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Use of forward osmosis in treatment of hyper-saline water

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ABSTRACT

Produced water is the largest waste stream in the oil and gas industry. The quality of produced water varies greatly, from near drinkable to highly contaminated (large amounts of inorganics and organics). Some of the most challenging produced waters in the world today are found in Iraq, where concentrations of dissolved solids can exceed 200,000 ppm and oil content can be near 100 ppm. In this work, forward osmosis is investigated as a suitable treatment method for hyper-saline produced water. Two draw solutions, ammonia-carbon dioxide (NH_3-CO_2) and magnesium chloride ($MgCl_2$), were evaluated for dewatering these brines. The NH_3-CO_2 draw solution, though easily recycled, demonstrated low flux and substantial scaling issues caused by pH changes and carbonate fluxes. $MgCl_2$ showed substantially higher fluxes due to higher osmotic efficiency and lower scaling propensity.

Keywords: Produced water; Brine treatment; Forward osmosis; Scaling

1. Introduction

Potable water scarcity is of a global concern, especially in the arid areas such as Iraq where about 97% of the country is in arid land with low and erratic rainfall [1]. Iraq's freshwater resources primarily come from the Tigris and Euphrates rivers that run through center of the country. About 98% of water consumption in Iraq depends on these two rivers, their tributaries, and their associated marshes. The country has recently passed through exceptionally dry and warm years with the lowest river discharges in decades [2]. This is caused partly from Turkish, Syrian, and Iranian dams built for over the past 30 years leading to a significant decrease in annual flow for both rivers. Combined with a lack of proper water management, high rate of evaporation, desertification, climate change, and salt inflow from the Gulf Sea, an unprecedented water crisis has emerged in southern Iraq. An annual water shortage of 430 million m^3 was estimated in this region [3].

In spite of this severe water shortage, large amounts of wastewater are produced every day from the production of oil in Iraq (produced water). This water, if treated efficiently and economically, may be used as a new water resource for many different purposes including irrigation, rangeland restoration, cattle and animal consumption, cooling towers, or enhanced oil recovery. One of the greatest challenges in treating Iraqi produced water is its high salinity [4]. High salinity complicates the treatment of produced waters since many treatment systems are unable to properly treat the water to a level allowable for direct use or discharge [5]. Yet without proper management, environmental and financial risks range from [6]: (1) degradation of ground and surface water quality; (2) death of plants and destruction of soil textures; (3) erosion of soils and siltation of nearby waterways; (4) blockage of produced water equipment; and (5) other adverse effects on ecosystems. These risks are only enhanced

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by the high salinity of Iraqi produced waters, which can in some fields reach salinity levels in excess of 240 g/L of total dissolved solids (TDS). Desalination of such hyper-saline water is considered as extraordinarily expensive because of large energy requirements [7].

Highly saline produced water often renders conventional desalination technologies, such as reverse osmosis, unusable due to thermodynamic limitations caused by osmotic pressure. Forward osmosis circumvents this issue by using osmotic pressure to drive water across a selective membrane. Using a high concentration draw solution, osmotic potential can force osmotic flow from even the highest salinity solutions [8]. This benefit has enabled FO to be used in brine concentration processes in a number of fields, most notably in the oil and gas industries [9,10]. The use of the FO combined with membrane distillation process in the treatment of produced water has been studied by Zhang et al. [11]. The authors used synthetic produced water with a salinity of about 12,000 ppm and an oil content of 4,000 ppm as the feed solution and 5 M NaCl as the draw solution for the FO-MD experiment. Both FO and MD showed more than 99.9% rejection for the oil and the salt [11]. One such study describes using forward osmosis in the treatment of drilling mud and hydraulic fracturing wastewater (with a TDS of 6,750 ppm) [12]. They found that FO can recover more than 80% of the water from drilling wastewater and reduce its volume to more than three times. Another, two projects were performed on a pilot scale to investigate using of forward osmosis in treatment of produced water in scalable and movable plant. The first one is the "Green Machine" from Hydration Technology Innovations (HTI). This system was tested with a feed solution from Haynesville shale gas field (3,500 ppm TDS). Its results showed that [13] the system recovered 85% of the feed solution using 1M NaCl draw solution and produced highly purified water for reuse. The other pilot plant used the ammonia-carbon dioxide draw solution in treatment of high salinity produced water (about 75,000 ppm TDS) from the Marcellus shale region [14]. This plant was able to run with energy 2.3 times less than that of the conventional mechanical vapor compression process for the same feed salinity. An additional stage after the draw solution recovery was necessary to remove the salts which crossed the membrane from the feed solution to the draw solution. The final product (permeate) was of high quality with TDS of about 300 ppm.

It is worth noting, however, that these early studies have focused on produced water streams salinities less than 100,000 ppm. This work adds to that by providing performance data using synthetic waters with 240,000 ppm TDS. We provide performance data using different draw solutions and evaluate which specific constituents of the feed and draw solution contribute to scaling potential. The results of this study can be valuable in designing integrated process of treatment of hypersaline streams and deciding the required pretreatment steps for high salinity produced waters and the preferred properties and chemistry of a chosen draw solute.

