feed solution. The maximum recovery rate at 0.8:0.8 LPM flow rate of the feed and the draw 266 solution was 1.4%, increased to 2.1% at 2.0:2.0 LPM flow rate of the feed and the draw 267 268 solution. The maximum recovery rate of 3% was achieved at 2.0 LPM: 0.8 LPM flow 269 rate of the feed and the draw solution, respectively. As explained earlier the higher recovery rate at 2.0 LPM: 0.8 LPM was due to the development of a positive hydraulic 270 pressure in the same direction of the draw solution, which promoted further permeation 271 flow across the membrane. 272

273

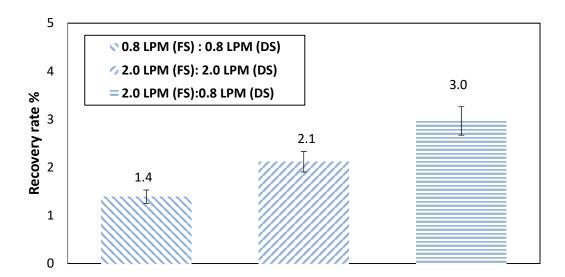


Figure 4. Impact of increasing FS and DS flow rates on recovery rate percentage at isothermal conditions (25°C).

277 3.1.3 Dilution of draw solution

The concentration of Ca^{2+} , Mg^{2+} and SO_4^{2-} ions were measured in the DS before and after 278 the experimental runs. As mentioned earlier, these ions are responsible for scale 279 280 formation and deposition in the MSF desalination plant. As shown in Table 2 at 0.8 LPM: 0.8 LPM flow rate of the feed solution and the draw solution and at room temperature, 281 the concentration of SO4²⁻, Mg²⁺, and Ca²⁺ ions in the draw solution was 5203.9, 2539.8 282 and 733.6 ppm, respectively. After the FO experimental run these concentrations became 283 5163.3, 2519.9 and 714.1 ppm for SO4²⁻, Mg²⁺ and Ca²⁺ ions, respectively. It was noticed 284 that the draw solution was diluted by 0.78%, 0.78% and 1.1% for SO₄²⁻, Mg²⁺, and Ca²⁺ 285 ions, respectively. The corresponding dilution in ions concentration at 2.0:2.0 LPM flow 286 rate of the feed solution and the draw solution was 2.6%, 1.3% and 1.7% for SO_4^{2-} , Mg^{2+} 287 and Ca^{2+} ions, respectively. Where the concentration of SO_4^{2-} , Mg^{2+} and Ca^{2+} ions in the 288 draw solution was 5052.9, 2493.7 and 729 ppm, respectively. After the FO experimental 289 run these concentrations became 4923.4, 2460.9 and 716.8 ppm for SO42-, Mg2+ and Ca2+ 290 ions, respectively. A further dilution of 2.9%, 1.8% and 2.2% for SO4²⁻, Mg²⁺ and Ca²⁺ 291 ions, respectively was achieved at 2.0:0.8 LPM flow rate of the feed solution and the 292 draw solution. Where the concentration of SO_4^{2-} , Mg^{2+} and Ca^{2+} ions in the draw solution 293 was 5712.2, 2601.6 and 726.2 ppm, respectively. After the FO experimental run these 294 concentrations became 5547.6, 2555.3 and 715.5 ppm for SO_4^{2-} , Mg^{2+} and Ca^{2+} ions, 295 respectively. It was noticed that the SO4²⁻ and Ca²⁺ ions exhibited higher dilution 296 percentage than the Mg²⁺ ions; this was attributed to several factors such as the FO 297 membrane rejection to ions and to the ions diffusion coefficient. Generally, SO4²⁻ is 298 highly rejected by FO membranes because of its negative charge and its large molecular 299 weight [10, 18]. FO membrane rejection to Ca^{2+} was higher than Mg^{2+} because of the 300 larger molecular weight of calcium ions compared to magnesium ions. It should be also 301 noted that SO_4^{2-} has a diffusion coefficient of $1.07*10^{-9}$ m²/s, which is higher than that of 302 Ca^{2+} (i.e. $0.793*10^{-9} \text{ m}^2/\text{s}$) and Mg⁺² (i.e. $0.703*10^{-9} \text{ m}^2/\text{s}$). This will affect ions reverse 303 salt diffusion across the membrane and hence concentration in solution. A high rejection 304 of SO4²⁻ ions by FO membranes is very important in the FO pretreatment of seawater to 305 prevent scale formation in the MSF plant since MgSO4 and CaSO4 are the main non-306 alkaline scale formations. It should be mentioned here that the initial concentrations of 307

- the studied ions slightly varied between each set of experiments due to the fact that fresh
- 309 samples were used for every set of experiments. New seawater samples and new brine
- 310 reject samples were used for every set of experiments.

