Journal of Environmental Management 365 (2024) 121517

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Innovative stimuli-responsive membrane MSF brine rejection dilution by tertiary treated sewage effluent

Daoud Khanafer [a], Ali Altaee [a,*], Alaa H. Hawari [b], John Zhou [a], Lilyan Alsaka [a]

[a] Centre for Green Technology, School of Civil and Environmental Engineering, University of Technology Sydney, 15 Broadway, NSW, 2007, Australia
[b] Department of Civil and Environmental Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

ARTICLE INFO

Keywords:
Pressure stimuli-responsive membrane
Desalination
Forward osmosis
Tertiary sewage effluent

ABSTRACT

In this study, treated wastewater and Multi-Stage Flash (MSF) brine were integrated into the Forward Osmosis (FO) system using pressure stimuli-responsive Nanofiltration (PSRNF) membranes to dilute magnesium, calcium, and sulfate MSF plant brine reject. The deposition of magnesium sulfate and calcium sulfate in the heat exchanger is one of the main issues affecting the performance and efficiency of MSF thermal desalination plants. Reducing the concentration of the divalent ions can minimize scale formation and deposition to a level that allows the MSF plant to operate at high top brine temperature (TBT) and without scale problems. The PSRNF membranes were chosen in the FO process because of their high water permeability, rejection of divalent and monovalent ions, small structure parameter (S), and inexpensiveness compared to commercial FO membranes. Three PSRNF membranes were tested in the FO process with the feed solution facing the active membrane layer to avoid active layer delamination. Although the PSRNF membrane exhibited negligible water flux at 0 bar, it increased when a 2–4 bar was applied to the feed solution. The wastewater temperature was set at 25 °C while 40 °C was the brine operational temperature to mimic the field situation. A maximum average water flux of 39.5 L/m^{2}h was recorded at 4 bar feed pressure when the PSRNF membrane was used for the brine dilution, achieving up to 42% divalent ions dilution at 0.02 kWh/m^3 specific power consumption. The average water flux in the PRSNF membrane was 35% higher than that in the commercial TFC FO membrane. Notably, the PSRNF membrane is ten times cheaper than commercial FO membranes. Notably, the PSRNF membrane is ten times cheaper than commercial FO membranes, achieving substantial cost reductions and pioneering advancements in FO purification technology.

1. Introduction

Despite the advantages of thermal desalination, it suffers from various drawbacks that can affect the overall process. MSF, one of the leading thermal-based desalination techniques, faces the problem of non-alkaline scale formation on the heat exchanger tube at high operating temperatures. The ionic species responsible for the non-alkaline scaling are mainly Ca^{2+}, Mg^{2+}, and SO_4^{2-}. The scale deposition results in an increase in power consumption and overall cost. Currently, different techniques are used to mitigate fouling, such as antiscalants and periodic physical cleaning of the MSF plant tubes. Feed water pretreatment using the membrane process was proposed as an alternative to these techniques. Ata initially proposed the NF separation process to remove the ions responsible for scaling (Hassan, 2006). It is a membrane technology intermediate between reverse osmosis (RO) and ultrafiltration in terms of pore size. The NF membranes have selectivity for various organic and inorganic microorganisms and divalent and multivalent ions. The NF technique is widely used in filtration applications, including industrial wastewater treatment to remove compounds and ions from water, the textile industry to remove colour, the food industry for concentration and recovery, and the water industry as a pretreatment for other desalination techniques (Mulyanti and Susanto, 2018). NF pilot plants were used for seawater filtration to the MSF plants in Saudi Arabia; this implementation successfully increased the top brine temperature (TBT) in the MSF to over 110 °C without scaling issues (Hamed et al., 2005).

A study by Wafi et al. (2019) in Qatar examined the three-year performance of RO and NF pilot plants for seawater desalination. The results demonstrated the dominance of the NF desalination process, where NF recorded 29 % less energy consumption and 29 % less cost.

* Corresponding author.
E-mail address: ali.altaee@uts.edu.au (A. Altaee).

https://doi.org/10.1016/j.jenvman.2024.121517
Received 19 February 2024; Received in revised form 25 April 2024; Accepted 16 June 2024
Available online 21 June 2024

The major drawback of the NF was the fouling problem, which was explained to be related to the membrane quality (Wafi et al., 2019). Despite the NF technique's characteristics of low energy consumption compared to the RO and the high rejection rate of a wide range of commercial NF membranes, the NF process is not yet commercialized in seawater treatment. Data collection based on studies and pilot-scale operations showed the feasibility of the NF technique in wastewater treatment when fouling, poor durability, instability, and low water flux can be controlled (Abdel-Fatah, 2018). To determine the suitability of the NF process as a pretreatment before desalination plants, Hilal et al. studied the performance of three commercially available membranes (NF90, N30F, NF270) in treating high salinity salt solutions similar to the seawater salinity. The results showed that NF90 achieved salt rejection of 95% at high salinity at a pressure of 9 bar (Hilal et al., 2005). Another study used an NF polypiperazine membrane for brackish groundwater treatment at a 6–10 bar pressure range. The NF membrane was able to remove 70–76 % of hardness; however, it only achieved 44–66% salinity removal.

Forward osmosis (FO) was applied for seawater pretreatment for Ca^{2+}, Mg^{2+}, and SO_4^{2-} ions removal and MSF brine reject dilution (Khanafer et al., 2021a). Unlike NF and RO processes, the FO process relies on osmotic pressure for permeation flow, reducing the operating cost and membrane fouling propensity. In the FO process, seawater or tertiary sewage effluent (TSE) was the feed solution to dilute the MSF brine reject draw solution. Due to its lower osmotic pressure, water flux in the TSE tests was more significant than in the seawater FO tests. With seawater feed and brine reject draw solution, the thin film composite (TFC) FO membrane achieved 7.7 L/m^2h water flux, increasing to 27.87 L/m^2h when TSE was the feed solution (Khanafer et al., 2021b). The results indicated the potential of using a wastewater stream to dilute the MSF brine reject in the thermal desalination process. Despite the advantages of the FO process, membrane cost and water flux are some drawbacks limiting the FO application in desalination and water purification.

This study used the concept of pressure stimuli-responsive NF (PSRNF) membranes, patent WO2023/038538 A1 (Altaee et al., 2023), in the FO process for seawater pretreatment for the MSF plant. The PSRNF membrane is a commercial NF membrane with specific characteristics, such as a small structure parameter (S), excellent water flux and rejection rate, and inexpensive to address the drawbacks of the FO membranes. As a pressure-driven membrane, water flux in the PSRNF membrane is insignificant when operating in the FO process, but it increases when slight pressure, 2–4 bar, is applied on the feed side. Besides, the membrane should operate with the feed solution facing the active membrane layer to avoid active layer delamination. The research questions are i) can the PSRNF membrane demonstrate competitiveness with commercial FO membranes in the dilution of the MSF brine reject? ii) what is the decline in water flux for the PSRNF membrane over successive filtration cycles, and iii) what is the specific energy is associated with the operation of the PSRNF membrane under a low-pressure condition? TSE was proposed to be used as the feed solution (FS) in the FO system with three commercially available NF membranes, TS80, XN45, and UA60, for diluting the MSF brine solution, i.e., the DS. The FO system was designed to reduce the divalent ions responsible for scale deposition in the MSF plants. The TSE temperature was maintained at 25 °C, and the brine was 40 °C. Since the NF process is pressure-driven, hydraulic pressures up to 4 bar were applied on the TSE side to stimulate water flux. The ALFS orientation was the operational mode in the FO experiments to avoid the delamination of the selective membrane layer at the applied feed pressure. The feed and draw solution was filtered using a microfilter of 20 μm to remove the turbidity and the organic matter. The performance of each membrane was represented by the water flux, flux reduction, ion concentrations in the brine reject, and specific energy consumption.