2. Materials and method

2.1. Forward osmosis membrane

The membrane used in this work was CTA (cellulose triacetate) forward osmosis membrane. This membrane was provided by HTI (Albany, OR). This membrane has been widely used for a number of FO applications including seawater desalination [15], wastewater treatment [16], and advanced life support systems [17]. Properties and images of the membrane can be found elsewhere [18].

2.2. Feed solution

Produced water composition (Table 1) was taken from Ref. [19]. These four waters represent the four largest oilfields in Iraq (about 85% of the total Iraqi oil production [3]). Each water has a TDS that is about eight times that of seawater while also having relatively low oil content. To study the effect of the different salts in the produced water on the FO process, we prepared feed solutions with different compositions (Table 2). NaCl (99.9% Fisher), $CaCl_2$ (Fisher), $MgCl_2.6H_2O$ (99% Acros organics), $MgSO_4.7H_2O$ (99.3% Fisher), $NaHCO_3$ (99%, J.T. Baker), and $FeCl_3.6H_2O$ (99 + % Acros organics) were used to prepare the feed solution. We tested the described recipe (PW-Full) and then individual recipes with a single component removed (PW-Ca lacks calcium, PW-Mg lacks Magnesium, PW-SO_4 lacks Sulfate, PW-HCO_3 lacks bicarbonate, and PW-Fe lacks iron). For solutions lacking one component, the osmotic pressure was kept constant by adding an appropriate amount of NaCl. The modified Van't Hoff equation [20] was used to calculate the osmotic pressures and retune the feed recipe after removal of one of the components.

2.3. Draw solutions

Two types of draw solutions were used in this study. A 6M ammonia-carbon dioxide draw solution was prepared by dissolving ammonium bicarbonate NH_4HCO_3 in mixture of ammonium hydroxide (29%, Fisher) and deionized water to get NH_3/CO_2 molar ratio of 2.2–1. Higher ratios of NH_3/CO_2 are required to prepare higher concentrations of NH_3-CO_2 draw solution [15]. A 4.8 $MgCl_2$ solution was prepared by dissolving the appropriate amount of $MgCl_2.6H_2O$ (99%, Acros organics) in DI water which was provided from a Millipore Integral 10 water system (Millipore Corporation, Billerica, MA, USA).

2.4. Forward osmosis tests

The FO experiments were run on a bench-scale laboratory system, a schematic diagram of the laboratory scale unit used in this study is provided elsewhere, [21]. The weight change of the feed solution was measured using a digital balance (Denver Instruments PI-4002, Denver Instruments Bohemia, New York, USA) connected to a computer. The water permeation flux was calculated by dividing the mass flow through the membrane by the area. Feed and draw solutions were maintained at 30°C ± 1°C. The pressure on both sides was 3 psi ($\Delta p = 0$). Cross-flow velocities of both the feed and draw solutions were 0.25 m/s. All experiments were conducted in the FO mode (the active layer facing the feed solution). A benchmarking test using a NaCl feed solution with an equivalent osmotic pressure to the produced water was used as a control for the experiment. All experiments were run in duplicate and the error bars are from the standard deviations of experimental data.

Table 1
Characteristics of the produced water in the south of Iraq

Analysis	North Rumaila	South Rumaila	Al-Zubair	West Qurna
pH	4.8	4.1	6.62	4.9
Conductivity (µS/cm)	280,000	278,000	268,000	300,000
TDS (mg/L)	247,000	246,000	238,000	264,000
TH (mg/L as $CaCO_3$)	54,000	40,000	50,000	43,000
Alkalinity (mg/L as HCO_3^-)	238	110	262	347
Oil content (mg/L)	36	53	66	57
SO_4^{-2} (mg/L)	108	116	104	94
Total Fe (mg/L)	98	110	50	2.4
Ca^{+2} (mg/L)	17,234	12,826	14,028	12,024
Mg^{+2} (mg/L)	2,655	1,930	3,632	3,148
Na^+ (mg/L)	89,000	91,000	87,000	98,000
Cl^- (mg/L)	138,000	141,000	134,000	151,000

TDS: total dissolved salts, TH: total hardness.

2.5. Analytical and imaging methods

The membrane surface was analyzed by Scanning Electron Microscopy-Energy Dispersive X-ray Apparatus JSM-6335F (FESEM, JEOL Ltd., Japan). Prior to imaging, the samples were sputter coated with a thin layer of gold. Imaging was done using an accelerating voltage of 10 kV and current of 12 µA.

Reverse ammonia/ammonium flux during the FO tests was measured gravimetrically using sodium tetraphenylboron to precipitate dissolved ammonia species as ammonium tetraphenylborate as described in our previous study [22]. The pH of the feed solutions before and after the experiments was measured by pH meter (accumet excel XL 50, Fischer scientific) calibrated using five buffer solutions of 2, 4, 7, 10, and 12.

