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Pressure assisted forward osmosis for shale gas wastewater treatment

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ABSTRACT

This study investigated the feasibility of using pressure assisted forward osmosis (PAFO) for shale gas wastewater treatment. PAFO combines osmotic gradient across a membrane with external pressure together, which was expected to obtain higher flux than forward osmosis (FO). Experiments were performed in a laboratory-scale PAFO system, which allows the application of external pressure up to 10 bar on the feed solution side. Deionized water and three kind of synthetic shale gas wastewater, including low range, medium range, and high range wastewaters, were used as feed solutions and NaCl was used as a draw solution. The water flux was improved up to 10–15% by applying external pressure to FO when low range and medium range wastewaters were treated. However, the effect of the external pressure was significantly reduced when the high-range wastewater was treated. After FO treatment, air gap membrane distillation was successfully applied to re-concentrate the draw solutes.

Keywords: Desalination; Forward osmosis; Pressure assisted forward osmosis; Pressure effect; Membrane distillation; Shale gas

1. Introduction

Shale gas is a natural gas, which is tightly locked in very small spaces within the reservoir rock. Shale gas can be used for heating, power generation, and raw materials for petrochemical industry. As conventional oil resources have been depleted, shale gas has become an increasingly important source of natural gas. The combination of horizontal drilling and hydraulic fracturing has allowed access to large volumes of shale gas that were previously uneconomical to produce. The production of natural gas from shale formations has rejuvenated the natural gas industry in the United States. Shale gas reservoir developments are a growing source of natural gas reserves across the United States [1].

However, hydraulic fracturing has raised environmental concerns and is challenging the adequacy of existing regulatory regimes. One of the main concerns is the production of wastewater containing high concentration of contaminants. Various chemicals have been used for hydraulic fracturing, resulting in

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environmental issues and human health problems [1–4]. Nevertheless, shale gas wastewater had been discharged without proper treatment until recently. This has led to water contamination on the vicinity of shale gas wells.

The conventional method to treat the shale gas wastewater is reverse osmosis (RO), which is widely used especially due to its advantage over conventional wastewater treatment [5,6]. Although RO has proven to be a robust method for shale gas waste water treatment, its major drawback is its high demand in electric energy [7,8] and severe fouling of the membranes. In addition, RO produces substantial amount of brine containing high salt contents, which should be properly disposed or treated [9].

In this context, forward osmosis (FO) has drawn attention as an alternative technology for shale gas waste water treatment. Instead of using electricity, FO uses an osmotic pressure, allowing the potential for reduced energy consumption. FO also offers additional advantages such as high water retention rates and overall sustainability. Nevertheless, the water production rate by FO is limited by the concentration of draw solution. This implies that a large amount of draw solutes should be used to obtain high flux in FO, which creates additional problems in the recovery of draw solute [10].

Recently, pressure assisted forward osmosis (PAFO) has been proposed as a novel method to increase flux through FO membranes [11]. PAFO adds a medium pressure pump to a conventional FO system. The system takes advantage of additional hydraulic pressure, resulting in water transport in both mechanisms: flux driven by hydraulic pressure (RO mechanism) and that by osmotic pressure (FO mechanism). Accordingly, PAFO has potential for the treatment of shale gas wastewater.

After FO process, the diluted draw solution must be reconcentrated, yielding potable water and recycling the draw solute. Accordingly, the development of an adequate and efficient method for recycling draw solution is crucial to achieve success for FO application. Among various techniques, membrane distillation (MD) has drawn attention as a novel method to recycle FO draw solution [12,13]. This is because MD can be operated using low grade waste heat, allowing the reduction of energy cost for draw solution recovery.

Therefore, the objectives of this study are to investigate the feasibility of FO and PAFO processes for shale gas wastewater treatment. The effect of external pressure on permeate flux was examined in PAFO for shale gas wastewater treatment. A hybrid system combining FO with MD for the continuous treatment of shale gas wastewater was also attempted to demonstrate the potential of FO and PAFO.