1.1. Materials and methods

1.1.1. NF membranes

This investigation utilized three commercial NF membranes, namely TS80, XN45, and UA60, sourced from TRISEP®. The TS80 membrane, recognized as a thin-film polyamide membrane, is commonly employed for water softening in diverse water purification applications. The XN45 and UA60 membranes comprise a thin-film polypiperazine with respective pore sizes of 300–500 Da and 1000 Da, respectively. Table 1 outlines the characteristics of each membrane, considering conditions of 2 g/L $MgSO_4$, 7.6 bar pressure, 25 °C temperature, and a 30-min operational duration. The membranes were chosen because of their high water permeability, hydrophilicity, and small structural parameters (130–170 μm). The latter parameter is crucial in mitigating the impact of internal concentration polarization in FO processes. XN45 and UA60 exhibit 96% and 80% $MgSO_4$ rejection, while TS80 demonstrates 99.6% rejection of divalent ions and 80% rejection of NaCl. Notably, the water permeability coefficients of the selected NF membranes surpass those of the Porifera TFC FO membrane by 4–6.7 times and the FTSH2O CTA FO membrane by 12.5–20 times, as detailed in Table 1. Additionally, the wettability and hydrophilic behavior of the Porifera TFC and FTSH2O CTA membranes were examined through contact angle measurements, revealing distinct characteristics in the active and support layers. Zeta potential measurements were also conducted using Malvern instruments for all membranes. The PSRNF membranes' surface charge was higher than commercial Porifera TFC and FTSH2O CTA membranes, offering better repulsion to positively charged divalent ions.

1.1.2. Stream solutions

In this study, treated wastewater (TSE) was the FS, and brine solution was the DS. The Blacktown wastewater treatment plant in Sydney (Australia) provided the TSE samples. The wastewater treatment processes include nitrification, denitrification, and phosphorus removal. The average daily concentrations of the total kjeldahl nitrogen (TKN) and total phosphorus (TP) are listed in Table 2. The brine concentration was 80 g/L, and a 40 °C temperature was maintained during the experiments. The TSE TDS was 0.967 g/L and maintained a temperature of 25 °C during the FO experiments.

The osmotic pressure of the DS was about 70.4, whereas the FS osmotic pressure was about 0.804 bar; the osmotic gradient between the two streams was remarkably high for promoting a considerable water flux. The characteristics of the TSE are presented in Table 2.

1.1.3. Lab-scale setup

A detailed description of the bench-scale FO system setup used in this study is presented in Fig. 1. A Sterlitech-manufactured CF042A-FO Cell served as the FO filtration unit. This unit, constructed from transparent cast acrylic, boasts dimensions of 5 × 4 × 3.25 inches, housing a membrane area of 42 cm^2 (equivalent to 6.5 square inches). It ensures robust performance with a maximum tolerance of 88 °C and resistance of up to 27.6 bars of hydraulic pressure. Each cell incorporates two flow meters, F-550 from Blue-White Industries Ltd., facilitating precise FS and DS flow rate measurement. Pressure gauges (USG US Gauge) are provided, offering readings between 0 and 4 bars to gauge hydraulic pressure on FS and DS. Cole-Parmer pumps, capable of delivering pressures of up to 5 bars, maintain water circulation within the system. For analyzing solution properties, an HQ 14 d portable conductivity and TDS meter (HACH, Australia) monitors conductivity, TDS, and salinity, while a HACH 2100 P turbidity meter assesses solution clarity. Additionally, a digital scale balance, linked to a computerized system, tracks variations in DS weight.

1.1.4. Experimental work

The first task was the prefiltration of the feed solutions. The TSE and brine solution were filtered using HP4750 dead-end stirred cell (Sterlitech, USA). A 20-μm Whatman membrane was placed perfectly against

Table 1
Characteristics of the PSRNF, TFC Porifera, and CTA FTSH2O membranes.

Membrane	A_w (L/m^{2}h.bar)	B (L/m^{2}h)	S (μm)	NaCl Rj (%)	$MgSO_4$ Rj (%)	Flux (L/m^{2}h)	Zeta potential (mV)	Contact angle
TS80	8.63	1.33	130–170	80	99.2	49.3–81.6	−55.6	17.4°±2.3[a]
XN45	7.96	2.51	130–170	20	96	47.6–73.1	−52	8.2°±2.8[a]
UA60	14.01	26.55	130–170	10	80	76.5–136	−60	15.7°±3.1[a]
Porifera TFC	2.1	1.2	344	96	–	–	−41.9 ± 2.4	68.5° ± 0.7[a] 53.9° ± 2[b]
FTS H_2 O (CTA)	0.69	0.34	707	90	–	–	−12.8 ± 1.2	68.1°± 1[a] 60.2°± 0.5[b]

[a] active layer.
[b] support layer.

Table 2
Characteristics of feed and draw solutions used in this study.

Ion/parameter	TSE	Brine solution	Measuring Instrument
Ca^{2+} (mg/L)	80 ± 3	1040.9	7900 ICP-MS
Mg^{2+} (mg/L)	65 ± 5	2199.6	7900 ICP-MS
SO_4^{2-} (mg/L)	–	6566	DIONEX AS-AP
Cl^- (mg/L)	–	22,351.6	7900 ICP-MS
Na^+ (mg/L)	139 ± 2	19,151.6	7900 ICP-MS
K^+ (mg/L)	–	872.3	7900 ICP-MS
Si^{4+} (mg/L)	6.9 ± 0.01	–	
TDS (g/L)	0.967	80.2	HQ14d Conductivity
Conductivity (mS/cm)	3.91 ± 0.27	106.7	HQ14d Conductivity
pH	7.2 ± 0.2	8.35	HQ40d multi
Temperature (°C)	21 ± 2	40 ± 3	
Nitrogen-TKN (mg/L)	3.5	–	
Phosphors-TP (mg/L)	2.4	–	
Turbidity (NTU)	7.1 ± 0.1	2.43	2100 P Turbidimeter
No prefiltration	1.76 ± 0.12	–	
With prefiltration			
TOC (mg/L)	49.69 ± 2	–	
No prefiltration	28 ± 1.3	–	
With prefiltration			

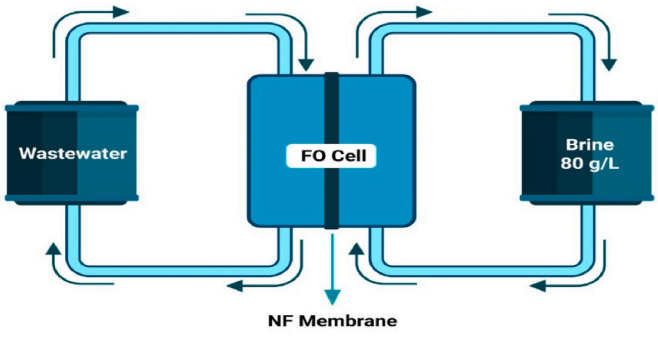

Fig. 1. Illustration of the experimental lab-scale setup.

the stainless steel porous disc, and filtration was run at <1 bar and 20 °C to remove colloidal and microparticles from the feed solutions. The active membrane area is 17.3 cm^3, and the diameter is 47–48 mm.

