A novel forward osmosis for treatment of high-salinity East Baghdad oilfield produced water as a part of a zero liquid discharge system

Miqat Hasan Salih*, Ahmed Faiq Al-Alawy

Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad, Iraq, emails: mekat.hassan@coeng.uobaghdad.edu.iq (M.H. Salih), drahmed@coeng.uobaghdad.edu.iq (A.F. Al-Alawy)

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ABSTRACT

This study investigated a novel application of forward osmosis (FO) for oilfield produced water treatment from the East Baghdad oilfield affiliated to the Midland Oil Company (Iraq). FO is a part of a zero liquid discharge system that consists of oil skimming, coagulation/flocculation, forward osmosis, and crystallization. Treatment of oilfield produced water requires systems that use a sustainable driving force to treat high-ionic-strength wastewater and have the ability to separate a wide range of contaminants. The laboratory-scale system was used to evaluate the performance of a cellulose triacetate hollow fiber CTA-HF membrane for the FO process. In this work, sodium chloride solution was used as a feed solution (FS) with a concentration of 76 g/L, while the draw solution (DS) was magnesium chloride solution, and the applied external pressure on the feed solution side was 2 bar. The impact of batch mode with a constant DS concentration (or continuous mode) and batch mode with dilution draw solution concentration (240, 300, and 400 g/L) on the FO performance for oilfield produced water treatment were investigated on normalized flux, recovery, feed solution concentration, reverse salt flux, and rejection. The recovery and feed solution concentration increased with increasing draw solution concentration and time. While the normalized flux increased with increasing the draw solution concentration and decreased with time. The reverse salt flux of Mg$^{2+}$ and the rejection of Na$^+$ decreased with time. The produced water feed solution was concentrated to 220 g/L at DS concentration of 400 g/L MgCl$_2$ in batch mode with a constant DS concentration after 16.5 h at which the recovery was 65.67%. The reverse salt flux of Mg$^{2+}$ was 0.06 g/m$^2$h after 10 h, at which the rejection of Na$^+$ reaches 99.84%.

Keywords: Forward osmosis; Zero liquid discharge system; Iraqi oilfield produced water

1. Introduction

The need for freshwater recovery from unconventional sources has been motivated by increasing water scarcity and limited clean water resources [1,2]. Produced water (PW) has the potential to be a significant alternative water resource for various needs, especially for oil producing countries [3,4]. PW treatment is necessary because it can pollute surface water, ground water, and soil [5].

With global estimated water to crude oil ratio of 3:1, PW is the largest amount of wastewater generated in the petroleum industry [6–8]. PW contains a variety of impurities that must be removed before it can be used. The total dissolved solids (TDS), grease, dispersed oil, organic compounds, salts, radionuclides, and heavy metals are widely present in PW. Most PW salinity is higher than seawater, with TDS concentrations ranging from 1,000 to 400,000 ppm [3,9]. Iraq is one of the top three oil-exporting and reserving countries in the world [4]. Midland Oil Company (Iraq) reported a production rate of $140 \times 10^3$ and $27.56 \times 10^3$ bbl/d of produced water and oil respectively in 2015, and it is

* Corresponding author.
expected to increase to $307.84 \times 10^3$ and $92.15 \times 10^3$ bbl/d in 2031 [7,10].

When treating the PW to a quality suitable for external reuse or discharge, the primary consideration is to reduce the TDS concentration. Significant pretreatment, such as skimming, gravity separation [11], centrifugation, a biological method [12], sedimentation, coagulation/flocculation [13], and electrochemical oxidation [14] is required to reduce scaling and fouling potential before PW can be treated using membrane or thermal technologies. In produced water commercial treatment systems, multiple technologies designed to remove different constituents are frequently combined [15].