2.6. Langelier saturation index

The Langelier saturation index (LSI) is calculated number used to predict the calcium carbonate stability in water. It indicates whether the $CaCO_3$ will precipitate, dissolve, or be in equilibrium. Precipitation occurs when LSI > 0 [23,24]. The value of LSI is calculated from the following equation:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_s} \tag{1}$$

where pH is the pH value of the feed solution and $\mathrm{pH_s}$ is the saturation pH which was calculated using Lenntech calculator [25].

3. Results and discussion

3.1. NH_3-CO_2 as a draw solution

3.1.1. Feed solution composition effect

Fig. 1 shows the water flux in LMH (L/m² h) for different feed compositions using NH_3-CO_2 as the draw solution for 20 h of operation. Details of the feed compositions are given in Table 2. As anticipated, the highest fluxes were observed in the baseline test which was a NaCl solution of 223 g/L (equivalent osmotic pressure as the produced water recipe. For better manifestation of the flux data, we present in Fig. 2 the average water flux for the different feed solutions.

Comparatively, the water flux when using a full composition feed solution (PW-full) was 60% lower than the baseline which contained only NaCl as the feed solution. When individual components of the PW were removed and replaced with NaCl, a number of conclusions can be drawn. Upon removing the divalent cations (i.e., calcium and magnesium) the water flux increased approximately 72% compared with water flux observed for the full composition feed solution. The behavior was particularly dependent on presence of calcium within solution and this suggests that calcium is mainly responsible for flux decline in this process. The flux decline is likely due to calcium scaling and more evidences will be discussed in the following sections. Omission of the anions (SO_4 and HCO_3) and iron from the feed solution showed minimal changes in the water flux. This is most likely because the saturation limits for these salts are higher than their concentrations in the feed solution.

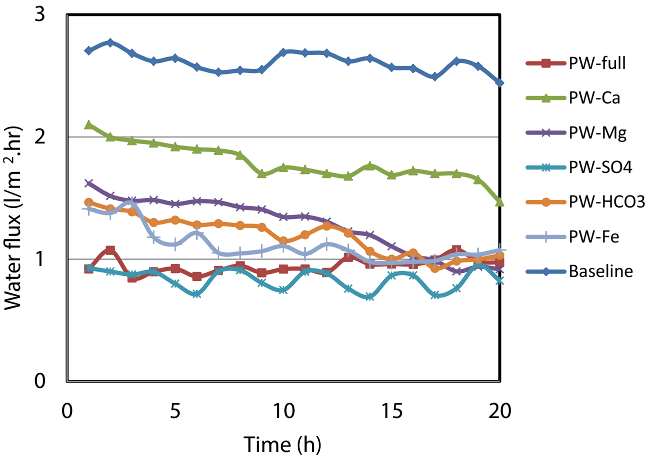

Fig. 1. Water flux at different feed solution composition. Experimental conditions: 6 M NH_3-CO_2 draw solution, HTI-CTA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

Table 2
Composition of the synthetic produced water and the corresponding osmotic pressure

Component	Concentration (g/L)							Osmotic pressure (atm)						
	Baseline	PW-full	PW-Ca	PW-Mg	PW-SO_4	PW-HCO_3	PW-Fe	Baseline	PW-full	PW-Ca	PW-Mg	PW-SO_4	PW-HCO_3	PW-Fe
NaCl	223	185	215	192	185	185	185	200.88	167	194	174	167	167	167
$CaCl_2$	–	45	–	45	45	45	45	–	26.92	–	26.92	26.92	26.92	26.92
$MgCl_2$	–	10	10	–	10	10	10	–	6.64	6.64	–	6.64	6.64	6.64
$MgSO_4$	–	0.12	0.12	–	–	0.12	0.12	–	0.05	0.05	–	–	0.05	0.05
$NaHCO_3$	–	0.25	0.25	0.25	0.25	–	0.25	–	0.15	0.15	0.15	0.15	–	0.15
$FeCl_3$	–	0.05	0.05	0.05	0.05	0.05	–	–	0.03	0.03	0.03	0.03	0.03	–
Total	223	240.42	225.23	237.71	240.36	240.33	240.41	200.88	200.88	200.88	200.88	200.88	200.88	200.88

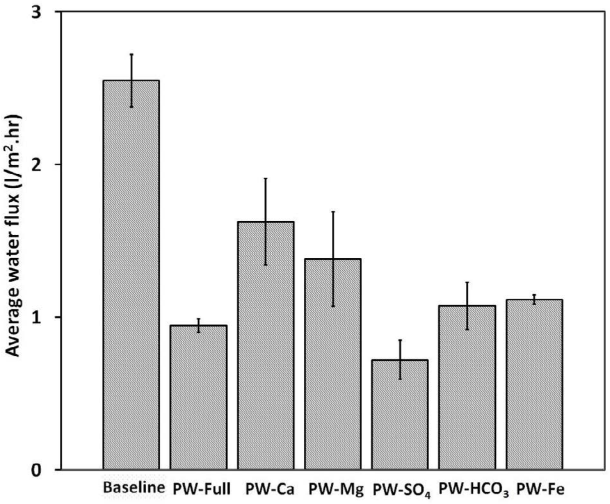

Fig. 2. Average water flux at different feed solution composition. Experimental conditions: 6 M NH_3-CO_2 draw solution, HTI-CTA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

3.1.2. Ammonia flux

Fig. 3 shows the Ammonia flux for the different feed solution compositions. Ammonia flux was measured between 1 and 2.5 mol/m^2 h. Ammonia flux from the draw into the feed solution will create substantial changes in feed solution chemistry during the course of a test.