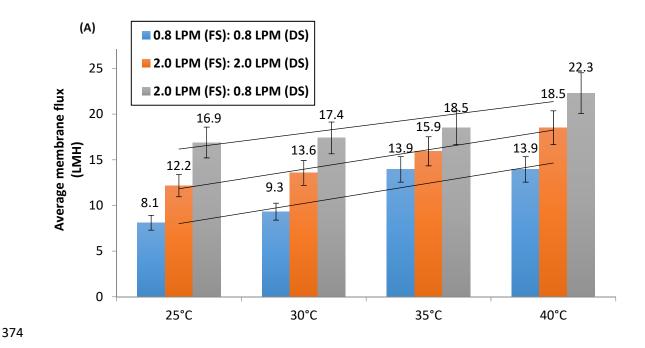
Table 2: Concentration of SO_4^{2-} , Mg^{2+} , and Ca^{2+} ions in the DS before and after the FO experiments at different DS and FS flowrates and at room temperature.

Ion (ppm)	Flow rates of FS and DS (LPM)	Initial ions concentration in DS (ppm)	Ions concentration in DS at the end of the run (ppm)	Reduction (ppm)	Reduction (%)
SO4 ²⁻	0.8 LPM (FS):	5203.9	5163.3	40.6	0.78
	0.8 LPM (DS)				
	2.0 LPM (FS):	5052.9	4923.4	129.5	2.6
	2.0 LPM (DS)				
	2.0 LPM (FS):	5712.2	5547.6	164.6	2.9
	0.8 LPM (DS)				
Mg ²⁺	0.8 LPM (FS):	2539.8	2519.9	19.9	0.78
	0.8 LPM (DS)				
	2.0 LPM (FS):	2493.7	2460.9	32.8	1.3
	2.0 LPM (DS)				
	2.0 LPM (FS):	2601.6	2555.3	46.3	1.8
	0.8 LPM (DS)				
Ca ²⁺	0.8 LPM (FS):	733.6	714.1	8.06	1.1
	0.8 LPM (DS)				
	2.0 LPM (FS):	729	716.8	12.2	1.7
	2.0 LPM (DS)				
	2.0 LPM (FS):	726.2	715.5	16.1	2.2
	0.8 LPM (DS)				

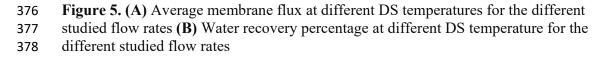
320 3.2. Impact of Draw Solution Temperature

Practically, the temperature of brine reject from an MSF desalination plant will be around 321 40°C. Therefore, we investigated the impact of the draw solution temperature on the 322 performance of the FO process. Increasing the temperature of the draw solution was 323 evaluated at different flow rates of the feed and the draw solutions. The experiments were 324 conducted at draw solution temperatures of 25°C, 30°C, 35°C, and 40°C while the 325 temperature of the feed solution remained constant at 25°C. Typically, the temperature of 326 MSF brine is about 40°C but using different brine temperature would help to understand 327 the impact of DS temperature on the performance of the FO process. The duration of each 328 experiment was 150 minutes in which the membrane active layer was facing the DS (i.e. 329 330 PRO mode). Figure 5 (A) presents the average membrane flux at the different draw solution temperatures and flow rates of feed and draw solutions. It was noticed that for 331 any given flow rates, the average membrane flux increased with the increase in the 332 temperature of the draw solution from 25°C to 40°C. At 0.8: 0.8 flow rate of the feed and 333 the draw solution, the average membrane flux was 8.1 L/m^2 .h at a DS temperature of 334 25°C which increased to 13.9 L/m².h at a DS temperature of 40°C, achieving 72% higher 335 average membrane flux due to the temperature increase of the DS. The corresponding 336 increase in the average membrane flux for 2.0 LPM: 2.0 LPM and 2.0 LPM: 0.8 LPM 337 338 flow rates for the FS and the DS was 52% and 32%, respectively. The increase of the 339 membrane flux at high draw solution temperature could be due to the lower water 340 viscosity and greater diffusivity across the membrane at higher temperatures. Furthermore, according to Van't Hoff equation, the osmotic pressure increases with the 341 increase of the draw solution temperature, therefore, the driving force in the process 342 increases. Figure 5(A) also shows that the impact of feeds' flow rates on the average 343 membrane flux remained unaffected with the variation in the temperature of the feed 344 solution. The FO process at flow rate equal to 2.0 LPM: 0.8 LPM for the feed solution 345 and the draw solution, respectively, exhibited the highest average membrane flux, which 346 reached 22.3 L/m².h at 40°C. According to a previous study by Hawari et al. [21], the 347 membrane flux in a FO process increased with increasing the draw solution temperature. 348 The membrane flux reached a maximum value at a draw solution temperature around 26 349 °C before it started to decrease again with further temperature increase of the draw 350