Membrane technology is an interesting alternative technology because it operates without the use of chemicals and has a low energy consumption [3,16]. Reverse osmosis (RO) is a widely used desalination technique in community water supply systems and industry [17]. Revert-osmosis TDS levels are limited to 40,000 mg/L (approximately seawater level) or lower because it is difficult to achieve high hydraulic pressure in order to overcome the osmotic pressure caused by the high salinity of produced water with high total dissolved solid levels [15,18–20]. The Midland Oil Company has high salinity produced water, which ranges from 2 to 5 times higher than seawater. High TDS levels may be better treated by forward osmosis (FO), membrane distillation (MD) [18], and mechanical vapor compression. During the membrane distillation and mechanical vapor compression processes, the permeate must undergo a phase change, which requires a high-energy that is not needed for FO treatment [3,15,20].

FO is a process that has the potential to significantly reduce the cost of desalinating saline water sources. FO is an osmotically driven membrane process in which the driving force for separation is the difference in chemical potential between a concentrated draw solution and a lower salinity feed solution (including contaminated wastewater) [21,22]. Water transports across a semipermeable, salt-impermeable FO membrane from low osmotic pressure feed solution to high osmotic pressure draw solution [23,24]. FO has attracted attention as an alternative technology for seawater desalination because they have several advantages over other technologies such as high rejection of many pollutants without the aid of pressure [24], low and reversible membrane fouling [20], low energy consumption because they use the osmotic pressure. Also, FO can treat high salinity waters using inexpensive and simple low pressure equipment, and it can be utilized to generate energy from the osmotic pressure gradient between seawater and freshwater. The concentration of the draw solution, however, limits the rate of water production by FO. Furthermore, reverse solute flux is a critical issue in FO [5,15,26].

In osmotically driven membrane processes, there are two types of concentration polarization phenomena: external concentration polarization (ECP) and international concentration polarization (ICP) [26]. If the draw solution comes into contact with the active layer of the membrane (Active Layer-Draw Solution orientation), the feed solution is concentrated in the support layer (concentrative ICP), while the draw solution is diluted in the active layer (dilutive ECP). If the feed solution comes into contact with the active layer of the membrane (Active Layer-Feed Solution orientation), the feed solution is concentrated in the active layer (concentrative ECP), while the draw solution is diluted in the support layer (dilutive ICP) [5,19]. ECP is generally thought to have less influence on FO performance than ICP [28].

A draw solution solute must simultaneously have specific properties to be effective, such as high osmotic efficiency (it has a low molecular weight and has to be highly soluble in water in order to generate high osmotic pressure) [29], non-toxic, easily and economically be separated and recycled [23], and minimal reverse draw solute flux [15,26]. Magnetic nanoparticles, polyelectrolytes, and stimuli-responsive polymer hydrogels are unsuitable for forward osmosis treatment of high salinity PW because they cannot generate high osmotic pressure [15]. MgCl₂, performed the best among the DS salts, with no considerable increase or decrease in flux performance. This is because it can generate high osmotic pressure with three ions, whereas others have only two [3]. MgCl₂ was used as the draw solution for the forward osmosis desalination of produced water because it can generate 65.8 percent more osmotic pressure than the same concentration of NaCl [18]. The nanofiltration (NF) process, which is a low pressure membrane process, can be used to effectively remove divalent ions and can be proposed as an alternative regeneration method for the MgCl₂ draw solution [30].

Recently, the zero liquid discharge (ZLD) system has received increased attention for its potential to improve sustainability in desalination [31,32]. The ZLD system completely recovers water from the highly saline solution and produces compressed solid waste [33,34]. The produced crystal, as well as the increased water recovery, have the potential to offset the entire operational costs. For brine concentration, FO, MD, and electroosmosis (ED)/electrodialysis reversal (EDR) have all been widely utilized [3]. FO was used to concentrate industrial brine to a salinity of 220,000 mg/L at a recently built ZLD plant. In addition to their high performance, FO provides opportunities for resource recovery, and therefore they could be attractive options for the ZLD system [35]. Zero liquid discharge consist of the following processes:

- Oil skimming followed by coagulation/flocculation, electrocoagulation, or chemical precipitation.
- Forward osmosis, nanofiltration, or reverse osmosis membrane.
- Crystallization.