The mechanism of mass transfer (water and ammonia fluxes) in the CTA membrane is governed by diffusion that happens due to the concentration difference across the membrane [26]. Interestingly, the ammonia flux results followed a similar trend to that of the water flux. The higher the

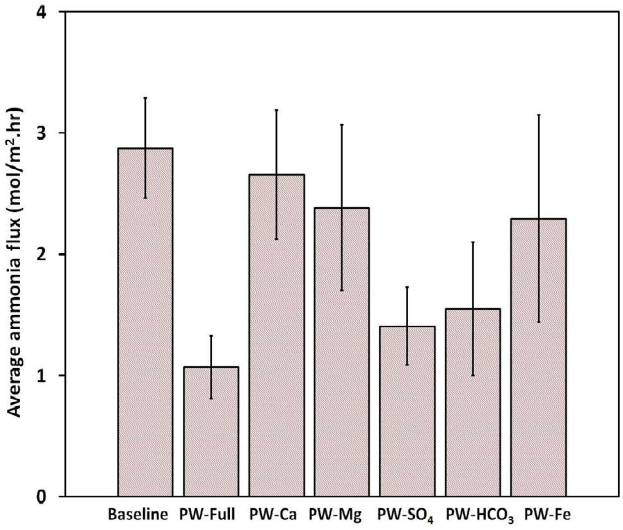

Fig. 3. Solute flux at different feed solution. Experimental conditions: 6 M NH_3-CO_2 draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

fouling will be the lower the flux (water and ammonia) will be. So, fouling has effect on the ammonia flux as the same as the effect on the water flux. The highest ammonia flux was for the baseline test while the lowest was for the full composition feed solution (PW-full). The difference in ammonia flux was most likely caused by scaling, which adds a layer of resistance to ammonia transport on the active layer of the membrane.

3.1.3. Scaling when using NH_3/CO_2 as draw solution

Scaling was observed on the active layer side of the membrane surface upon the removal of the membrane from the test cell when using NH_3-CO_2 as a draw solution. The main component of the scaling in this process is calcium carbonate ($CaCO_3$). There is an abundance of carbonate ions (i.e., 6M) in the NH_3-CO_2 draw solution which will diffuse into the feed solution where the carbonate ions are relatively low (i.e., 250 ppm). Fig. 4 shows the scaling layer which formed on the membrane surface with PW-full as the feed solution. The composition of this layer is provided in part by EDX is the calcium carbonate.

The solubility of $CaCO_3$ depends largely on the pH of the solution with higher pH lowering the solubility [27]. During the test, pH (of the feed solution increased from 6 to more than 8 (Fig. 5) due to the ammonia flux through the membrane. The precipitation of $CaCO_3$ is also supported by its LSI increasing from –0.44 to 1.7 (confirming saturation) after the FO experiment for 20 h as the pH changed and the concentration of solutes increased. Further confirmation that the scaling is $CaCO_3$ is demonstrated that when Ca was removed from the feed, no scaling was observed (Fig. 6). This lack of scaling is likely part of the reason that the average fluxes from these tests were higher than with feed solutions containing Ca.

When feed solutions without bicarbonate were evaluated, scaling was still observed (Figs. 7(a)–(c)). At first, one might think that this scaling is from $CaSO_4$, however, EDX detected

