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Xue-Mei Li

Chinese Academy of Sciences

Baolong Zhao

Chinese Academy of Sciences

Zhongwei Wang

Chinese Academy of Sciences, zw702@uowmail.edu.au

Ming Xie

University of Wollongong, mx504@uowmail.edu.au

Jianfeng Song

Chinese Academy of Sciences

See next page for additional authors

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Water reclamation from shale gas drilling flow-back fluid using a novel forward osmosis-vacuum membrane distillation hybrid system

Abstract

This study examined the performance of a novel hybrid system of forward osmosis (FO) combined with vacuum membrane distillation (VMD) for reclaiming water from shale gas drilling flow-back fluid (SGDF). In the hybrid FO-VMD system, water permeated through the FO membrane into a draw solution reservoir, and the VMD process was used for draw solute recovery and clean water production. Using a SGDF sample obtained from a drilling site in China, the hybrid system could achieve almost 90% water recovery. Quality of the reclaimed water was comparable to that of bottled water. In the hybrid FO-VMD system, FO functions as a pre-treatment step to remove most contaminants and constituents that may foul or scale the membrane distillation (MD) membrane, whereas MD produces high quality water. It is envisioned that the FO-VMD system can recover high quality water not

Keywords

distillation, back, flow, fluid, membrane, novel, water, reclamation, shale, forward, gas, drilling, osmosis, system, hybrid, vacuum

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Authors

Xue-Mei Li, Baolong Zhao, Zhongwei Wang, Ming Xie, Jianfeng Song, Long Nghiem, Tao He, Chi Yang, Chunxia Li, and Ghang Chen

**Water reclamation from shale gas drilling flow-back
fluid using a novel forward osmosis (FO) – vacuum
membrane distillation (VMD) hybrid system**

Water Science and Technology

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Xue-Mei Li^{1,*}, Baolong Zhao¹, Zhouwei Wang¹, Ming Xie², Jianfeng Song¹, Long D.
Nghiem², Tao He^{1,*}, Chi Yang¹, Chunxia Li¹, and Gang Chen¹

¹ Membrane Materials and Separation Technology, Shanghai Advanced Research
Institute, Chinese Academy of Sciences, Shanghai, China

² Strategic Water Infrastructure Laboratory, School of Civil, Mining and Environmental
Engineering, University of Wollongong, Wollongong, NSW 2522, Australia

* Corresponding authors: Xue-Mei Li(lixm@sari.ac.cn), Tao He (het@sari.ac.cn); Ph +862120325162

Abstract

This study examined the performance of a novel hybrid forward osmosis (FO) – vacuum membrane distillation (VMD) system for reclaiming water from shale gas drilling flow-back fluid (SGDF). In the hybrid FO-VMD system, water permeated through the FO membrane into a draw solution reservoir and the VMD process was used for draw solute recovery and clean water production. Using SGDF sample obtained from a drilling site in China, the hybrid system could achieve almost 90% water recovery. **Quality** of the **reclaimed** water is comparable to that of bottled water. In the hybrid FO-VMD system, FO functions as a **pre-treatment** step to remove most contaminants and **constituents** that may foul or scale the MD membrane, whereas MD produces high quality water. It is envisioned that the FO-VMD system can recover high quality water not only from SGDF but also other wastewaters with high salinity and complex compositions.

Key words : water reclamation; water reuse; forward osmosis; shale gas; drilling and fracturing fluid; membrane distillation.

1. Introduction

Hydraulic fracturing of oil and gas wells has attracted significant attention for contributing toward energy security as well as potential environmental impact (Shaffer *et al.* 2013). Hydraulic fracturing is a water intensive process (Dahm *et al.* 2011) and can produce a large volume of saline wastewater known as shale gas drilling flow-back fluid (SGDF) which can account for 30 to 70% of the original fracturing fluid volume. SGDF contains various dissolved constituents including organic matters and inorganic salts. The treatment of the SGDF is a major challenge for the oil and gas industry because of the stringent regulations and discharge limits (Hickenbottom *et al.* 2012).