In a previous work Salih et al. [36], the treatment of real oilfield produced water from the East Baghdad oilfield using two stages of ZLD system namely oil skimming process followed by a coagulation/flocculation process were studied. The best temperature and time for oil skimming were 40°C and 2.5 h. which gave 95.8%, 94.9%, 31.5%, and 33.2% removal for oil content, COD, turbidity, and TSS respectively. In the coagulation/flocculation process, the optimum PAC dosage and pH were 55 mg/L and 6.4 which gave 99.9%, 96.5%, and 97.7% removal for oil content, turbidity, and TSS respectively. Table 1 represents the real East Baghdad oilfield produced water after pretreatment in previous work by Salih et al. [36]. This research
aims to apply a FO process as the third part of the ZLD system to generate clean water extracted from diluted draw solution and a concentrated feed solution of about 220 g/L. The efficiency of FO will be estimated with MgCl$_2$ as draw solution and simulated oilfield produced water from the East Baghdad oilfield as a feed solution with different DS concentrations. The possibility of using a CTA hollow fiber membrane with AL-FS orientation to generate pure water from the FO process will be investigated with regard to water flux and reverse salt flux.

2. Experimental work

2.1. Materials and Membrane

All of the chemicals were analytic reagent grade and used without further treatment. NaCl (99%, India) to prepare the feed solution has the same conductivity and TDS concentration as the real East Baghdad oilfield produced water, MgCl$_2$$\cdot$6H$_2$O (99%, India) to prepare draw solution has different concentrations. The distilled water of conductivity 1.7 µS/cm was used to prepare the draw and feed solution.

The presented work employs a cellulose triacetate hollow fiber membrane CTA-HF (TOYOBO, Japan) membrane. The membrane’s effective surface area is 0.15 m$^2$, module length is 20 cm, module diameter is 13 mm, the outer diameter of hollow fiber is 200 µm, inside diameter of hollow fiber is 105 µm, the number of hollow fibers is 1260, and the thickness of the support layer is 47.5 µm. At the HF membrane’s outer surface, the active layer has existed. Thus, for AL-FS orientation (FO mode), the draw solution has been pumped to the lumen-side of the hollow fiber membrane, while the feed solution has been pumped to the shell-side.

2.2. Forward osmosis process

The experimental setup for the FO process used in this work is shown in Fig. 1. The membrane orientation was AL-FS. The experiments were conducted on counter-current flows in which the feed solution and draw solution

<table>
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<td>SO$_4^{2-}$, mg/L</td>
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<tr>
<td>Cl$^{-}$, mg/L</td>
<td>40,657.6</td>
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<tr>
<td>Na$^+$, mg/L</td>
<td>27,950</td>
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Fig. 1. The experimental setup of forward osmosis process (FO).
flowed in opposite directions. The initial volumes of the feed and the draw solution in the FO process were 1,000 and 500 mL, respectively. Two diaphragm pumps (PJ-1611, China) were used for recirculating draw solution through the HF module’s lumen side, pressurizing and recirculating feed solution through the shell side. The NaCl solution with a concentration of 76 g/L was employed as FS, and MgCl₂ was employed as DS with different concentrations (240, 300, and 400 g/L). For the experiments with constant DS concentration, the DS vessel was intermittently dosed with a 500 g/L MgCl₂ solution in order to maintain constant concentration.

Two rotameters were used to measure the feed solution volumetric flow rate as well as the draw solution volumetric flow rate. Feed and draw solution flow rates have been held constant at 2 and 0.1 L/min, respectively. Throughout the tests, the cooling/heating coils were immersed in the draw and feed solution containers to control the temperature (35°C ± 1°C). The inlet and outlet pressures of the feed and draw solution were measured using a pressure gauge. The pressure of 2 bar was applied on the FS side (shell side) and it was adjusted by using valve 3. Concentrations of the draw and feed solutions were measured through a conductivity meter (EC-Meter Basic 30, CRISON, Spain). Mg²⁺ ions concentrations were measured by chemical analysis (titration method), Na⁺ ions concentrations were measured by a flame photometer (FLAMEPHOTOMETER CL 378, India). The water permeation flux ($J_w$) was calculated by measuring the weight change of the feed solution with a digital mass balance. $J_w$ (L/m² h, expressed as LMH) was calculated using Eq. (1) [37].

$$J_w = \frac{\Delta V}{A_e \Delta t} \quad (1)$$

where $\Delta V$ is the permeate water over test duration $\Delta t$. $A_e$ represents the effective area of the membrane.