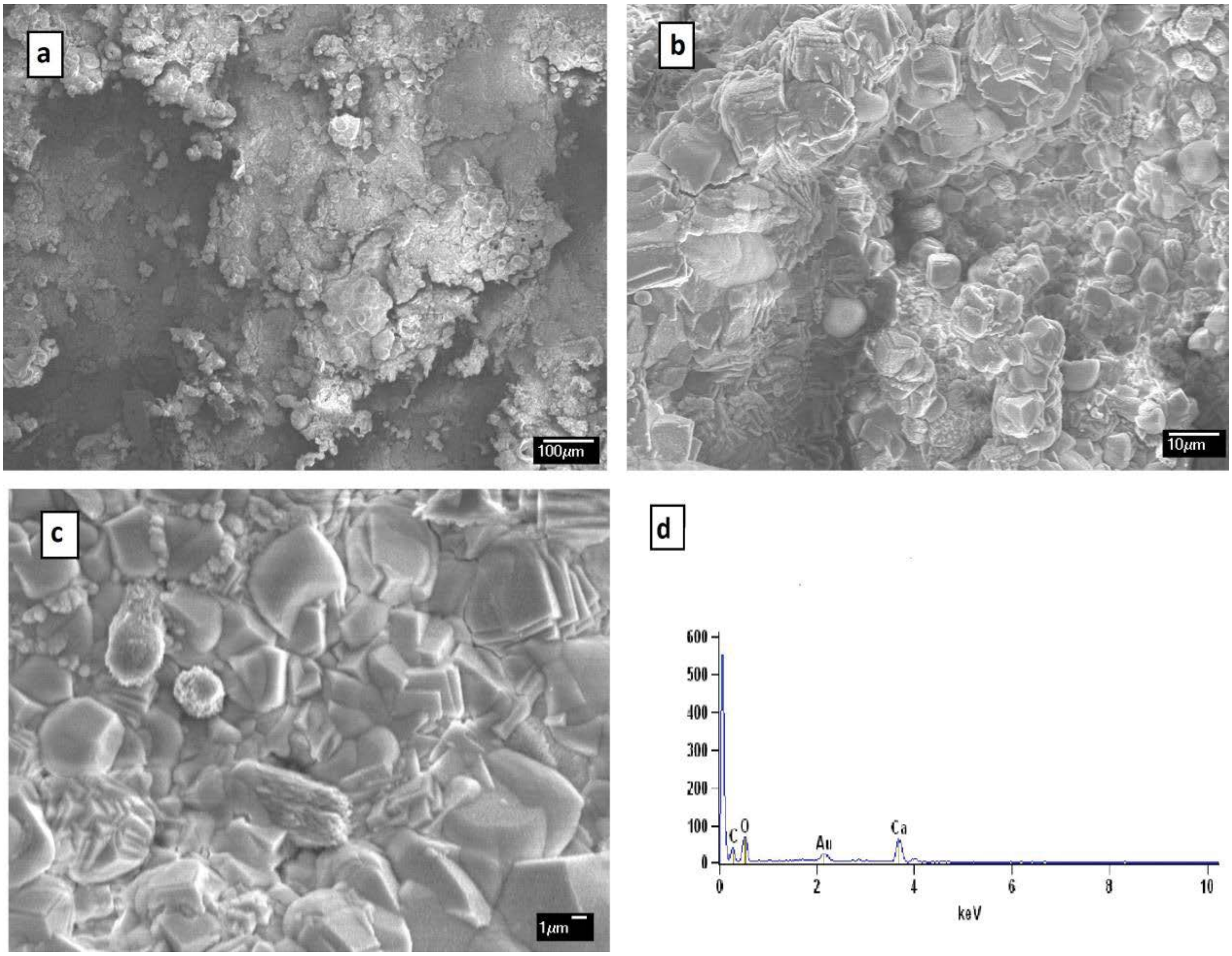

Fig. 4. SEM image of CTA membrane at magnification of (a) 100×, (b) 500×, (c) 5,000×, and (d) EDX of the scaling. Experimental conditions: PW-full feed solution, 6 M NH_3-CO_2 draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

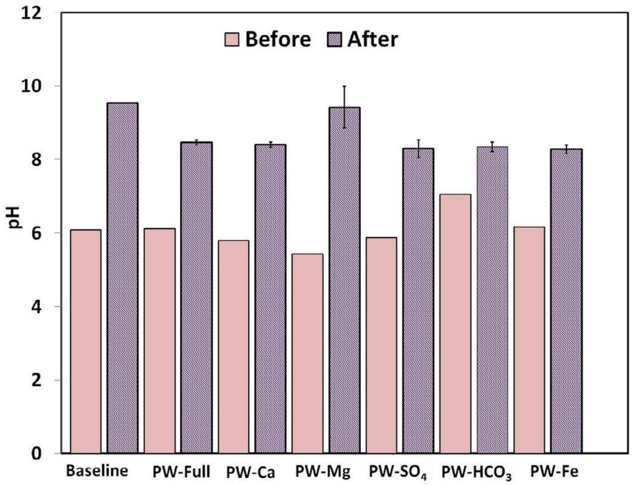

Fig. 5. pH change of the feed solution for the different feed solution composition. Experimental conditions: 6 M NH_3-CO_2 draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

no sulfur (Fig. 7(d)). This suggests that bicarbonate is diffusing into the feed from the draw solution, which contains 6M carbonate species. A similar mechanism of scaling formation was reported by Li et al. when using NH_3-CO_2 draw solution in desalination of seawater [28].

3.2. $MgCl_2$ as a draw solution

$MgCl_2$ has been considered by a number of groups to be a high-performance draw solution [29–31]. This draw solute is simple compared with the complex speciation of the ammonia-carbon dioxide system. An important feature of this draw solution is that it will not appreciably change pH of the feed solution when used. It also lacks scalable species like carbonate. Moreover, a 4.8 M $MgCl_2$ solution has osmotic pressure of 1,057 atm (Based on modified Van't Hoff equation) compared with 250 atm for 6 M of NH_3-CO_2 [15].

From an applications perspective, $MgCl_2$ has its challenges. It cannot be recycled thermolytically. Nanofiltration has been reported as an efficient method to concentrate solutions up to 0.6 M $MgCl_2$ [31], but this would not be suitable for high salinity feeds. Membrane distillation can be used for separation of very high concentration solutions, but the energy requirement for doing so would exceed that of recycling the NH_3-CO_2 for the same feed concentration [7]. Nevertheless, it is worth exploring this draw solution to better identify draw solution properties that are preferred for treating high salinity waters with scalable components. Other types of draw solutions such as polyelectrolytes [32], gluconate salts [33], and magnetic nanoparticles [34] should be considered in the future researches.