solution up to 32°C. On the contrary, the membrane flux in this study kept increasing as 351 the temperature of the DS increased. Where at the highest draw solution temperature of 352 40°C the highest membrane flux was obtained. This could be due to the increase of the 353 flow rates of the feed solution and the draw solution that resulted in i) reducing the 354 impact of concentration polarization which could have overcame the thermal-osmosis 355 effect ii) developing a positive hydraulic pressure across the FO membrane that promoted 356 permeation flow. Where at flow rates 2.0 LPM for FS and 0.8 LPM of DS a 0.15 bar 357 hydraulic pressure was measured across the membrane. This can be clearly seen in Figure 358 5 (A) where at the flow rates of 0.8 LPM: 0.8 LPM for the FS and DS there was no 359 enhancement in the membrane flux when the temperature increased from 35°C to 40°C. 360 In effect, the effect of CP decreased at high flow rates of the feed and draw solution, 361 362 leading to a noticeable increase in the water flux from the feed to draw solution which 363 reduced the counter water flux due to the thermal-osmosis. It should be noted that the obtained average membrane flux was found to be very promising and it is 2.3 to 5.5 times 364 more than the theoretically anticipated water flux in previous studies [22–26]. However, 365 water flux between 25 and 33 L/m2h was reported in FO experiments treating feed water 366 367 at 32 oC [20]. Figure 5B also show that, depending on the temperature of draw solution, increasing the flow rate of feed solution from 0.8 LPM to 2.0 LPM resulted in 33 to 368 369 100% increase in water flux. On the other hand, increasing the temperature of draw solution (using same flow rates) resulted in up to 71% increase in water flux. As such, 370 increasing flow rate of feed solution resulted in a larger improvement in the water flux. 371 372



(B) 0.8 LPM (FS): 0.8 LPM (DS) 4.6 2.0 LPM (FS): 2.0 LPM (DS) 5 2.0 LPM (FS):0.8 LPM (DS) 3.4 4 Recovery rate % 3.4 3.3 3.1 <u>3</u>.0 2.8 2.7 2.7 3 2.1 1.8 2 1.4 1 0 25°C 30°C 40°C 35°C



- increasing the temperature of the draw solution from 25°C to 40°C and was always higher
- at 2.0:0.8 LPM flow rate of the feed and the draw solution. At the 2.0:0.8 LPM flow rate,

Figure 5 (B) shows the recovery rate of the FO process at different flow rates of the draw

solution and the feed solution. The recovery rate of the FO process increased with