The MSF brine solution is prepared by heating the seawater to reach the salinity of the real brine reject of the MSF plants. Each FO experiment was operated at a **2 LPM** flow rate for 180 min, repeated three times on the same membrane with physical cleaning of the membrane after each filtration cycle. The cleaning was performed with DI water for 30 min and at 40 °C. All the experiments were operated in the FO mode, where membrane AL faces FS, to avoid the delamination of the active membrane layer when slight pressure was applied to the feed solution. For the TS80 NF membrane, each set of experiments was conducted at 0, 2, and 4 bars. For XN45 and UA60, the four cycles of the FO process were operated at 4 bar to compare the results with the TS80 NF membrane.

1.1.5. Analytical methods

To study the impact of the FO technique conducted in the experiments, the specific power consumption (E_s, kW h/m^2) in the standalone FO process as per the following:

$$E_S = \frac{P_f\, Q_f + P_D\, Q_D}{n\, Q_p} \quad \text{(Equation 1)}$$

Concerning the prefiltration stage, the energy expended in the prefiltration technique, which can be included in the FO process where applicable, was determined by evaluating the following expression:

$$E = \frac{P_f\, Q_f}{n\, Q_p} \quad \text{(Equation 2)}$$

P_f: wastewater hydraulic pressure in bar, Q_f: FS flow rate in m^3/h, P_D: brine hydraulic pressure in bar, Q_D: DS flow rate in m^3/h, n: the pump efficiency (assumed 0.8 in this study), Q_p: permeation flow in m^3/h.

The rate of water passage through the membrane over a given time is referred to as the permeation flux or water flux, denoted as Jw (L/m^{2}h). Water flux is determined by measuring the change in weight of the FS throughout the process, as described by the equation below:

$$J_W = \frac{\Delta W}{A.\Delta t} \quad \text{(Equation 3)}$$

In equation (3), ΔW is the difference in the weight of FS in kg, A is the membrane area in m^2 and Δt is the time interval in hours (h).

The estimation of the recovery rate involves calculating the ratio of permeate flow to feed flow using the following expression:

$$Re = \frac{Q_p}{Q_f} 100\% \quad \text{(Equation 4)}$$

In Equation (4), Q_p and Q_f are the flow rates of permeate and FS (L/min), respectively. After each cleaning method, the reduction in water flux (FR) was calculated to assess the efficacy of these methods in restoring water flux. The calculation of water flux recovery was determined using the following expression:

$$FR = \left(1 - \frac{J_c}{J_f}\right) \times 100 \quad \text{(Equation 5)}$$

J_c is the average water flux after cleaning, and J_f is the average water flux before cleaning. The water permeability coefficient (A_w) of the PSRNF membrane was obtained from the following expression:

$$A_w = \frac{J_w}{(P_f - \Delta\pi)} \quad \text{(Equation 6)}$$

In Equation (6), $\Delta\pi$ is the osmotic pressure of the feed solution (bar). Equation (7) calculates the membrane salt permeability coefficient (B) from the water flux (J_W) and the membrane rejection rate (Rj):

$$B = \frac{(1 - Rj)}{Rj} J_W \quad \text{(Equation 7)}$$

At the outset and conclusion of each FO test, the concentrations of

Ca^{2+} and Mg^{2+} in the brine solution were measured using an Agilent Technologies 7900 ICP-MS ion chromatography machine. Meanwhile, the SO_4^{2-} concentrations were determined using an HPIC-manufactured Dionex VWDIC. Subsequently, all ion concentrations were documented, and the reduction percentages were individually calculated and disclosed for each ion in the FO experiments.

1.2. Results and discussion

1.2.1. Water flux

The FO-MSF system was tested under the draw and feed solution characteristics listed in Table 2 to resemble the field situation. Furthermore, the FO tests were conducted in the ALFS mode only since hydraulic pressure applied to the membrane support layer in the ALDS would delaminate the active layer of the PSRN NF membrane. Commercial NF membranes are designed to operate in a pressure-driven process for wastewater treatment. Since the FO system is an osmotically-driven separation process, a slight pressure range from 1 to 4 bar was applied on the feed side facing the active membrane layer. This feed pressure is used to overcome membrane resistance, and it is much lower than the hydraulic pressure required in the NF membrane for seawater softening, from 15 to 25 bar (Hassan, 2006). The NF TS80 membrane was tested at 0, 2, and 4 bar in multiple filtration cycles to evaluate membrane performance and fouling over time. The operating conditions of the PSRNF membrane were at a 2 LPM flow rate of the feed, and the draw solutions, 40 °C draw solution temperature, 21 °C feed solution temperature, and the active membrane layer were against the feed solution.