The pure water recovery measures how much of the feed is recovered as permeate. It is reported as a percentage. Recovery was determined by using Eq. (2) [38]:

$$\text{Recovery} = \left( \frac{V_p}{V_f} \right) \times 100 \% \quad (2)$$

where $V_p$ is the permeate (or product) volume of water and $V_f$ is the volume of water in the feed vessel.

The reverse solute flux $J_s$ (g/m² h) of Mg²⁺ ions was determined by using Eq. (3) [39]:

$$J_s = \frac{V_C - V_{C_f}}{A_e \Delta t} \quad (3)$$

where $C_i$ and $V_i$ are the Mg²⁺ ions concentration in the feed solution and volume at time $t$, respectively, and $C_f$ and $V_f$ are the initial Mg²⁺ ions concentration and volume of the feed solution.

The Na⁺ ions rejection (Na⁺ transferred from feed to draw solution) was obtained by using Eq. (4) [23]:

$$R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \quad (4)$$

where $C_p$ is the concentration of Na⁺ ions on the draw solution side, $C_f$ is the concentration of Na⁺ ions on the feed solution side.

3. Results and discussions

3.1. Baseline Experiments

Pure water flux and recovery using deionized water and PW with 76 g/L NaCl as FS with 400 g/L MgCl₂ as DS was measured and presented in Fig. 2 in the case of batch mode (osmotic dilution mode). This experiment shows the difference in the performance when the FS is deionized water or PW with initial TDS = 76 g/L. Fig. 2 shows that the initial water flux of the PW as FS was significantly lower than the initial flux in the baseline experiment (deionized water DW as FS). This is due to the interaction of high salinity, external concentration polarization, and feed solution viscosity. These findings are agreed with Hickenbottom et al. [24]. The initial water flux of the experiment with PW feed solution was lower than that of the baseline experiment by 74.13%. The recovery with PW feed solution reached 13.59% after 2 h while the recovery of the baseline experiment reached 64.98% after 2 h of operation.

3.2. Batch mode (osmotic dilution mode)

The recovery, normalized flux (NF), FS concentration, and DS concentration were measured in FO using three DS concentrations (240, 300, 400 g/L). These concentrations were diluted by water that transfers from the feed solution during the experiment until the equilibrium was approximately reached between feed and draw solution. As shown in Fig. 3, the recovery increased with time for all three DS concentrations.

For $C_{DS,i} = 400$ g/L, the recovery reached 55.29% after 22.5 h of operation, for the same time of 22.5 h the recovery of the $C_{DS,i} = 300$ and 240 g/L were lower than that of 400 g/L by 13.67%, and 35.25% respectively. For $C_{DS,i} = 400$ g/L, the recovery reached to 59.58% after 26 h of operation, for $C_{DS,i} = 300$ g/L the recovery reached to 47.73% after 22.5 h of operation while reached to 39.17% after 26 h of operation for $C_{DS,i} = 240$ g/L. Fig. 4 shows the normalized flux declined with time for all three DS concentrations, and increased slightly or remained constant at some experiments. For $C_{DS,i} = 400$ g/L, the NF reached 0.18 after 26 h of operation; for $C_{DS,i} = 300$ g/L the NF reached 0.35 after 26 h of operation for $C_{DS,i} = 240$ g/L. Because the experiments were carried out in the batch mode, which resulted in the dilution of the draw solution and the concentrate of the feed solution, the difference in the osmotic pressure between the two solutions decreased, and thus the driving force for water permeation decreased. These findings are supported by Blandin et al. [21].