Fig. 8 shows the water flux for the two different draw solutions when using DI water and PW-full as feed solutions. The $MgCl_2$ draw solution produced higher water flux than the NH_3-CO_2 solution when using DI water as a feed solution because it generates a far greater osmotic pressure. When using PW-full as a feed solution, the flux for both draw solutions decreased dramatically due to the decrease in driving force. However, $MgCl_2$ still has higher water flux than that of the NH_3-CO_2 draw solution. There is also much less scaling when using $MgCl_2$ as a draw solution. This is largely attributed to the lack of a pH change (Fig. 9) during the test which kept the LSI of the feed solution negative (changed from –0.44 to –0.29). The lack of scale is noticeable on the SEM image (Fig. 10) which shows a clean active side of the CTA membrane. The existence of some impurities on the membrane surface can be explained as follows: The After finishing the tests, we take the membrane out of the membrane module and keep it for some time before doing the SEM test. During this time, the water on the membrane surface is getting dried and leaving some salts on the membrane surface. The membrane texture can be seen clearly and that means

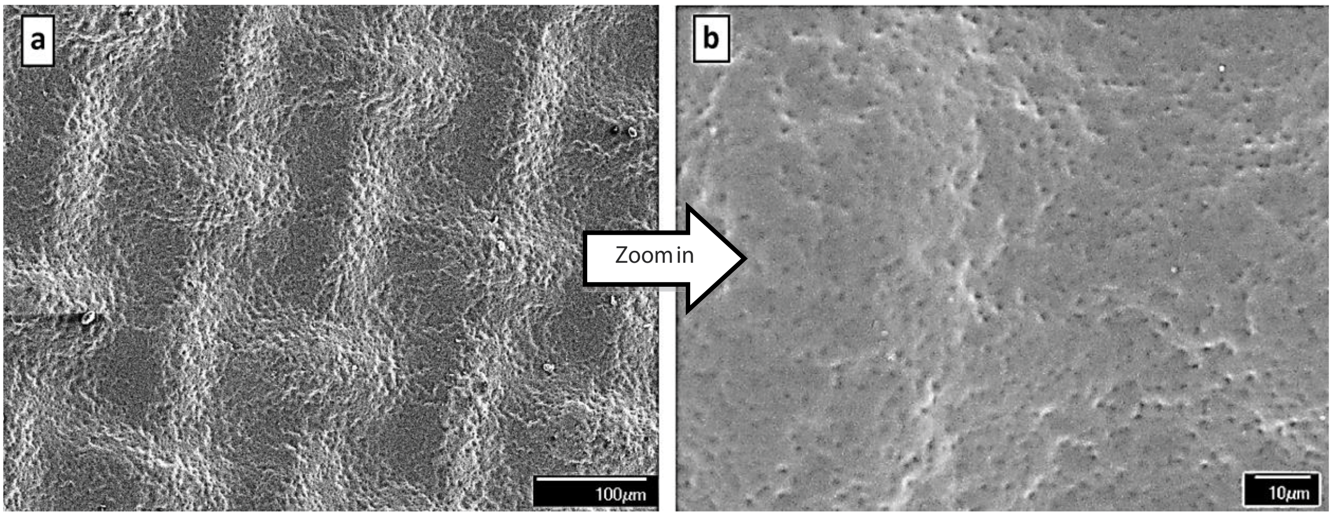

Fig. 6. SEM image of CTA membrane at magnification of (a) 200× and (b) 500×. Experimental conditions: PW-Ca feed solution, 6 M NH_3-CO_2 draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