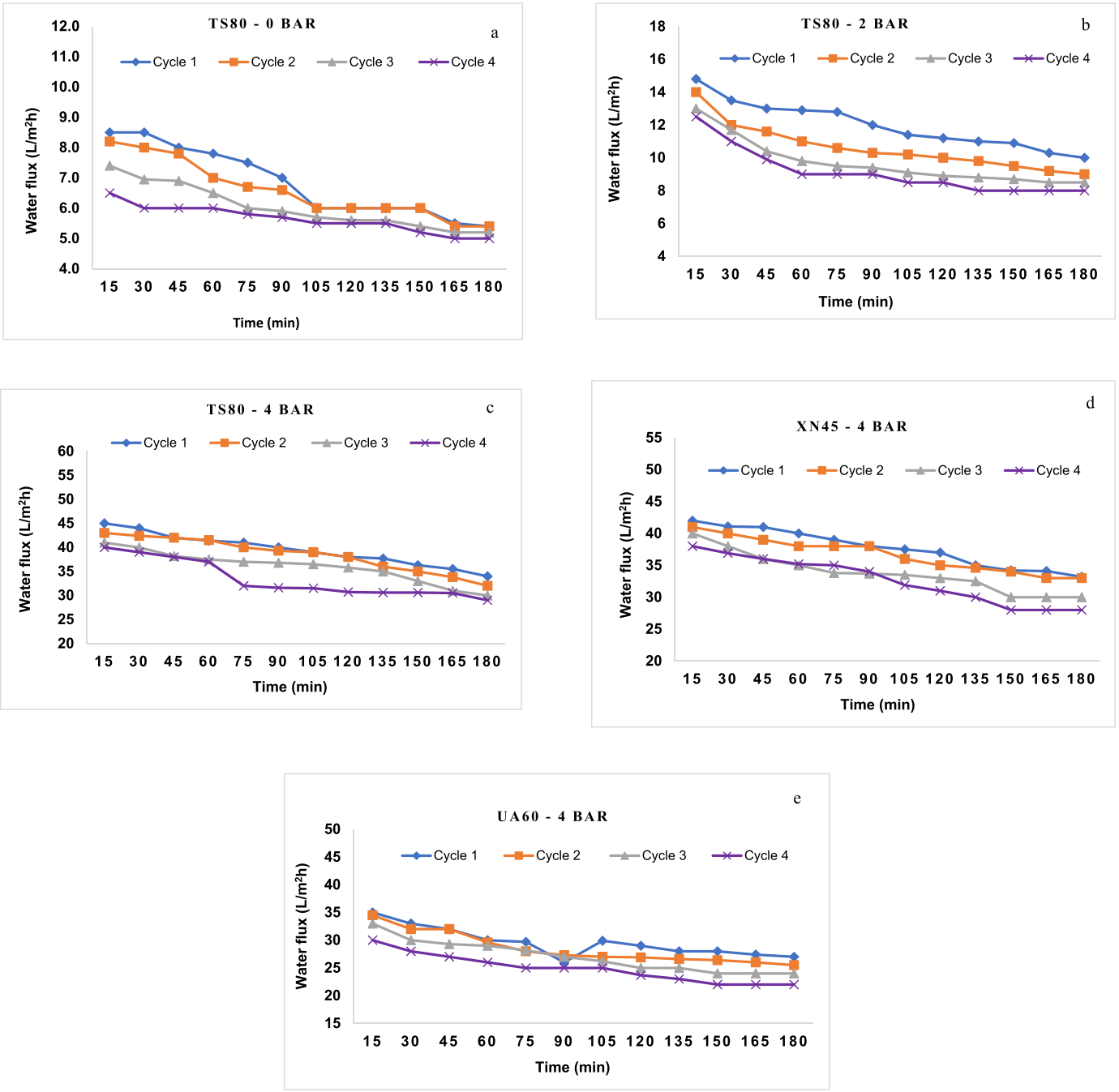

Fig. 2. The water flux of the FO system in four filtration cycles with the pressure stimuli-responsive membrane at a) 0 bar TS80, b) 2 bar TS80, c) 4 bar TS80, d) 4 bar NX45, and e) 4 bar UA60.

Fig. 2 displays the variation of the water flux with time and the applied feed pressure. The water flux was calculated according to **Equation (3)**. Results show that the highest water flux recorded for the first cycle at 0 bar was 8.5 L/m^{2}h but increased to 14.8 L/m^{2}h and 45 L/m^{2}h at 2 and 4 bar, respectively. At the end of the filtration cycle one, water flux decreased to 5.4, 10, and 34 L/m^{2}h for the FO process conducted at 0, 2, and 4 bar, respectively. The membrane was cleaned with DI water at 40 °C for 30 min to remove fouling materials before filtration cycle two started (Ibrar et al., 2020). Despite membrane cleaning, membrane fouling water was inevitable, leading to a decline in the water flux in the consecutive filtration cycles 2 to 4 (Fig. 2). Following three consecutive 30-min cleanings with 40 °C DI water, cycle 4 showed that the initial water flux was 6.5, 12.5, and 40 L/m^{2}h at 0, 2, and 4 bar, respectively, recording 23.5%, 15.6%, and 11.11% decline in the water flux for FO experiments conducted at 0, 2, and 4 bar. It is concluded that the TS80 membrane performed better at 4 bar than at 0 and 2 bar tests. Although the PSR TS80 membrane produced moderate water flux at 0 bar feed pressure, there was 1.7 and 5.3 times more water flux when 2 bar and 4 bar pressure was applied to the feed side. The slight pressure applied on the feed side of the PSR TS80 membrane promoted water flux several times compared to a 0 bar test. Fig. 2c also shows that in all cases, the water flux decreased over time with a remarkable slight decrease at 4 bar compared to 0 and 2 bar. The reduction in water flux was 19, 24, and 15 % at 0, 2, and 4 bar, respectively. Chemical cleaning, osmotic backwash, or more sophisticated pretreatment could be applied to alleviate membrane fouling since cleaning with 40 °C DI water was inadequate to remove fouling materials from the membrane surface.

Since water flux at 0 and 2 bar feed pressure was insignificantly less than at 4 bar, NX45 and UA60 membranes in the FO system were tested at 4 bar only. Table 1 shows that the NX45 membrane loose NF membrane rejects 20% of NaCl while the UA60 in a tight UF membrane only rejects 10% of NaCl. As shown in Fig. 2d, the membrane XN45 recorded a maximum water flux of 42 L/m^{2}h for the first cycle, which decreased to 33.2 L/m^{2}h at the end of the cycle. Despite membrane cleaning with 40 °C DI water for 30 min at the end of each cycle, water flux slightly decreased in the consecutive filtration cycles 2 to 4 due to membrane fouling. The initial water flux using XN45 in cycle 4 was 38 L/m^{2}h (Fig. 2d), indicating a 9.5% reduction in water flux compared to the first cycle. In contrast, 35 L/m^{2}h was the initial water flux in cycle 1 for the UA60 membrane and decreased to 27 L/m^{2}h after 180 min filtration time. Following cleaning with 40 °C DI water at the end of each filtration cycle, the initial water flux for cycle 4 was 30 L/m^{2}h (Fig. 2e). For filtration cycle 4, the water flux reduction in the UA60 membrane was 14.3% compared to cycle 1. Generally, the decline in water flux after 4 filtration cycles was 11.11% for the TS80 membrane, 9.5% for the NX45 membrane, and 14.3% for the UA60 membrane. The results reveal that the decline in water flux increased with the membrane surface charge shown in Table 2, probably due to the interaction between the organic matter and the membrane surface, leading to membrane fouling. Also, the interaction between positively charged divalent ions, such as Ca^{2+} and Mg^{2+}, and the negatively charged membrane surface would promote organic matter fouling due to the interaction between divalent ions and the organic matter. For example, the UA60 membrane with −60 mV zeta potential exhibited the largest water flux decline among all membranes.

The performance of the NF TS80 membrane outweighed the NX45 and UA60 membranes, knowing that the former membrane's salt permeability factor of 1.33 L/m^{2}h is much lower than that of the other membranes (Table 1). The TS80 membrane's tight structure retains the draw solution better than other membranes, maintaining a steady osmotic pressure across the membrane.

Water flux is considered remarkably high in the PSR NF membrane compared to the maximum water flux achieved in the commercial Porifera TFC FO membrane at the same experimental conditions with MSF brine draw solution and TSE feed solution. To better understand the behavior of the PSR NF membranes in the FO system, the average water flux in the PSR membranes was compared with that in the commercial Porifera FO TFC membrane tested with the same feed and draw solutions and temperatures (Fig. 3a). The latter membrane was tested in both orientations, i.e., ALFS and ALDS. The average water flux in the PSR membrane with ALFS was 29.5, 37.6, and 29.5 L/m^{2}h, respectively, whereas the Porifera TFC FO membrane's corresponding values were 27.8 L/m^{2}h in the ALDS and 29.2 L/m^{2}h in the ALFS. Indeed, FO membrane fouling intensifies and becomes challenging to mitigate when the feed solution faces the support membrane area, explaining the lower average water flux in the ALDS (Chun et al., 2017). In general, water flux in the PSRNF membranes was higher than in the Porifera TFC membrane due to their better water permeability and hydrophilic surface. The membrane's contact angle was 17.4° for the TS80, 8.2° for the NX45, and 15.7° for the UA60. The corresponding values for the CTA and TFC membranes were 68.5° and 68.1°, respectively, exhibiting 3.9 to 8.3 times less hydrophilic membrane surface compared to the PSRNF membranes (Table 2). Table 2 also shows that the water permeability coefficient of the PSRNF membranes was several times higher than the commercial CTA and TFC membranes, giving them the advantage of better water flux. The TS80 membrane stands out with the best average water flux of 39.5 L/m^{2}h when the FO operates at 4 bar.