2. Theory

2.1. Water transport mechanism

There are two kinds of concentration polarization phenomena in osmotically driven membrane processes, including the international concentration polarization (ICP) and the external concentration polarization (ECP) [14]. Depending on the orientation of the membrane, the mechanism for concentration polarization may be different. If the active layer of the membrane contacts with draw solution (Al-DS orientation), feed solution is concentrated in the support layer (concentrative ICP) and draw solution is diluted in the active layer (dilutive ECP). If the active layer of the membrane contacts with feed solution (Al-FS orientation), feed solution is concentrated in the active layer (concentrative ECP) and draw solution is diluted in the support layer (dilutive ICP). Assuming that the solute rejection is sufficiently high, the following equation can be used to describe these phenomena [15]:

$$J_w = A(\pi_{D,b}e^{-J_wK_D} - \pi_{F,b}e^{J_w/K_F}) \quad \text{for AL-FS} \tag{1}$$

$$J_w = A(\pi_{D,b}e^{-J_w/K_F} - \pi_{F,b}e^{J_wK_D}) \quad \text{for AL-DS} \tag{2}$$

where J_w is the water flux, A is the water permeability of the membrane, $\pi_{D,b}$ is the osmotic pressure of the draw solution, $\pi_{F,b}$ is the osmotic pressure of feed solution, K_F is the mass transfer coefficient in the boundary layer, $K_D = t\tau/D\varepsilon$ is the solute resistance to diffusion in the support layer, t is the membrane thickness, τ is the tortuosity, D is the diffusion coefficient of solute, and ε is the porosity. $S = t\tau/\varepsilon$ is the structure parameter of the membrane, which is closely related to the extent of internal concentration polarization.

On the other hand, the water flux in RO process is described as:

$$J_w = A(P_{feed} - \pi_{F,b}e^{J_w/K_F}) \tag{3}$$

Combining the Eqs. (1), (2), and (3), the generalized equation for pressurized FO processes can be derived:

$$J_w = A(\pi_{D,b}e^{(-J_wK_D)} - \pi_{F,b}e^{(J_w/K_F)} + P_{feed} - P_{draw}) \quad \text{for AL-FS} \tag{4}$$

$$J_w = A(\pi_{D,b}e^{(-J_w/K_F)} - \pi_{F,b}e^{(J_wK_D)} + P_{feed} - P_{draw}) \quad \text{for AL-DS} \tag{5}$$

If P_{feed} is positive and P_{draw} is zero, this process is defined as the PAFO. If P_{feed} is zero and P_{draw} is positive, this process is defined as the pressure retarded osmosis (PRO). Fig. 1 illustrates the fundamental mechanisms of FO, PRO, RO, and PAFO. Using Eq. (4) or (5), any osmotic process can be theoretically analyzed.

To consider the effect of cross-flow velocity, following equations may be used.

$$\mathrm{Sh} = 1.85\left(\mathrm{ReSc}\frac{d_h}{L}\right)^{0.33} \quad \text{for laminar flow} \tag{6}$$

$$\mathrm{Sh} = 0.04\mathrm{Re}^{0.75}\mathrm{Sc}^{0.33} \quad \text{for turbulent flow} \tag{7}$$

where Sh is the Sherwood number, Re is the Reynolds number, and Sc is the Schmidt number, d_h is the hydraulic resistance, and L is the channel length.

3. Material and methods

3.1. Feed and draw solutions

During FO and PAFO tests, sodium chloride (Sigma–Aldrich, St. Louis, MO) was used as a draw solute. The concentration of the draw solution is 5 M. Deionized water (D.I. water) and three synthetic shale gas wastewaters were used as the feed solutions. The chemical compositions of the synthetic wastewaters were determined based on those of real shale gas water in Marcellus, which are reported in literature [1]. Table 1 summarizes the characteristics of the synthetic wastewaters used in this study. Although TDS for real shale gas wastewaters varies from 1 to 10%, we focused on the treatment of high TDS shale gas wastewaters, which have TDS ranging from 6 to 25%.

3.2. FO membrane

FO membrane manufactured by Hydration Technology Innovations (X-Pack, HTI, USA) was used for all FO and PAFO tests. According to the manufacturer, the total thickness of the membrane is approximately 100 μm and it has asymmetry structure [16].

3.3. FO and PAFO systems

A schematic diagrams and detailed description of the experimental systems are shown in Fig. 2. A laboratory-scale membrane cell was used for all FO and PAFO tests. The length, width, and depth of the channel of the membrane cell were 87, 35.5, and 1 mm, respectively. The effective membrane area was 0.00306 m^3. Spacers were used on both sides of the membrane channel to support the membrane. The membrane orientation was AL-FS.

Experiments were carried out on count-current flows where feed solution and draw solution flow in opposite directions to each other. Variables speed gear pumps (Micropump, Vancouver, WA) was used to pump feed water and draw solution. High pressure nitrogen gas was used to add the hydraulic pressure on feed solution. Feed water tank was made of stainless steel, type 304SS, to stand the high pressure. Hydraulic pressure was put into the completely sealed feed water line of feed water tank by high-pressure charged nitrogen gas. The pressure was adjusted by gas regulator. The pressure of both sides of membrane was monitored and recorded by pressure sensors connected at computer.