the recovery rated increased by 35%, from 3% to 4.6%, due to the increase of DS

- temperature from 25° C to 40° C. The reason for a greater membrane flux at a draw
- solution temperature of 40° C is due to the higher diffusivity of water molecules at
- elevated temperatures and higher osmotic pressure of draw solution. The FO process
- resulted in 2.9%, 1.8% and 2.2% dilution of SO_4^{2-} , Mg^{2+} , and Ca^{2+} ions in the draw
- solution, respectively at 25°C and 2.0:0.8 LPM flow rate. The dilution of SO_4^{2-} , Mg^{2+} ,
- and Ca^{2+} ions in the draw solution increased to 7.7%, 4.9%, and 8.5%, respectively at
- 40° C and 2.0:0.8 LPM flow rate. As indicated before, SO₄²⁻ and Ca²⁺ ions exhibited
- higher dilution by the FO than Mg^{2+} ion but most important that SO_4^{2-} ions are reduced in
- the solution since it is the main component in non-alkaline scale formations in the MSF
- 393 plant.
- 394 3.3. Impact of membrane orientation
- 395 The membrane orientation is one of the factors that would affect the performance of the FO process [20]. The membrane flux was evaluated in the PRO mode (DS-AL) and in the 396 FO mode (FS-AL). Figure 6 shows that the membrane flux was generally higher in the 397 PRO mode than in the FO mode. This is due to the lower effect of concentration 398 399 polarization in the PRO mode. This is in agreement with previous studies, which demonstrated better controllable concentration polarization effects when the FO process 400 operates in the PRO mode [20,27–29]. Figure 6 shows that the average membrane flux in 401 402 the FO mode was equal to that in the PRO mode at low flow rates, i.e. 0.8:0.8 LPM, and feed temperatures 30°C to 40°C. Whilst the average membrane flux in the PRO mode was 403 higher than that in the FO mode at 2.0:2.0 LPM and 2.0:0.8 LPM. This suggest that at 404 low feeds' flow rates, the FO process has no preference to operate on either mode, i.e. FO 405 or PRO, whereas at high feeds' flow rate it is desirable to operate the process at the PRO 406 mode to increase the membrane flux. In case of seawater contains high fouling materials, 407 it is suggested to operate the process in the FO mode and hence 0.8:0.8 LPM would be 408 more energy-efficient and easier to clean the membrane. However, 2.0:0.8 LPM FO 409 process operating at the PRO mode generated 1.6 times more water flux than 0.8:0.8 410 LPM FO process and should be considered when seawater quality does not promote 411 412 membrane fouling.
 - 18

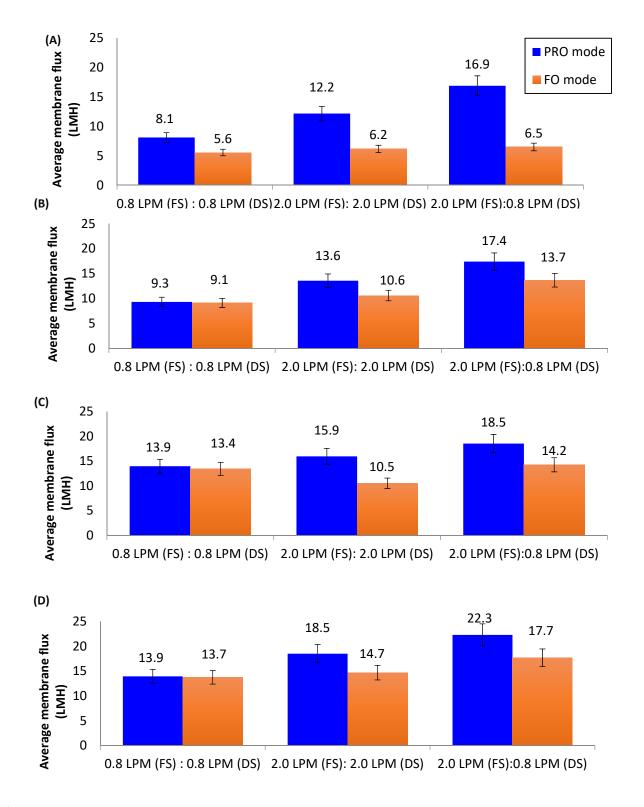


Figure 6. Impact of membrane orientation on average membrane flux (**A**. At DS temperature of 25°C, **B**. At DS temperature of 30°C, **C**. At DS temperature of 35°C, **D**. At DS temperature of 40°C)