Despite the excellent average water flux of NX45 and UA60 membranes, there is a concern about their loose structure, which would promote the leakage of draw solute to the feed side. On the contrary, the TS80 membrane exhibited the highest water flux due to its excellent rejection rate to monovalent and divalent ions, preventing the draw solution leakage to the feed solution. Compared to the TFC FO membrane, the average water flux in the TS80 membrane operating at 0 bar feed pressure is much lower than that in the TFC FO membrane and slightly increased at 2 bar, although incomparable to the average water

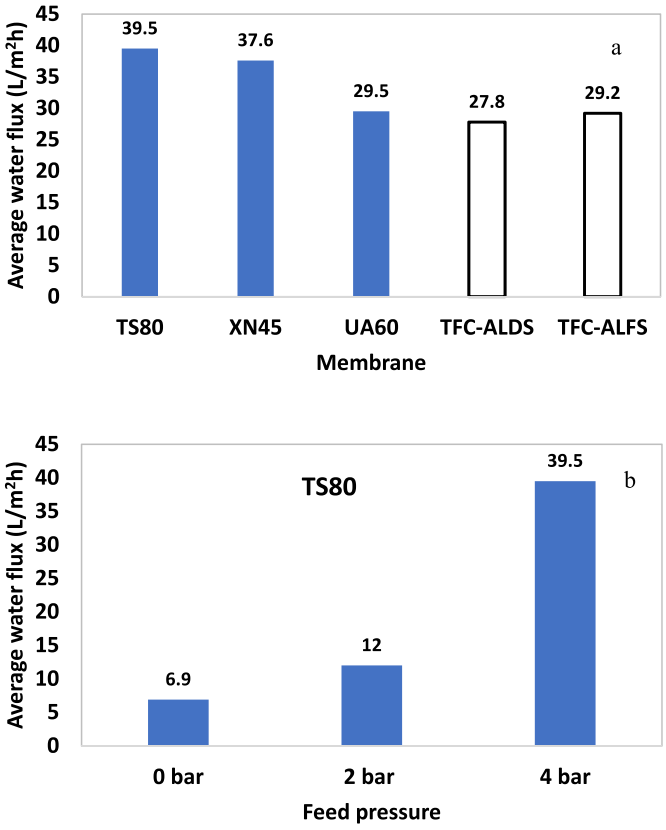

Fig. 3. Average water flux of the PSRNF and TFC and CTA membranes a) comparison of the average water flux in the first cycle of the PSRNF (TS80, XN45, UA60) and TFC and CTA FO membranes, and b) the average water flux in the TS80 membrane operating at 4 bar.

flux in the TFC FO membrane (Fig. 3b). Nevertheless, the TS80 membrane exhibited an outstanding average water flux 1.3 times higher than the Porifera TFC membrane at 4 bar feed pressure. With the increase in feed pressure, the water flux in the PSR membrane exponentially increased, showing extraordinary performance compared to conventional FO membranes.

1.2.2. Cleaning efficiency and fouling reversibility

In the physical cleaning, DI water at 40 °C was circulated in the FO cell for 30 min to wash the fouled membrane after each filtration cycle. The washed membrane was then reused in three consecutive cycles. DI water flushing is widely used and considered adequate to restore the water flux in the FO membrane operated by the osmotic pressure (Ibrar et al., 2020); however, its effectiveness for cleaning PSR NF membrane operated at 0–4 bar should be evaluated. As shown in Fig. 4, the average water flux reduction was the lowest after the first wash in the second filtration cycle, with only 2.5, 3.1, and 3.7 % reduction for membranes TS80, XN45, and UA60, respectively. A decline in average water flux was observed after the second wash, recording 8.9, 10.6, and 8.5% reductions in the average water flux. The higher water flux decline in the second cycle was probably attributed to the building up of fouling materials on the membrane surface. The fouling layer from the previous washing cycle played a crucial role in being the substrate for fouling development. After the final wash, the average water flux decline reached 15.5, 13.6, and 15.9 % in the TS80, NX45, and UA60 membranes. Following three consecutive cleaning with hot water at 40 °C, the percentage of water flux reduction was the highest after the third cleaning cycle due to the accumulative fouling effect on the membrane surface in the consecutive filtration cycles. Unlike the TFC and CTA FO membranes, PSR NF membranes are probably less amenable to cleaning with 40 °C DI water due to their surface negative charge, between −52 and −60, compared to a surface negative charge of −12.8 for the CTA FO and 41.9 for the TFC FO membrane (Table 1). Interaction between divalent ions and membrane surface increases with the negative surface charge, triggering inorganic fouling. Divalent ions also bridge between the membrane surface and organic matter in the feed solution, resulting in more stubborn fouling that requires advanced cleaning methods. It is noteworthy that under the same FO operating conditions, membrane fouling in the first filtration cycle would be dictated by the feed solution, draw solution, and membrane surface characteristics. Once the membrane surface is fouled, membrane fouling in the consecutive filtration would be partially or entirely dictated by the fouling layer characteristics.

The fouled and washed membranes were tested using a scanning Electron Microscope (SEM). The fouling materials were clearly shown on the surface of the active membrane layer of the NF membranes (Fig. 5 a, c&e). After flushing with hot DI water for 30 min, the fouling materials were primarily removed, explaining the reversibility of the fouling (Fig. 5 b, d&f). The results of the water flux reduction following the membrane cleaning agreed with the SEM images (Fig. 5). FT-IR (Thermo Scientific Nicolet spectrometer) and EDX (Bruker SDD X flash 5030) analysis of the TS80 were performed to identify the fouling of the best-performance PSRNF membrane. The FT-IR spectrum of the TS80 membrane reveals crucial information about its functional groups; broad absorption bands around 3300 cm-1 often indicate hydroxyl groups, suggesting the presence of water or hydrogen-bonding interactions. In comparison, sharp absorptions near 1650 cm-1 could denote carbonyl functionalities like those in amides or esters. The fingerprint region, below 1500 cm-1, provides a unique pattern that identifies specific molecular structures, which is particularly useful for understanding the cross-linking and polymer backbone within the membrane. Changes in peak intensities and shapes might indicate surface functionalization or degradation of the membrane. N–H stretching is typically marked by a peak around 2800–3100 cm-1, suggesting hydrogen bonding, and is often associated with amides in polyamide membranes. The C–N stretch, indicative of aliphatic amines or amides, generally appears between 1400 and 1550 cm-1 and provides information on the nitrogen-containing compounds in the membrane (Fig. 1) (Tajuddin et al., 2019). The C]O stretch, a key feature of carbonyl groups in various chemical structures, shows a strong absorption near 1550–1650 cm-1. These peaks' exact position and shape reveal the extent of hydrogen bonding and the degree of cross-linking within the membrane, which are critical factors in the membrane's selective permeability and overall performance in filtration applications.

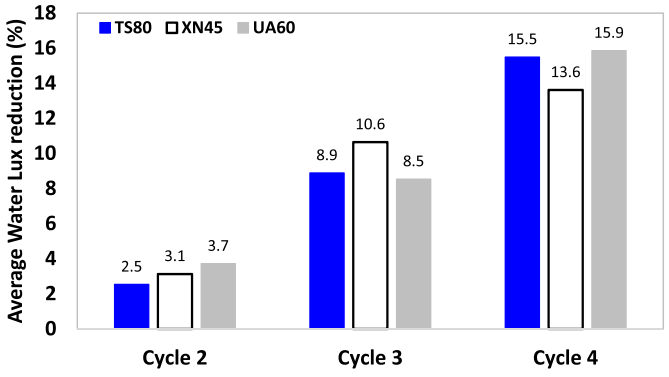

Fig. 4. Illustration of flux reduction after each cycle for each membrane at 4 bar applied feed pressure.