3.4. FO-AGMD hybrid system

A laboratory-scale flat-sheet membrane cells were used for both FO and air gap membrane distillation (AGMD). A schematic diagram describing the experimental setup is shown in Fig. 3. The channel dimension of FO and AGMD module were 2 mm long, 6 mm wide, and 1 mm deep. The air gap of permeate side of AGMD was 1 mm. In the FO system, the flows of both sides of membrane were counter-current flows of the feed water and draw solutions. Variables speed gear pumps (Micropump, Vancouver, WA) were used to pump feed water and draw solution. Only draw

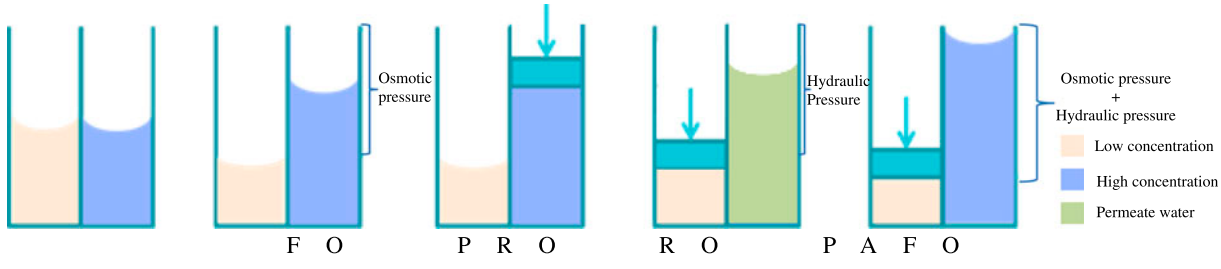

Fig. 1. Basic concepts for FO, PRO, RO, and PAFO.

Table 1
Chemical compositions and osmotic pressure

Reagents	Low (g/L)	Medium (g/L)	High (g/L)
NaBr	0.93	1.55	2.06
$BaCl_2$	3.49	5.01	7.13
Na_2SO_4	0	0.01	0.74
$CaCl_2$	8.33	27.20	86.03
$MgCl_2$	0.406	0.59	0.79
NaCl	45.26	83.05	110.13
Total TDS	68.3	149.0	247.0
Osmotic pressure at 25℃	41.2 bar	82. 3 bar	139. 8 bar

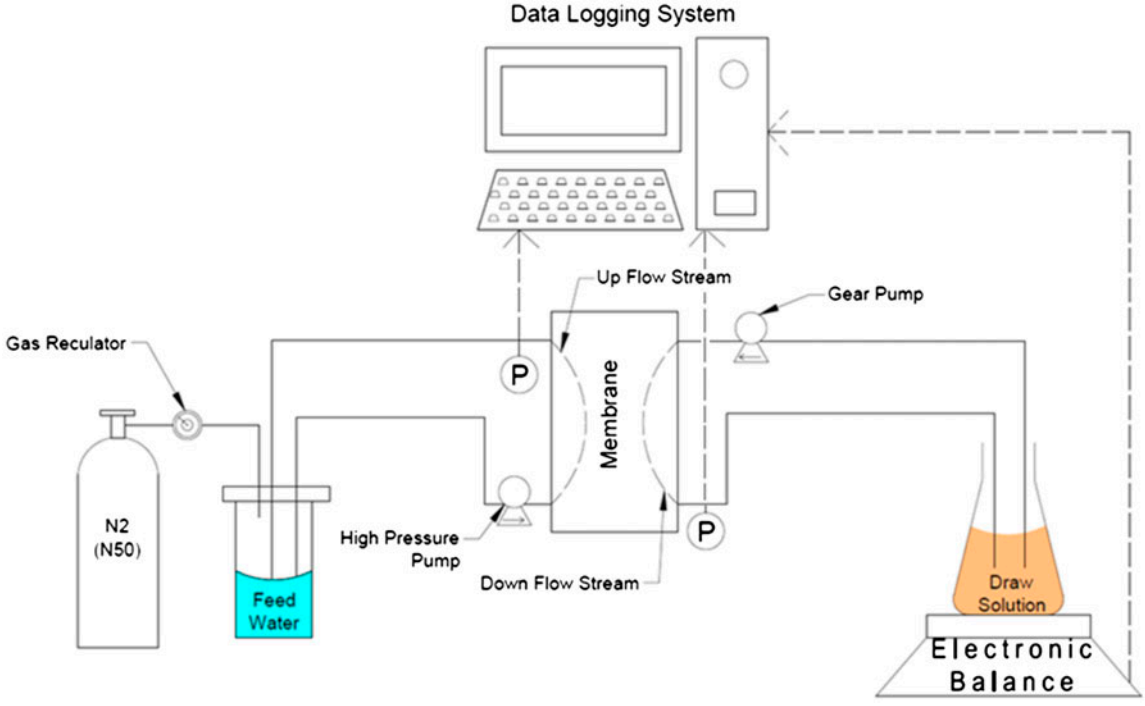

Fig. 2. Schematic diagram for experimental set-up for FO and PAFO test.