414 **4.** Conclusions

415

The feasibility of employing the forward osmosis (FO) process in the pretreatment of 416 417 Multi Stage Flashing (MSF) desalination plant feed solution was evaluated in the present study. Brine reject from real MSF desalination plant and seawater were the draw and feed 418 solutions. The impact of increasing the FS flow rate and the DS flow rate on the 419 420 membrane flux was evaluated. It was found that the highest membrane flux was 16.9 L/m^2 .h at a flow rate of 2.0 LPM for the FS and 0.8 LPM for the DS. The maximum 421 membrane flux was 22.3 L/m².h at 40°C draw solution temperature, this actually three 422 423 times more than the theoretical flux expected in the previous studies that suggested FO process for treatment of feed solution to the MSF. The study showed that water flux was 424 425 generally higher in the PRO mode than in the FO mode. In fact, this is not a problem in the FO process for seawater pretreatment for the MSF desalination plant since results 426 demonstrated that the membrane flux can be fully recovered by washing the membrane 427 428 with distilled water for 30 minutes. This indicates that the fouling was not severe and 429 mainly reversible. In general, the study showed the promising application of FO process for pretreatment of seawater to MSF plant. A pilot plant test is planned to take place in 430 the very near future. 431

432

433 Acknowledgments

- 434 This research is made possible by NPRP award (NPRP10-0117-170176) from Qatar
- 435 National Research Fund (QNRF). The statements made herein are solely the
- 436 responsibility of the authors. In addition, the authors wish to thank Qatar Foundation for
- the financial support provided to one of the co-authors through a graduate sponsorship
- 438 research award (GSRA4-2-0402-17013). The authors also wish to thank Qatar Electricity
- and Water Company (QEWC) for the supply of brine.

440 **References**

- Budhiraja P, Fares AA. Studies of scale formation and optimization of antiscalant
 dosing in multi-effect thermal desalination units. Desalination. 2008;220(1–3):313–
 25.
- 444 2. Ghani S, Al-Deffeeri NS. Impacts of different antiscalant dosing rates and their

thermal performance in Multi Stage Flash (MSF) distiller in Kuwait. Desalination 445 2010;250(1):463-72. Available 446 [Internet]. from: http://dx.doi.org/10.1016/j.desal.2009.09.077 447 3. El Din AMS, Mohammed RA. Brine and scale chemistry in MSF distillers. 448 Desalination. 1994; 99(1):73-111. 449 Hamed OA, Al-Otaibi HA. Prospects of operation of MSF desalination plants at 450 4. high TBT and low antiscalant dosing rate. Desalination [Internet]. 2010;256(1-451 3):181-9. Available from: http://dx.doi.org/10.1016/j.desal.2010.01.004 452 Tijing LD, Woo YC, Choi JS, Lee S, Kim SH, Shon HK. Fouling and its control in 5. 453 membrane distillation-A review. J Memb Sci [Internet]. 2015;475:215-44. 454 Available from: http://dx.doi.org/10.1016/j.memsci.2014.09.042 455 6. Amjad Z. Calcium sulfate dihydrate (gypsum) scale formation on heat exchanger 456 surfaces: The influence of scale inhibitors. J Colloid Interface Sci. 1988;123(2):523-457 36. 458 7. Lyster E, Kim M man, Au J, Cohen Y. A method for evaluating antiscalant 459 retardation of crystal nucleation and growth on RO membranes. J Memb Sci 460 2010;364(1-2):122-31. Available from: [Internet]. 461 http://dx.doi.org/10.1016/j.memsci.2010.08.020 462 Warsinger DM, Swaminathan J, Guillen-Burrieza E, Arafat HA, Lienhard V JH. 463 8. 464 Scaling and fouling in membrane distillation for desalination applications: A review. Desalination [Internet]. 2015;356:294-313. Available from: 465 http://dx.doi.org/10.1016/j.desal.2014.06.031 466 467 9. Nicoll PG. Forward osmosis as a pre-treatment to reverse osmosis. Int Desalin Assoc World Congr Desalin Water Reuse 2013 [Internet]. 2013;1–21. Available from: 468 469 http://www.modernwater.com/assets/downloads/Papers/Forward Osmosis as a Pretreatment to Reverse Osmosis.pdf 470 10. Hassan AM, Al-Sofi MAK, Al-Amoudi AS, Jamaluddin ATM, Farooque AM, 471 472 Rowaili A, et al. A new approach to membrane and thermal seawater desalination processes using nanofiltration membranes (Part 1). Desalination. 1998;118(1-473 474 3):35-51. Abdel Nasser Mabrouk, Hassan Fath MD and HA. Techno-Economics of Hybrid 11. 475 NF / FO with Thermal Desalination Plants. World 's largest Science, Technology 476 & Medicine Open Access book publisher. 2015 p. 477 12. Eriksson P, Kyburz M, Pergande W. NF membrane characteristics and evaluation 478 for sea water processing applications. Desalination. 2005;184(1-3):281-94. 479 Mezher T, Fath H, Abbas Z, Khaled A. Techno-economic assessment and 480 13. environmental impacts of desalination technologies. Desalination. 2011;266(1-481 482 3):263-73. 14. Altaee A. Forward Osmosis: Potential use in Desalination and Water Reuse. J 483 Membr Sep Technol. 2012;1(Md):79-93. 484 485 15. Altaee A, Mabrouk A, Bourouni K, Palenzuela P. Forward osmosis pretreatment of seawater to thermal desalination: High temperature FO-MSF/MED hybrid system. 486 Available from: 487 Desalination [Internet]. 2014;339(1):18-25. http://dx.doi.org/10.1016/j.desal.2014.02.006 488 Petty JD, Huckins JN, David A. (12) Patent Application Publication (10) Pub . No 16. 489 .: US 2002/0187020 A1. 2002;1(19). 490