The EDX analysis of the TS80 membrane indicates the TFC membrane is composed mainly of carbon (62.53%) and oxygen (21.91%), with Nitrogen (5.06%) and Sulphur (4.88%) present, reflecting a polymeric structure with functional groups for selectivity and permeability. After washing, carbon decreased slightly to 62.35%, probably due to fouling materials deposited on the membrane surface. In contrast, oxygen increased to 23.58% and sulphur to 5.77%, indicating the removal of surface-bound substances and a concentration of sulphur elements. The trace silicon (1.21%) and aluminium (0.61%) suggest inorganic fouling resistant to washing by DI water (Fig. 2a and b). Physical cleaning by DI water at 40 °C is probably insufficient to remove silica fouling, causing a decline in the membrane water flux after multiple filtration cycles. Therefore, chemical cleaning is recommended for silica fouling removal.

Mitigating the fouling matters with physical cleaning at 40 °C for 30 min is inadequate to remove the fouling materials from the surface, and hence the NF membranes suffer irreversible fouling. It is recommended that more sophisticated cleaning processes with acid and alkaline solutions be conducted for fouling mitigation in the PSRNF membrane. Fortunately, PSRNF membranes can tolerate a wide range of feed pH from pH 1 to pH 12, making them amenable to chemical cleaning. Also, more advanced TSE pretreatment with microfiltration could help in removing organic matter and reduce membrane fouling.

1.2.3. Dilution of ionic species

The PSR NF membranes were investigated for their potential to remove or reduce the divalent ions from the MSF brine. Divalent ions are amenable to NF membrane treatment for seawater softening but have never been tested for removal by the PSR NF membranes. Therefore, TS80, XN45, and UA60 NF membranes were tested for rejecting ions responsible for non-alkaline scale deposition on the heat exchanger, i.e., Ca^{2+}, Mg^{2+}, and SO_4^{2-}. The diluted draw solutions from the experiments were analyzed for these ions at the end of the FO experiments. The ions dilution in percentage at 4 bar for each TS80, NX45, and UA60 membranes are presented in Fig. 6. The results revealed that the dilution of Mg^{2+}, $Ca^{2+}$and SO_4^{2-} using TS80 membrane was 40, 42 and 32 %, respectively. The corresponding dilution percentages for the XN45 membrane were 28, 25, and 27 %, and for the UA60 membrane were 19, 16 and 23%, respectively. The significant divalent ions dilution achieved by the TS80 membrane is attributed to its high water flux compared to NX45 and UA60 (Fig. 3a). The elevated ions dilution in the TS80

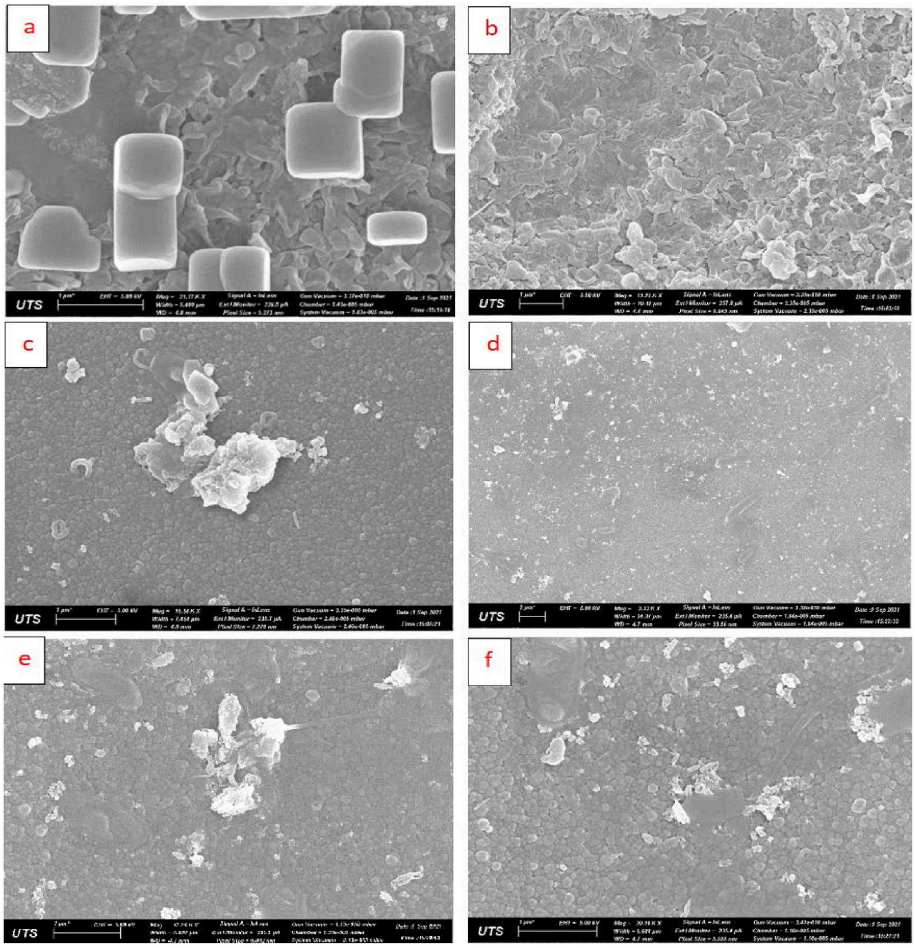

Fig. 5. SEM images of the fouled and cleaned NF membranes at 4 bar: a) TS80 fouled, b) TS80 washed, c) XN45 fouled, d) XN45 washed, e) UA60 fouled, f) UA60 washed, g) FT-IR of new and fouled TS80, h) EDX of new TS80, and i) EDX of fouled TS80.

membrane compared with the NX45 and UA60 is attributed to its excellent water flux (Fig. 3a) and high rejection to divalent ions (Table 1). The NF TS80 membrane rejects 99.2% of divalent ions, responsible for membrane fouling, compared to 96% for the NX45 and 80% for the UA60.

Notably, the desired dilution percentage for the brine reject through the FO process is 14% or greater, aligning with the recovery rate of the MSF plant when its performance ratio equals 8 (Morin, 1993). The findings illustrated in Fig. 6 indicate that PSRNF membranes have successfully achieved the desired 14% dilution necessary for the MSF plant, with the TS80 membrane exhibiting the most effective dilution performance.

The TS80 NF membrane outstands the Porifera TFC FO membrane for its capacity to reduce the concentration of divalent ions in the brine solution using the TSE feed solution. A previous study by Khanafer et al. (2021b) showed that the maximum dilution percentage of divalent ions in the FO process using TSE feed solution and Porifera FO membrane was 37%, 41%, and 25% for Mg^{2+}, $Ca^{2+,}$ and SO_4^{2-}, respectively. The corresponding dilution percentages for the TS80 membrane are 40% for the Mg^{2+}, 42% for the $Ca^{2+,}$ and 32% for the SO_4^{2-}, indicating better performance. Notably, NX45 and UA60 membranes also achieved the desired ion dilution for the MSF, albeit to a lesser extent than the Porifera TFC membrane.