solution of FO system was circulated inside of feed side of AGMD system. Variables speed gear pump (Micropump, Vancouver, WA) was use to pump draw solution of FO inside feed water line of AGMD.

To control the temperature of draw solution and the air, a hot plate was set up on a flask of draw solution of FO and a chiller was used to cool down the air inside permeate side of AGMD. The temperature of both sides of draw solution and the air was monitored and recorded. Water flux values of both draw solution of FO and permeate water of AGMD were continuously monitored using two electronic balances connected to a personal computer.

3.5. Test protocols: FO and PAFO tests for treatment of shale gas wastewater

Pure water flux in FO and PAFO was measured with using the D.I. water as feed water and sodium chloride solution of 5 M as draw solution. After measuring the pure water flux, to measure a permeate flux, the D.I. water was changed to three kinds of synthetic shale gas wastewater. In PAFO mode, external pressure was applied on the feed side, which ranges from 5 to 10 bar while in FO mode, there was no external pressure. Details in the operating conditions are described in Table. 2.

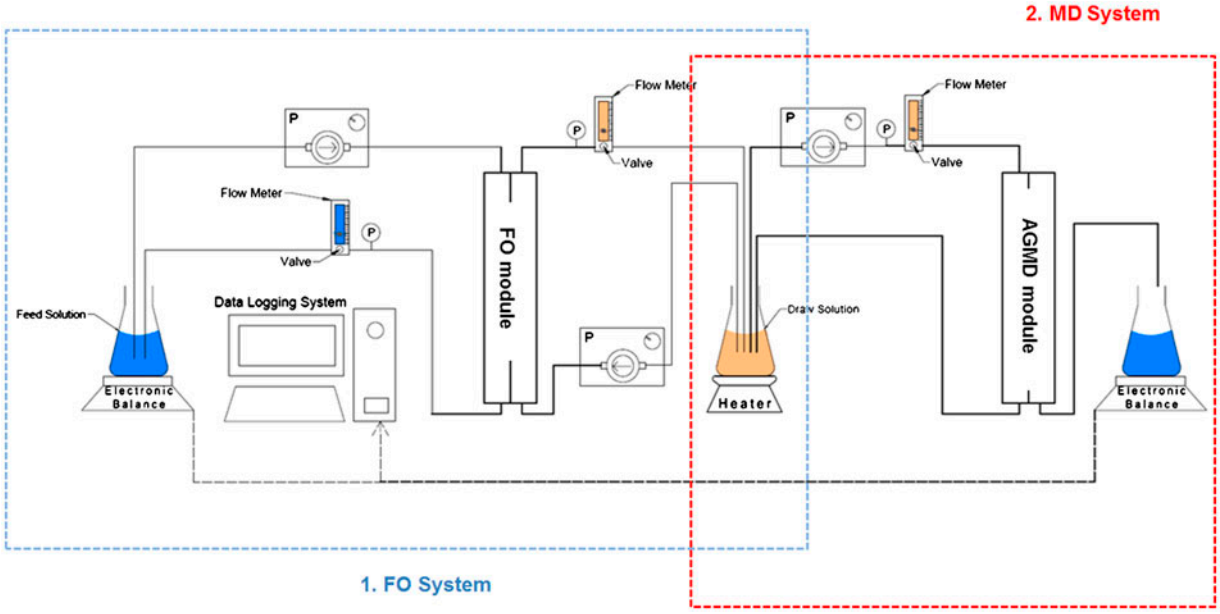

Fig. 3. Schematic diagram for experimental set-up for FO-MD hybrid system.

3.6. Test protocols: FO-MD hybrid system for investigation of feasibility of MD

The test conditions for FO-AGMD hybrid system are listed in Table 3. The draw solution of FO was the feed solution of MD. Accordingly, the temperature of the draw solution was 60°C. The cross flow rate for FO was 1 L/min while that for MD was 0.4 L/min. The membrane areas for FO and MD were same.