Several techniques can be used for the treatment and disposal of SGDF including deep well injection, thermal evaporation–distillation, and reverse osmosis (Xu & Drewes 2006; Xu *et al.* 2008). Deep well injection permanently eliminates the water from water cycle, while the treatment cost associated with the other techniques are high due to high energy consumption or fouling/scaling. Therefore, the development of novel treatment processes to manage SGDF is essential for the oil and gas industry. Recently, forward osmosis (FO) technology has been pursued as an alternative for the treatment of SGDF. FO is an osmotically driven membrane process. During the FO process, water diffuses spontaneously from a stream of low osmotic pressure (the feed solution) to a hypertonic (draw) solution having a very high osmotic pressure through a semipermeable membrane (Cath *et al.* 2006). Hickenbottom *et al.* (2012) successfully demonstrated an osmotic dilution process for the treatment of drilling mud with a water recovery of up to 80%, where the diluted draw solution was utilized directly as the

fracturing fluid reducing the fresh water demand in the hydraulic fracturing process. Osmotic dilution has shown considerable advantages in minimal energy input without the recovery of draw solute.

To reclaim water from SGDF, McGinnis et al (2013) has constructed an FO membrane brine concentrator (FO-MBC) pilot system using NH_3/CO_2 as the draw solution. In their FO-MBC system, clean water was recovered by heat treatment of the draw solution, which showed much less energy demand than a conventional evaporator. We have reported a concept of FO integrated membrane distillation (MD) process for water recovery from synthetic high salinity water with TDS of 10 wt%, where the FO process concentrates the feed water and MD claimed fresh water from the diluted draw solution (He 2012). The advantages of FO, especially fouling resistant, rejection towards organic matters, and the capability of MD to treatment of high TDS are shown. Moreover, because the feed to the MD process is pre-treated by FO, membrane fouling and scaling can be managed, and thus the integrated process is promising in the treatment of wastewaters with high salinity and fouling propensity. Although the integrated FO-MD processes have been demonstrated for treatment of various forms of wastewater (Cath *et al.* 2005a; Cath *et al.* 2005c; Yen *et al.* 2010; Wang *et al.* 2011; Ge *et al.* 2012), to date, their application for treating SGDF has not been reported.

Currently, there is a lack technical guideline and regulations in China in terms of SGDF management (Tong *et al.* 2013). More concerning, most shale gas drilling sites are located in densely populated southwest China (e.g. Sichuan, Chongqing, and Guizhou) where water crisis could be further exacerbated (Chang *et al.* 2012).

In this paper, a systematic study on the hybrid process for water reclamation is reported using SGDF from a mining site at the southwest China. Commercially available FO membranes were used in the FO process. The FO process was optimized with respect to the selection of draw solutes and operation conditions. A vacuum membrane distillation MD process was applied for draw solution recovery. The product water quality and the feed wastewater quality were analysed to assess the feasibility of the integrated process for the treatment of highly complicated feed wastewater streams.

2. Materials and Methods

2.1 Membranes and Chemicals

An asymmetric, cellulose triacetate membrane from Hydration Technology Innovations (Albany, OR) was used for the FO process. The FO membrane, embedded in a polyester mesh for mechanical support, has a dense, moderately hydrophilic cellulose triacetate active layer. More details on the FO membrane are provided elsewhere (Cath et al. 2006; McCutcheon & Elimelech 2008). A CF₄-plasma modified polyvinylidene fluoride (PVDF, Millipore 0.22 μm GVHP) microporous membrane was used for the VMD process. SGDF sample was collected from a drilling field in southwest China. Analytical grade sodium chloride (NaCl, CAS No.: 7647-14-5), potassium chloride (KCl, CAS No.: 7447-40-7) and magnesium chloride (MgCl₂, CAS No.: 7791-18-6) acquired from Sinopharm Chemical Reagent (Shanghai, China) were used as draw solutes in the FO process.

2.2 Pre-treatment of SGDF

Pre-treatment of SGDF was conducted to remove suspended particles, including coagulation and ultrafiltration. Two types of coagulants ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) were assessed at various concentrations and sedimentation time (mixing and sediment). SGDF after coagulation was ultra-filtered by a polyethersulfone hollow fiber membrane with molecular weight cut-off of 70 kDa (Altrateck, Nanjing, China) (Song *et al.* 2013). After the pre-treatment, the SGDF was further treated by an FO-VMD hybrid system.

2.3 FO-VMD hybrid system

A lab-scale flat-sheet cross-flow FO-VMD setup was employed to treat the SGDF after coagulation and ultrafiltration (Figure 1). The length, width and depth of the FO membrane cell were 100, 30 and 4 mm, respectively. Two variable speed gear pumps were used to circulate the feed and draw solutions concurrently. Flow rates of the feed and draw solutions were monitored with rotameters and kept constant at 0.6 L/min. Temperatures of both feed and draw solutions were controlled using thermostatic bath.