The PSRNF membranes offer an exceptional opportunity to enhance the performance of the FO in various desalination and purification technologies. PSRNF membranes are applicable to wastewater treatment where fouling is a concern since the PSRNF TS80 membrane is made specifically for wastewater treatment. Water flux in the PSRNF membrane is comparable to or better than in the FTSH2O CTA and Poreifera TFC membranes because of the hydrophilic nature of these membranes. For example, the water permeability coefficient of the TS80 membrane is 12 times more than the CTA membrane and 4 times more than the TFC membrane (Table 1). Additionally, membrane cost is a limiting issue, with commercial FO membranes being exorbitantly more expensive than reverse osmosis and nanofiltration membranes (Altaee et al., 2014). The PSR concept uses commercial NF membranes, which offers a cost-effective solution to this problem. Future work should consider the potential application of the PSR concept in various FO applications, including wastewater treatment, seawater desalination, fertilizer draw solution, and brine concentration.

1.2.4. *Energy consumption*

The energy consumption was calculated using **Equation (1)**, and the results are presented in Fig. 7. The experimental work at 4 bar with TS80, XN45, and UA60 membranes using TSE feed solution and 80 g/L brine reject showed that the specific power consumption was only 0.02, 0.02 and 0.03 kWh/m^3, respectively (Fig. 7). The highest specific power consumption recorded in the UA60 membrane is attributed to its low permeation flow (Fig. 3a), which adversely affects the power consumption in the FO process (Equation (1)). UA60 membrane is a loose NF membrane with a low rejection of monovalent ions and moderate rejection of divalent ions, causing draw solution loss and compromised water flux. As permeation flux increased in TS80 and NX45 membranes, the power consumption accordingly decreased to 0.02 kWh/m^3.

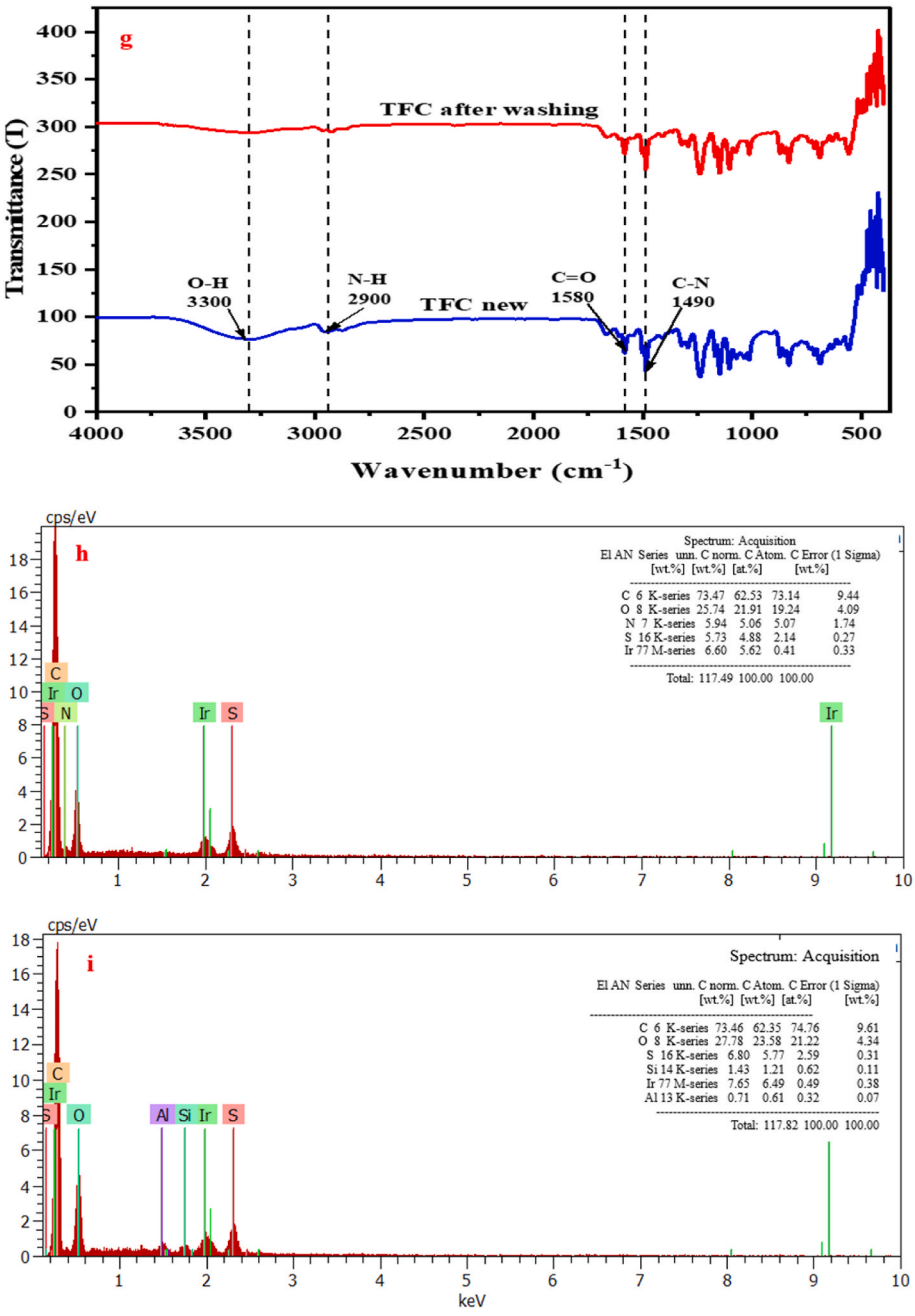

Fig. 5. (*continued*).

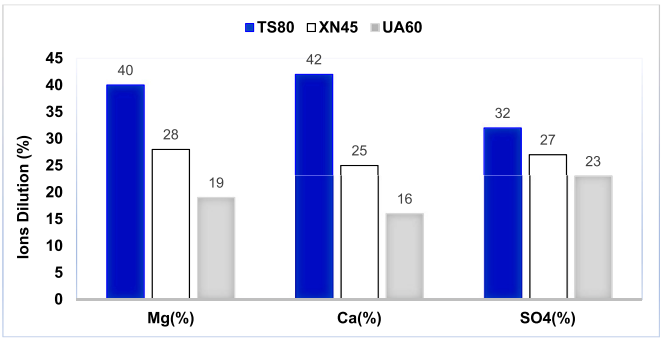

Fig. 6. The percentage of Mg, Ca, and SO_4 ions dilutions at 4 bar using TS80, XN45, and UA60. The PSR NF membranes were tested at 4 bar feed pressure.