4. Result and discussion

4.1. FO and PAFO tests for treatment of shale gas wastewater

A pure water flux with using D.I. water as feed solution was measured and presented in Fig. 4. The pure water flux range from 11.5 to 14 L/m^2-h as the external pressure increases from 0 to 10 bar. The increases in flux were 17% at 5 bar and 22% at 10 bar, respectively.

The permeate water flux was also measured in FO and PAFO with using three kinds of synthetic shale gas wastewaters. As shown in Fig. 5(a), the permeate flux (11.5 L/m^2-h) for the low range wastewater was smaller than the pure water flux (6.9 L/m^2-h). This is attributed to the osmotic pressure in the synthetic wastewater. When the external pressure was applied, the permeate flux increased by 17% at 5 bar and 21% at 10 bar, respectively. Similar results were obtained using medium and high range wastewaters as the feed solution, as shown in Fig. 5(b) and (c). These results suggest that the application of external pressure is effective to obtain high flux in the osmotically driven membrane processes.

Table 2
Operating conditions: FO and PAFO tests for treatment of shale gas wastewater

Item		Condition
Operation type		FO, PAFO
Membrane		HTI's CTA FO membrane
Effective membrane area		30.6 cm^2
Cross flow velocity	Feed	1.3 L/min
	Draw	1 L/min
Solution	Feed	Low, medium, high range flowback water
	Draw	Sodium chloride 5 M
Applied pressure	Feed	0, 5, 10 bar(PAFO condition)
	Draw	0

Table 3
Operating conditions: FO-MD hybrid tests for investigation of feasibility of MD

Item		Condition	
Operation type		Air gap MD	Forward osmosis
Membrane		PVDF 0.22 μm	CTA FO membrane
Effective membrane area		12.22 cm^2	12.22 cm^2
Cross flow velocity	Feed	0.4 L/min	1 L/min
	Draw	–	1 L/min
Solution	Feed	Sodium chloride 2.5 M (FO draw solution)	Low range wastewater
	Draw	–	Sodium chloride 2.5 M
Temperature	Feed	60℃	50℃
	Draw	20℃	60℃

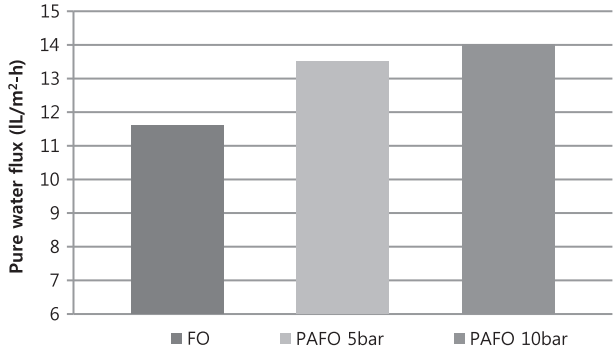

Fig. 4. Pure water flux for FO and PAFO.

The results in Figs. 4 and 5 were obtained in AL-FS mode. Experiments were also carried out in AL-DS mode. The FO flux values using different feed solutions are compared in Fig. 6. The pure water flux in AL-DS mode was much higher than that in AL-FS mode due to less severe internal concentration polarization. However, the permeate flux for the synthetic wastewaters in AL-DS mode was even smaller than that in AL-FS mode. Since the osmotic pressures of the synthetic wastewaters are substantially high, the internal concentration polarization is likely to be become severe. Moreover, membrane fouling could also occur.

Moreover, the application of external pressure was not possible in the AL-DS mode. In contrast to the AL-FS mode, the membrane was easily damaged even with 5 bar of applied pressure. This is attributed to the difference in the direction of pressure between AL-DS and AL-FS mode. In the AL-DS mode, the external pressure is applied to the support side of the membrane, which leads to the breakage of the thin active layer. However, in AL-DS mode, the pressure is applied to the feed side of the membrane and the support layer can provide enough mechanical strength to overcome the pressure. Thus, the active layer can be