Water flux, J_w , was determined as the weight change (ΔW) of the feed solution at a certain time interval (Δt) at unit membrane area (A).

$$J_w = \frac{\Delta W}{A \Delta t} \quad (1)$$

Reverse draw solute flux, J_s , was determined using mass balance calculation:

$$J_s = \frac{(C_t V_t - C_0 V_0)}{A t} \quad (2)$$

where C_0 and C_t are the concentrations of the draw solute in the feed at time 0 and t , respectively; V_0 and V_t are the volumes of the feed at time 0 and t , respectively; A is the membrane area, and t is the operating time of the FO experiment.

Prior to the operation of the FO-VMD hybrid system, this FO unit was employed to assess the treatment efficiency of SGDF by varying key parameters, including type and concentration of draw solution, temperature and cross-flow velocity of feed and draw solution, and membrane orientation. [Each type of draw solution was used separately to evaluate and compare the process efficiency by the FO unit.](#)

For VMD unit, dimensions of the VMD membrane cell were 100 mm in length, 30 mm in width and 4 mm in depth, respectively. A diamond shape spacer was used to prevent the deformation of the CF_4 -modified PVDF membrane (Wei *et al.* 2012). The vacuum pressure for distillate side was - 40 kPa and sweeping air was used at a flow rate of 6.0 L/min to facilitate water condensation at the distillate side. To reduce the energy consumption for heating draw solution (3 L in the FO unit), an overflow design was used to connect the FO and VMD units in this hybrid system. Specifically, only a small amount of draw solution (500 mL) was heated and concentrated in the VMD unit, and then the concentrated draw solution was overflow to the draw solution tank in the FO unit. Basic performance of the FO-VMD hybrid system, including water permeate flux, temperature, vacuum pressure and electrical conductivity of the product water, was recorded by a data logger.

[Figure 1]

2.4 Water quality analysis

Basic water parameters (including pH, electric conductivity, turbidity, total hardness, chemical oxygen demand (COD) and ammonia) of the SGDF sample before and after pre-treatment and product water were tested following standard methods. Ions concentrations were determined by an Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) (ICPE-9000, Shimadzu, Kyoto) and an Ion Chromatography (LC20AT, Shimadzu, Kyoto), respectively. The ICP-AES utilises the wavelength and intensity of electromagnetic emission to determine the concentration of each target element. Calibration was conducted prior to each batch of analysis. The linear regression coefficients (R^2) for all calibration curves were greater than 0.99. Osmotic pressure of varying draw solutions were analysed by an osmometer (Osmomat 030, Gonotec GmbH, Germany) using freezing point method.

3 Results and Discussion

3.1 Pre-treatment of SGDF

Systematic analysis showed that SGDF was highly saline with total dissolve solid (TDS) of 6700 mg/L. NaCl was the dominant inorganic salt with concentration of 2072 mg/L in the SGDF sample. The organic matter was also significant with COD of 259 mg/L.

Pre-treatment using coagulation and ultrafiltration was effective to remove colour, suspended particles and some soluble contaminants, thereby improving feed water

quality before FO-VMD treatment (Table 1). Specifically, the initial SGDF was yellowish and turbid, and after pre-treatment with coagulation (80 mg/LFeCl₃·6H₂O and 30 min sedimentation) and ultrafiltration, the pre-treated SGDF became clear and transparent. TDS removal by coagulation and UF pre-treatment was negligible as expected. However, COD removal was 25% and the removal of Si, Sr, and Ca was in the range of 20 to 40%.

[Table 1]

3.2 SGDF treatment efficiency by FO

3.2.1 Types of Draw solution

Water fluxes induced by KCl, NaCl and MgCl₂ were compared in FO mode (i.e., membrane active layer contacts feed solution). [To minimise the impact on the permeate flux caused by the dilution of the draw solution, the operating time for each experiment was 30 min \(corresponding to a cumulative permeate volume of 80 mL\).](#) To produce the same osmotic pressure of 180 atm, the required concentrations of KCl, NaCl and MgCl₂ are 3, 3.26, and 1.75 M, respectively (Figure 2a). However, at the same osmotic pressure of 180 atm, the water flux in FO mode was in the order of KCl>NaCl>MgCl₂ (Figure 2b). This order of water flux is mainly driven by the effective diffusion coefficient of the draw solutes when the osmotic pressures of three draw solutions were the same (Lay *et al.* 2012). In fact, diffusion coefficients of three draw solutes were in the same order as water fluxes, namely, KCl>NaCl>MgCl₂ (Tang & Ng 2008; Xu *et al.* 2010; Lay *et al.* 2012).