- 491 17. Altaee A, Mabrouk A, Bourouni K. A novel Forward osmosis membrane
 492 pretreatment of seawater for thermal desalination processes. Desalination [Internet].
 493 2013;326:19–29. Available from: http://dx.doi.org/10.1016/j.desal.2013.07.008
- Hassan AM. Review of Development of the New Nf-Seawater Desalination Process
 From Pilot Plant To. Engineering. 2002;2(December):14–7.
- 496 19. Torrey S, Scott J. Membrane and ultrafiltration technology: developments since
 497 1981 [Internet]. Noyes Data Corp.; 1984. (Chemical technology review). Available
 498 from: https://books.google.com.qa/books?id=JoA3AQAAIAAJ
- 499 20. Hawari AH, Kamal N, Altaee A. Combined influence of temperature and flow rate
 500 of feeds on the performance of forward osmosis. Desalination. 2016;398:98–105.
- 501 21. Mengual JI, García López F, Fernández-Pineda C. Permeation and thermal osmosis
 502 of water through cellulose acetate membranes. J Memb Sci. 1986;26(2):211–30.
- 503 22. Wilke CRC. A.I.Ch.E.J. 1955;
- Phuntsho S, Vigneswaran S, Kandasamy J, Hong S, Lee S, Shon HK. Influence of
 temperature and temperature difference in the performance of forward osmosis
 desalination process. J Memb Sci [Internet]. 2012;415–416:734–44. Available from:
 http://dx.doi.org/10.1016/j.memsci.2012.05.065
- Zhao P, Gao B, Yue Q, Liu S, Shon HK. Effect of high salinity on the performance of forward osmosis: Water flux, membrane scaling and removal efficiency.
 Desalination [Internet]. 2016;378:67–73. Available from: http://dx.doi.org/10.1016/j.desal.2015.09.028
- 512 25. Xie M, Price WE, Nghiem LD, Elimelech M. Effects of feed and draw solution
 513 temperature and transmembrane temperature difference on the rejection of trace
 514 organic contaminants by forward osmosis. J Memb Sci. 2013;438:57–64.
- 51526.Zhao S, Zou L. Effects of working temperature on separation performance,516membrane scaling and cleaning in forward osmosis desalination. Desalination517[Internet].2011;278(1-3):157-64.518http://dx.doi.org/10.1016/j.desal.2011.05.018
- 519 27. Gray GT, McCutcheon JR, Elimelech M. Internal concentration polarization in 520 forward osmosis: role of membrane orientation. Desalination. 2006;197(1–3):1–8.
- 521 28. Tang CY, She Q, Lay WCL, Wang R, Fane AG. Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration. J Memb Sci [Internet]. 2010;354(1–2):123–33. Available from: http://dx.doi.org/10.1016/j.memsci.2010.02.059
- 525 29. Xu Y, Peng X, Tang CY, Fu QS, Nie S. Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis
 527 performance in a spiral wound module. J Memb Sci. 2010;348(1–2):298–309.
- 528 529