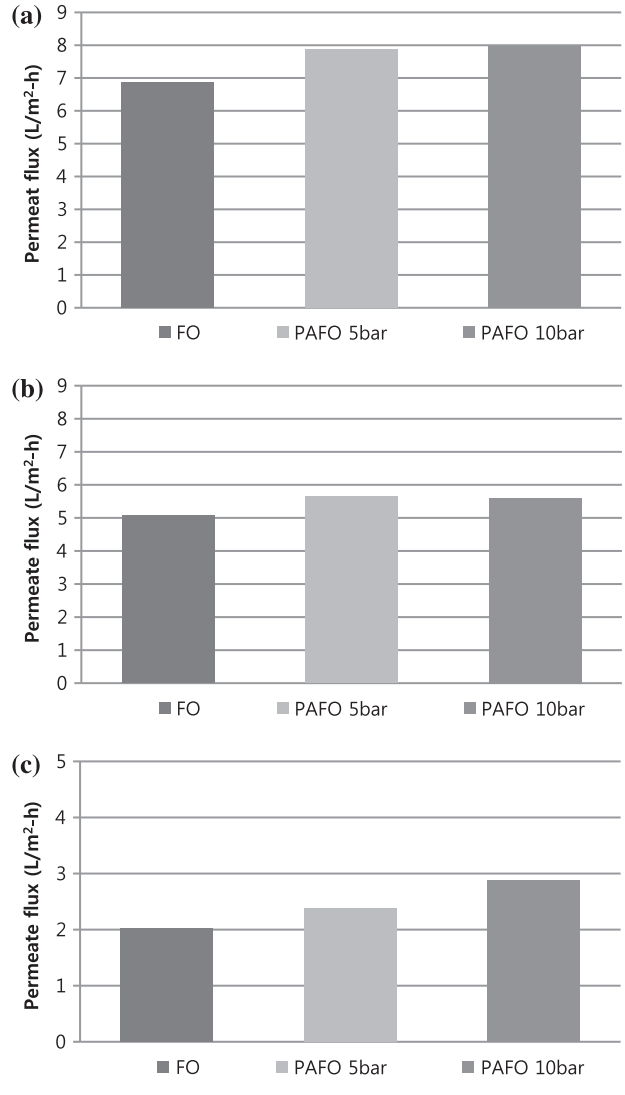

Fig. 5. Permeate flux for different synthetic feed solutions (a) low range, (b) medium range, and (c) high range synthetic shale gas wastewaters in FO and PAFO.

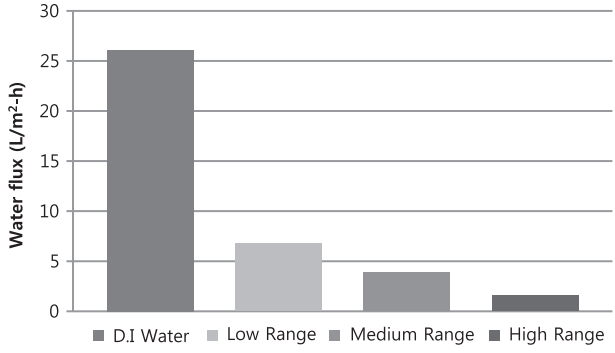

Fig. 6. Permeate flux of FO in AL-DS mode with sodium chloride solution of 5 M as draw solution.

intact under high pressure (up to 10 bar). These results suggest that AL-DS mode is not appropriate for PAFO operation.

4.2. Prediction of water flux in PAFO

The theoretical model was applied to predict the water flux in PAFO. RO experiments was carried out to determine the A (water permeability) and the B (solute permeability) values of the membrane. The operating pressure of RO was 35 bar. D.I water was used as the feed water to estimate A and 10% NaCl solutions was used to calculate B. It was found that the A and B values were 0.438 L/m^2-h-bar and 5.015×10^{-9} m/s, respectively. The model parameters K_F, and K_D were obtained from a separate set of experiments and used for this model prediction. Using Eq. (4), the water flux values for FO and PAFO using different feed solutions were calculated and shown in Fig. 7. The non-linear equation was solved using an iteration method. The model appears to be useful to estimate the flux in PAFO. As shown in Fig. 8, the R^2 value was 0.988.

As shown in Fig. 7, PAFO showed higher flux than FO by increasing driving force for water transport. However, the increased effective driving force in PAFO is less than the applied hydraulic pressure. According to the model calculations, the effective pressure increases by 2–2.7 L/m^2-h with an increase in hydraulic pressure by 10 bar. Accordingly, only 20–27% of the applied pressure is used to increase the flux. This is attributed to an increase in ICP with increasing driving force by the additional hydraulic pressure, which is explained in Eqs. (4) and (5).