Compared to seawater feed solution tests, the FO process combined brine reject and the low-salinity TSE feed solution achieved a higher permeation flux (Khanafer et al., 2021b). TSE, abundant wastewater found in various Middle Eastern countries, is subject to restrictions preventing its discharge into the sea according to environmental guidelines. Combining the TSE with the brine reject has the following advantages: i) reduces the cost of TSE management and ii) converts wastewater to a valuable source of freshwater. With the TSE feed solution and ALFS, the specific power consumption of the FO process was increased from 0.005 kWh/m^3 in the TFC FO membrane (ALFS) to 0.02 kWh/m^3 in the TS80 membrane (Table 3). As for the FO process with seawater feed solution, the TS80 membrane was more energy efficient than the commercial TFC and CTA membranes due to the limited permeation flux in the FO process with seawater feed solution. The TDS of the seawater in the Middle East region could reach 48 g/L compared to 0.967 mg/L for TSE (Table 2), compromising the osmotic pressure

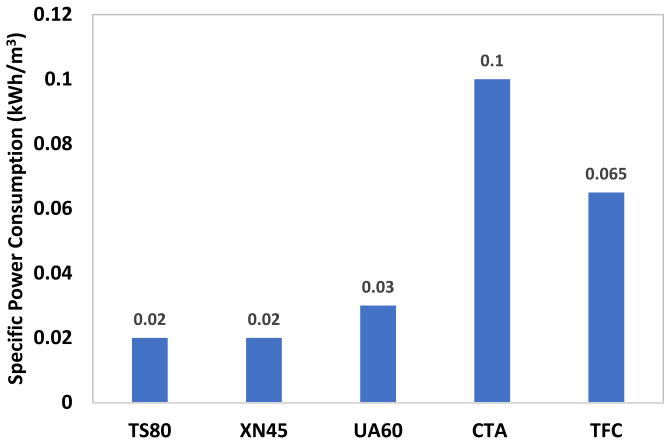

Fig. 7. TS80, XN45, and UA60 NF membranes' power consumption in the FO processes of PSRNF, FTSH2O CTA, and Porifera TFC membranes. All experiments were at 4 bar.

Table 3
Specific power consumption in PSR NF, FTSH2O CTA, and Porifera TFC membrane using MSF brine reject of 80 mg/L TDS at 40 °C draw solution.

Membrane	Feed solution	Orientation	Feed pressure (bar)	Es (kWh/m^3)	Ref
TS80	TSE	ALFS	4	0.02	This study
TFC	TSE	ALDS	0	0.006	Khanafer et al. (2021b)
		ALFS	0	0.005	
TFC	Seawater	ALFS	0	0.023	Khanafer et al. (2021a)
		ALFS	4	0.065	
CTA	Seawater	ALFS	0	0.026	Khanafer et al. (2021a)
		ALFS	4	0.1	

driving force and permeation flow in the FO process. Nevertheless, commercial TFC FO membranes experience a shortcoming represented by their prohibited cost, which could be up to 10 times more than the reverse osmosis or nanofiltration membranes. For instance, commercial TFC or CTA FO membranes are approximately $1900 per m^2, whereas pressure-driven membranes, such as TS80 NF, are just $260 per m^2 based on retail prices. The significant cost gap between the commercial FO and PSR TS80 membranes favours using the latter in the FO processes.

1.3. Conclusions

To further investigate the feasibility of the FO system in the pretreatment of the feed water to the MSF plants, treated wastewater and brine reject solution were the FS and DS in the FO system. This study evaluated three NF membranes, TS80, XN45, and UA60, in the FO system instead of the FO membranes. The TS80 membrane achieved the highest water flux of 45 L/m^{2}h in cycle one at 4 bar. The maximum average flux generated by the TS80 membrane during the four cycles was considerably higher than the TFC FO membrane under the same operational parameters. It was recorded at 39.5 L/m^{2}h for the TS80 membrane compared to 16.7 L/m^{2}h for the TFC membrane. The physical cleaning using hot DI water flushing for 30 min effectively reduced the fouling that was considered reversible and not severe. The dilution of the brine draw solution using TS80 reached up to 42%. The proposed PAFO system delivers a promising energy-saving outcome with a maximum of 0.02 and 0.03 kWh/m^3 energy consumed at 4 bar. To sum up, the proposed system provides a high water flux, a steady flux decrease, a considerable decrease in the ion count, and low energy consumption. The potential of the PAFO system in diluting the brine solution by integrating TSE FS with the NF membrane in the FO process is revealed in this study, and additional research is required in a broader spectrum.

CRediT authorship contribution statement

Daoud Khanafer: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ali Altaee:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Funding acquisition, Data curation, Conceptualization. **Alaa H. Hawari:** Writing – original draft, Validation, Formal analysis, Data curation, Conceptualization. **John Zhou:** Writing – review & editing, Writing – original draft, Validation, Supervision, Formal analysis, Data curation. **Lilyan Alsaka:** Formal analysis, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

This research is made possible by a food security research award (MME03-1015-210003) from the Qatar National Research Fund (QNRF) in partnership with the Ministry of Municipality. The statements made herein are solely the responsibility of the authors.

References

Abdel-Fatah, M.A., 2018. Nanofiltration systems and applications in wastewater treatment. Ain Shams Eng. J. 9 (4), 3077–3092.
Altaee, Ali, Khanafer, Daoud, Hawari, Alaa, 2023. Method, Apparatus and System for Seawater Treatment patent WO2023/038538 A1.
Altaee, Ali, Zaragoza, Guillermo, Sharif, Adel, 2014. Pressure retarded osmosis for power generation and seawater desalination: performance analysis. Desalination 344, 108–115.
Chun, Y., Kim, S.-J., Millar, G.J., Mulcahy, D., Kim, I.S., Zou, L., 2017. Forward osmosis as a pre-treatment for treating coal seam gas associated water: flux and fouling behaviour. Desalination 403, 144–152.
Hamed, O.A., Al-Shail, K., Ba-Mardouf, K., Al-Otaibi, H., Hassan, A.M., Farooque, A., Al-Sulami, S., Al-Hamza, A., 2005. Nanofiltration (NF) Membrane Pretreatment of SWRO Feed & MSF Makeup. Saline Water Desalination Research Institute, Saline Water Conversion Corporation (SWCC), Saudi Arabia, Research Activities and Studies Book, Volume No fifteen-1425-1426 H.
Hassan, A., 2006. Fully Integrated NF-Thermal Seawater Desalination Process and Equipment. Google Patents.
Hilal, N., Al-Zoubi, H., Mohammad, A., Darwish, N., 2005. Nanofiltration of highly concentrated salt solutions up to seawater salinity. Desalination 184 (1–3), 315–326.
Ibrar, I., Yadav, S., Altaee, A., Samal, A.K., Zhou, J.L., Nguyen, T.V., Ganbat, N., 2020. Treatment of biologically treated landfill leachate with forward osmosis: investigating membrane performance and cleaning protocols. Sci. Total Environ. 744, 140901.
Khanafer, D., Yadav, S., Ganbat, N., Altaee, A., Zhou, J., Hawari, A.H., 2021a. Performance of the pressure assisted forward osmosis-MSF hybrid desalination plant. Water 13 (9), 1245.
Khanafer, D., Ibrahim, I., Yadav, S., Altaee, A., Hawari, A., Zhou, J., 2021b. Brine reject dilution with treated wastewater for indirect desalination. J. Clean. Prod., 129129
Morin, O., 1993. Design and operating comparison of MSF and MED systems. Desalination 93 (1–3), 69–109.
Mulyanti, R., Susanto, H., 2018. Wastewater Treatment by Nanofiltration Membranes. IOP Publishing, 012017.
Tajuddin, M.H., Yusof, N., Wan Azelee, I., Wan Salleh, W.N., Ismail, A.F., Jaafar, J., Aziz, F., Nagai, K., Razali, N.F., 2019. Development of copper-aluminum layered double hydroxide in thin film nanocomposite nanofiltration membrane for water purification process. Front. Chem. 7, 3.
Wafi, M.K., Hussain, N., Abdalla, O.E.-S., Al-Far, M.D., Al-Hajaj, N.A., Alzonnikah, K.F., 2019. Nanofiltration as a cost-saving desalination process. SN Appl. Sci. 1 (7), 1–9.