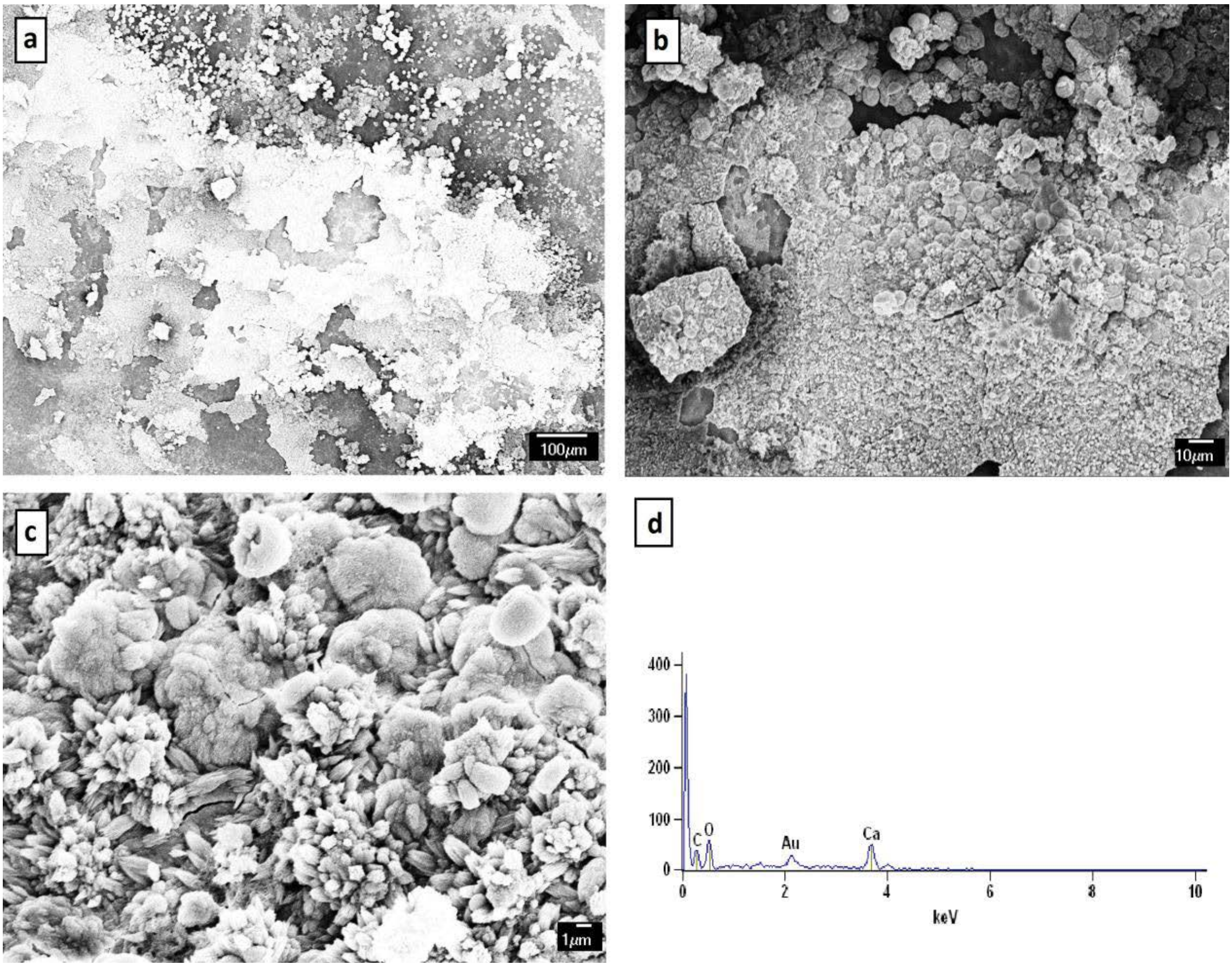

Fig. 7. SEM image of CTA membrane at magnification of (a) 100×, (b) 500×, (c) 5,000×, and (d) EDX of the scaling. Experimental conditions: PW-HCO_3 feed solution, 6 M NH_3-CO_2 draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

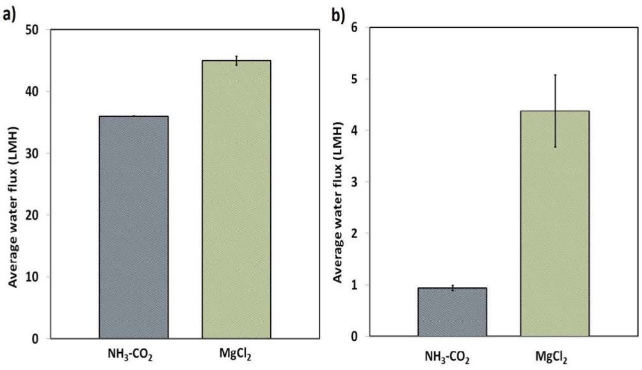

Fig. 8. Comparison between NH_3-CO_2 and $MgCl_2$ as draw solutions in CTA membrane. Experimental conditions: Feed solution (a) DI water and (b) PW-full, FO mode, cross-flow velocity of 0.25 m/s, temp 30°C, and zero transmembrane pressure.

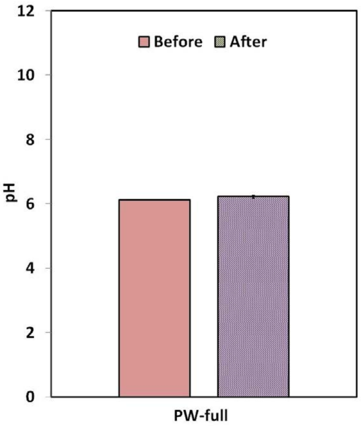

Fig. 9. pH change of the feed solution. Experimental conditions: PW-full feed solution, 4.8M $MgCl_2$ draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