4.3. FO-AGMD hybrid system for continuous treatment of shale gas wastewater

As the final step, the hybrid system consisting of FO and AGMD was investigated as a stand-alone treatment

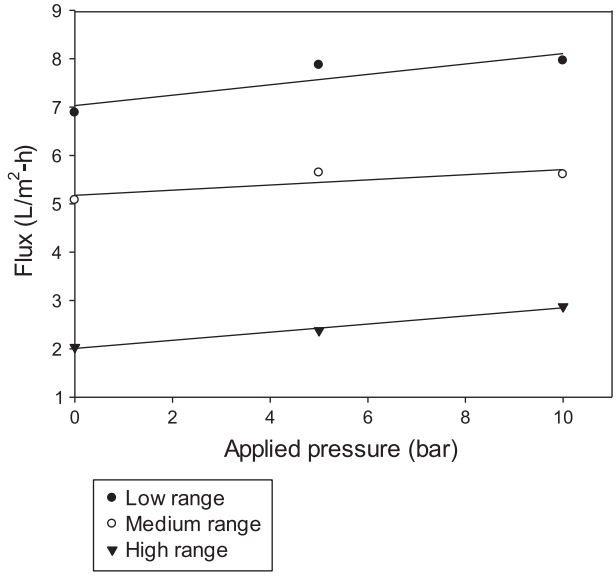

Fig. 7. Effect of external pressure on flux in PAFO.

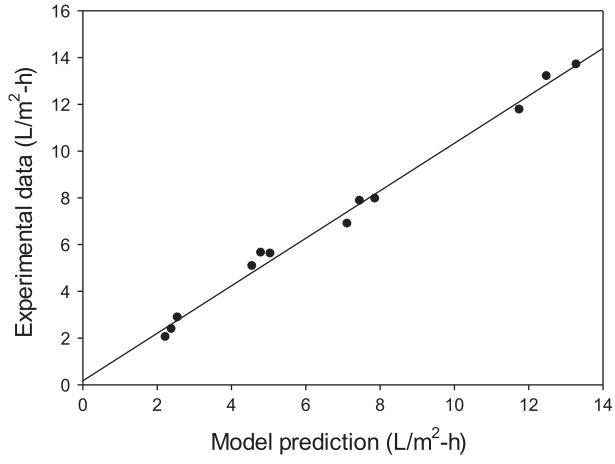

Fig. 8. Model prediction vs. experimental data.

system for shale gas wastewater. In this system, the draw solution was continuously re-concentrated by AGMD. Since AGMD is insensitive to the osmotic pressure of feed solution, it is efficient to recover draw solution. Fig. 9 illustrates the results of pure water flux of the FO-AGMD hybrid experiment. The temperature difference was 40˚C and the draw solution was 2.5 M NaCl solution. Despite the high concentration of the draw solution, the water flux through MD was stable. Moreover, the TDS of the product water was approximately 200 mg/L and salt reaction was over 99.99%. As shown in Fig. 9(a), the flux was instable for first few minutes, which is attributed to initial changes in the feed temperature. Except for the initial period, the FO flux is stable and continuously maintained.

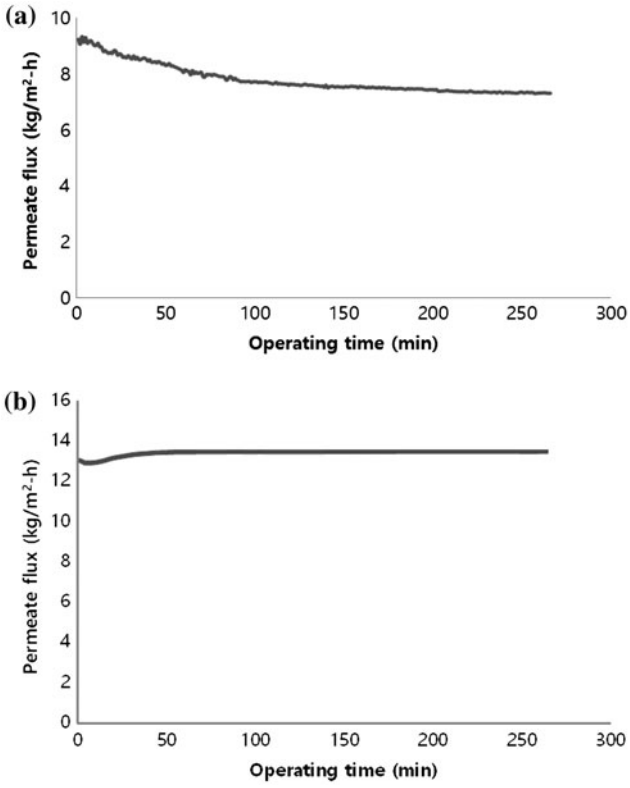

Fig. 9. Permeate flux of FO-MD hybrid system using low range synthetic shale gas wastewater and 2.5 M sodium chloride solution. The pure water flux of FO is (a) and AGMD is (b).