Fig. 5 shows that FS concentration increased and DS concentration decreased with time for all three DS
concentrations. For $C_{DS,i} = 400$ g/L, the FS concentration reached 170 g/L after 22.5 h of operation, for the same time of 22.5 h, the FS concentration of the $C_{DS,i} = 300$, and 240 g/L was lower than that of 400 g/L by 14.42%, and 30.12% respectively. For $C_{DS,i} = 400$ g/L, the FS concentration reached to 177 g/L after 26 h of operation, for $C_{DS,i} = 300$ g/L, the FS concentration reached to 145.49 g/L after 22.5 h of operation; while it reached to 124.7 g/L after 26 h of operation for $C_{DS,i} = 240$ g/L. This result is agreed with Hickenbottom et al. [24]. For $C_{DS,i} = 400$ g/L, the DS concentration reached 186.9 g/L after 26 h of operation, for $C_{DS,i} = 300$ g/L, the DS concentration reached to 153.7 g/L after 22.5 h of operation; while it reached to 134.36 g/L after 26 h of operation for $C_{DS,i} = 240$ g/L. The DS concentration decreased over time while the feed solution concentration increased, resulting in a decrease in the net osmotic pressure. These findings are proved by Jamil et al. [40].

The reverse solute flux ($J_s$), which is resulted from the draw and the feed solution high concentration difference, and the rejection were measured in FO using DS concentrations 400 g/L in an osmotic dilution mode for 10 h of operation. As shown in Fig. 6, the reverse salt flux and the rejection decreased with time. The $J_s$ of Mg$^{2+}$ at the first two hours was 0.2 g/m$^2$h and thus, the specific reverse flux was 0.1 g/m$^2$h.

Fig. 2. Water flux and recovery as a function of time for deionized water (DW) and PW as FS with MgCl$_2$ as DS for FO process.

Fig. 3. Recovery as a function of time for simulated PW as FS ($C_{FS,i} = 76$ g/L) and MgCl$_2$ as DS for FO process.
Fig. 4. Normalized flux as a function of time for simulated PW as FS ($C_{FS,i} = 76$ g/L) and MgCl$_2$ as DS for FO process.

Fig. 5. (a) Feed solution concentration and (b) draw solution concentration as a function of time for simulated PW as FS ($C_{FS,i} = 76$ g/L) and MgCl$_2$ as DS for FO process.
salt flux ($J_s$) was 0.57 g/L. Then it decreased by 70% at the end of 10 h ($J_s = 0.4$ g/L). The rejection of Na$^+$ was very high at 99.93% at 2 h and declined to 99.84% at 10 h. High ionic strength water (high salinity feed solution) has the potential to reduce the pore size of the membrane and thus reduce RSF. Ions may also neutralize the pore charge, reduce electrostatic repulsion within the pores, pore size, and water and solute diffusion. Applying pressure to FS was predicted to increase water flux, which alters the solute concentrations at the membrane boundary layer on both sides of the membrane due to enhanced CP effects and limits the reverse solute flow. The DS concentration decreased due to increase dilution, while the FS concentration increased due to an increase in the feed solute rejection, decreasing the $\Delta C$ and, ultimately, the SRSF. FO membranes can reject all particulate matter and almost all dissolved contaminants. The rejection of Na$^+$ reached above 99%, which is a reasonable result because the CTA membrane was not designed specifically for high salt removal. These findings agreed with Bell et al. [41].

3.3. Batch mode with a constant DS concentration

The recovery, normalized flux, and FS concentration were measured in FO using three DS concentrations (240, 300, 400 g/L). These DS concentrations were kept constant during the experiment. Fig. 8 shows that the recovery of pure water increased with time for all three DS concentrations.