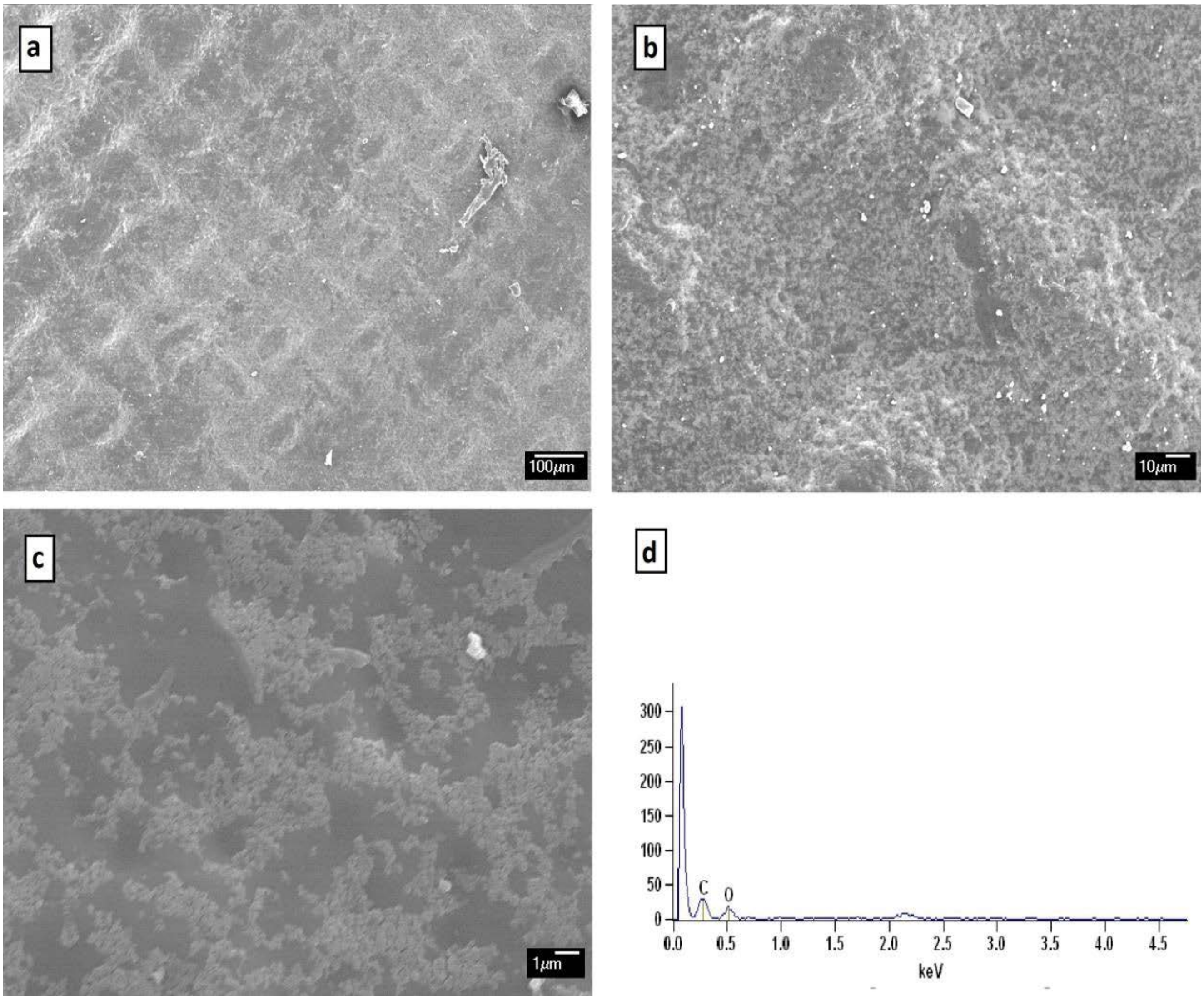

Fig. 10. SEM image of CTA membrane at magnification of (a) 100×, (b) 500×, (c) 5,000×, (d) EDX of the membrane. Experimental conditions: PW-full feed solution, 4.8 $MgCl_2$ draw solution, HTI-CA membrane, FO mode, cross-flow velocity of feed and draw 0.25 m/s, temp 30°C, and zero transmembrane pressure.

that the membrane is not covered with a fouling layer it is just some salt crystals on the membrane surface.

4. Conclusions

FO is a feasible treatment option for hyper-saline produced waters where other treatment methods fail or consume high amount of energy. The performance of FO systems is highly dependent on the choice of draw solutions, however. The draw solution impacts not only the osmotic potential of such systems, but has been shown here to impact other parameters like pH and scaling due to its composition. This means that draw solutions like NH_3-CO_2, which have been popularized in the literature due to its thermolytic regenerability, may have drawbacks when used in produced water systems that scale at high pH. Such concerns would extend to any hard water system that involved FO. Using a draw solution that does not impact pH, such as the $MgCl_2$ described here, certainly eliminates this problem. However, that problem is replaced by the limited recycling option for these types of inorganic salt draw solutions.

What this study shows is that selecting of a draw solute is not trivial. Such a solution must not only work well with a particular membrane (as other studies have discussed), it must work with a particular feed solution. This added complexity may cause some to dismiss FO as a poor choice for managing these kinds of waters, but the complexity of choosing a draw solute is really a double-edged sword. Yes, it means that another variable is included in the process design. However, given the number of solutes that are available and the numerous recycling methods that can be used to regenerate these solutes, options are plentiful. We as scientists and engineers studying applications of FO must keep this in mind as we continue to publish in this area. The wide variety of draw solution options today is both a blessing and a curse for the field.

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