As shown in Fig. 9, the FO flux and the MD flux were not balanced. Since the experiments were carried out in a relatively short time (less than 5 h), the flux values were not precisely controlled. However, it seems that the effect of flux difference on the system behavior is not significant because of relatively small membrane areas (12.22 cm^2). Moreover, if the MD flux is higher than FO flux, the draw solution is concentrated, leading to increase in FO flux due to the high osmotic pressure. Accordingly, the FO-MD system may reach its steady-state condition without additional control. Nevertheless, it is practical to match the MD flux with FO flux for long-term operations. In this case, the feed temperature in MD may be adjusted to balance the FO flux.

5. Conclusions

In this study, the applicability of FO and PAFO as a treatment option for shale gas wastewater was investigated. The following conclusions were withdrawn:

(1) FO was applied for the treatment of shale gas wastewater. Using a draw solution of 5 M at 25˚C, the permeate flux ranges from 2 to 8 L/m^2-h, depending on the characteristics of the synthetic feed waters.
(2) As the external pressure up to 10 bar was applied, the flux increased up to 22%. A theoretical model was applied to predict the effect of pressure on flux in PAFO operations. The Model matches the experimental data well.
(3) A hybrid system consisting of FO and AGMD was developed and applied to treat synthetic wastewater. The operation was stable and the final water TDS was less than 200 mg/L. A PAFO-AGMD system will be also examined in our future works.

Acknowledgments

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References

[1] J.D. Arthur, B. Bohm, M. Layne, Hydraulic fracturing considerations for natural gas wells of the Marcellus Shale. in: Groundwater Protection Council Annual Forum, Cincinnati, OH, 2008.
[2] A. Alkhudhiri, N. Darwish, N. Hilal, Produced water treatment: Application of air gap membrane distillation, Desalination 309 (2013) 46–51.
[3] K.B. Gregory, R.D. Vidic, D.A. Dzombak, Water management challenges associated with the production of shale gas by hydraulic fracturing, Elements 7(3) (2011) 181–186.
[4] K.L. Hickenbottom, N.T. Hancock, N.R. Hutchings, E.W. Appleton, E.G. Beaudry, P. Xu, T.Y. Cath, Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations, Desalination 312 (2012) 60–66.
[5] T.Y. Cath, S. Gormly, E.G. Beaudry, M.T. Flynn, V.D. Adams, A.E. Childress, Membrane contactor processes for wastewater reclamation in space, J. Membr. Sci. 257(1–2) (2005) 85–98.
[6] R.L. McGinnis, M. Elimelech, Energy requirements of ammonia–carbon dioxide forward osmosis desalination, Desalination 207(1–3) (2007) 370–382.
[7] R. Semiat, Energy issues in desalination processes, Environ. Sci. Technol. 42(22) (2008) 8193–8201.
[8] S. Liang, C. Liu, L. Song, Two-step optimization of pressure and recovery of reverse osmosis desalination process, Environ. Sci. Technol. 43(9) (2009) 3272–3277.
[9] J.M. Arnal, M. Sancho, I. Iborra, J.M. Gozálvez, A. Santafé, J. Lora, Concentration of brines from RO desalination plants by natural evaporation, Desalination 182(1-3) (2005) 435–439.

[10] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia—Carbon dioxide forward (direct) osmosis desalination process, Desalination 174(1) (2005) 1–11.
[11] G. Blandin, A.R. Verliefde, C.Y. Tang, A.E. Childress, P. Le-Clech, Validation of assisted forward osmosis (AFO) process: Impact of hydraulic pressure, J. Membr. Sci. 447 (2013) 1–11.
[12] X.-M. Li, B. Zhao, Z. Wang, M. Xie, J. Song, L.D. Nghiem, T. He, C. Yang, C. Li, G. Chen, Water reclamation from shale gas drilling flow-back fluid using a novel forward osmosis-vacuum membrane distillation hybrid system, Water Sci. Technol. 69(5) (2014) 1036–1044.
[13] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, A forward osmosis-membrane distillation hybrid process for direct sewer mining: System performance and limitations, Environ. Sci. Technol. 47(23) (2013) 13486–13493.
[14] J.R. McCutcheon, M. Elimelech, Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis, J. Membr. Sci. 284(1–2) (2006) 237–247.
[15] S. Loeb, L. Titelman, E. Korngold, J. Freiman, Effect of porous support fabric on osmosis through a Loeb-Sourirajan type asymmetric membrane, J. Membr. Sci. 129(2) (1997) 243–249.
[16] HTI, Military/X Pack, 2005. Available from: <http://www.hydrationtech.com>.