For $C_{DS} = 400$ g/L, the recovery reached 65.67% after 16.5 h of operation; for the same time of 16.5 h, the recovery of the $C_{DS} = 300$, and 240 g/L are less than that of 400 g/L by 26.87%, and 31.61% respectively. For $C_{DS} = 300$ g/L, the recovery reached 66.66% after 26.5 h of operation, while it reached 65.69% after 31.5 h of operation for $C_{DS} = 240$ g/L as shown in Fig. 7. Fig. 8 shows the normalized flux declined

![Fig. 6. Reverse salt flux of Mg$^{2+}$ and rejection of Na$^+$ as a function of time for simulated PW as FS ($C_{FS,i}$ = 76 g/L) and MgCl$_2$ as DS ($C_{DS,i}$ = 400 g/L) for FO process.](image1)

![Fig. 7. Recovery as a function of time for simulated PW as FS ($C_{FS,i}$ = 76 g/L) and MgCl$_2$ as DS for FO process.](image2)
with time for all three DS concentrations, and increased slightly or remained constant at some experiments. For $C_{DS} = 400$ g/L, the NF reached 0.1 after 16.5 h of operation. For $C_{DS} = 300$ g/L, the NF reached 0.31 after 26.5 h of operation, while it reached 0.2 after 31.5 h of operation for $C_{DS} = 240$ g/L. Higher draw solution concentrations may generate a higher osmotic driving force, resulting in an increase in water flux across the membrane. Increasing the osmotic pressure due to an increase of the DS concentration causes an increase in permeate water flux. The increase in flux should be linear with the osmotic pressure difference, $\Delta \pi = \pi_{DS} - \pi_{FS}$, but the flux exhibits a non-linear phenomenon, especially at higher driving forces. This phenomenon is attributed to the internal concentration polarization, which is most likely caused by the microporosity of the membrane permeate side. Water flux rapidly decreased due to a decrease in the osmotic pressure driving force, which corresponded to an increase in feed solution concentration, which decreased the osmotic driving force. It is, therefore, very possible that the increase of feed concentration also increases the external concentration polarization of the active layer surface. Also, scaling caused by feed and draw solutions could also accumulate on the membrane surface and reduce flux. These findings are proved by Yun et al. [27], Liden et al. [19], and Jamil et al. [40].

As shown in Fig. 9, FS concentration increased with time for all three DS concentrations. For $C_{FS} = 400$ g/L, the FS concentration reached 220.42 g/L after 16.5 h of operation. For the same time of 16.5 h, the FS concentration of the $C_{DS} = 300$, and 240 g/L are less than that of 400 g/L by 30.22%, and 37.52% respectively. For $C_{DS} = 300$ g/L, the FS concentration reached 221.07 g/L after 26.5 h of operation, while it reached 221 g/L after 31.5 h of operation for $C_{DS} = 240$ g/L. This result is agreed with Hickenbottom et al. [24].

Through the experiments carried out in this study, the aim was achieved which is obtaining a high concentration of the PW feed solution as well as obtaining a high recovery of pure water as shown in Table 2.

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**Fig. 8.** Normalized flux as a function of time for simulated PW as FS ($C_{FS} = 76$ g/L) and MgCl$_2$ as DS for FO process.

**Fig. 9.** Feed concentration as a function of time for simulated PW as FS ($C_{FS} = 76$ g/L) and MgCl$_2$ as DS for FO process.
4. Conclusion

This work shows that Forward osmosis (FO) is a viable option as a part of the ZLD system for the treatment of oilfield produced water (i.e., East Baghdad oilfield). Forward osmosis can be utilized to extract water from high salinity oilfield produced water, thereby concentrating the produced water for further processing. MgCl₂ osmotic agent was effective for PW treatment in the FO process due to the good solubility of MgCl₂ that provided effective osmotic pressure to draw water from PW and reduced salt flux significantly to 0.06 g/m² h. FO operated in a batch mode with a constant DS concentration can effectively concentrate feed solution three times their initial value after 16.5 h of operation and recover more than 65% of the oilfield PW. While, FO operated in the osmotic dilution mode can concentrate feed solution 2.33 times their initial concentration after 26 h of operation and recover more than 59% of the oilfield PW, with a high rejection of Na⁺ reached to 99.84%.

References


Table 2

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<tr>
<th>Cᵢₒs, g/L</th>
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Best results of continuous and batch mode with Cᵢₒs = 400 g/L.