Reverse salt flux selectivity (*RSFS*), J_w/J_s , was determined by properties of membrane active layer (water and draw solute permeabilities) and thermodynamic properties of draw solutions (osmotic pressure) (Phillip *et al.* 2010; Xie *et al.* 2013c). The *RSFS* can be considered as the volume of water produced per the moles (or mass) of draw solute lost, which is an important parameter to evaluate the draw solution efficiency in an FO process. The *RSFS* of three draw solutions were in the order of $\text{MgCl}_2 > \text{NaCl} > \text{KCl}$ (Figure 2b), which was consistent with their diffusion coefficients. This is because under the same draw solution osmotic pressure (i.e., 180 atm), the *RSFS* is related to the membrane solute permeability or solute diffusivity (Phillip *et al.* 2010; Xie *et al.* 2013c).

[Figure 2]

3.2.2 Draw solution concentration and key operating conditions

Water flux increased significantly as the feed and draw solution temperature increased from 15 to 45 °C (Figure 3a). This thermally-induced increase in water flux was largely driven by the increase in water and KCl diffusivities at an elevated temperature (Phuntsho *et al.* 2012; Xie *et al.* 2013c).

Water flux increased as the draw solution concentration increased, as expected (Figure 3b). However, it is noteworthy that increase in water flux was non-linear when the draw KCl solution concentration was beyond 2.5 M. This water flux behaviour is mainly ascribed to dilutive internal concentration polarization where the draw solution in porous support layer was diluted by the permeate, thereby reducing the effective

osmotic pressure difference across the membrane (McCutcheon & Elimelech 2006; Xie *et al.* 2013c).

There was negligible difference in water flux as the cross-flow rate increased from 0.5 to 2 L/min (Figure 3c). Despite the increase in Reynolds number from 578 to 2312, water flux was largely unchanged, indicating that the external concentration polarization was insignificant (McCutcheon & Elimelech 2007). This result was consistent with a previous study by Kim *et al.* (2012).

[Figure 3]

3.2.3 Membrane orientation

FO membrane could be operated in either FO mode (i.e., active layer faced feed solution) or PRO mode (i.e., active layer faced draw solution). Water flux behaviour was significantly different under two membrane orientations (Figure 4). Water flux was stable at 22 L/m²h in the FO mode; whereas water flux decline gradually from 30 to 12 L/m²h in the PRO mode. Water flux in the PRO mode was higher than that in the FO mode at the initial stage. Specifically, the dilutive internal concentration polarization in the FO mode is more pronounced than concentrative internal concentration polarization in the PRO mode, which substantially reduces the effective osmotic driving force for water flux (Xie *et al.* 2012). In addition, the gradual decline in water flux in the PRO mode could be attributed to the build-up of membrane fouling in the porous support layer (Tang *et al.* 2010; Liu *et al.* 2011; Zhao & Zou 2011; Zhao *et al.* 2011; Jin *et al.* 2012). In the PRO mode, foulants in the SGDF were trapped in the porous support layer

and led to severe internal concentration polarization, thereby substantially decreasing water flux. Indeed, a brownish fouling layer was observed at the conclusion of the PRO experiment. By contrast, in the FO mode, membrane fouling was insignificant due to the absence of trans-membrane hydraulic pressure (Xie *et al.* 2013b), thereby leading to a stable water flux. These results highlighted that FO mode performed better than PRO mode in treating feed solution with high fouling propensity.

In summary, SGDF treatment efficiency by the FO process was better when the FO mode was used. Thus, the FO mode was used in the FO-VMD hybrid system for SGDF treatment. In addition, draw solution was 3 M KCl, cross-flow rates and temperatures for both feed and draw solutions were 0.5 L/min and 30 °C, respectively.

[Figure 4]

3.3 SGDF treatment efficiency by FO-VMD hybrid process

The FO-VMD hybrid process was employed to reclaim freshwater from SGDF. In this hybrid system, freshwater in the pre-treated SGDF was first extracted into 3 M KCl draw solution by FO process and then was produced by VMD process. At the same time, the diluted draw solution was concentrated and re-circulated back to the FO process. Comparing to similar design in previous studies (Cath *et al.* 2005b; Altaee *et al.* 2013), the unique design in the FO-VMD was that a draw solution over-flow connection allowed for only heating a small volume of the draw solution in VMD process, thereby substantially reducing the energy consumption and carbon footprint of the FO-VMD system.

Water flux in the FO process was stable at 18 L/m²h during 15 hours of operation, reaching water recovery of 88%. It is noteworthy that water flux was fully restored to the initial one after draw KCl solution was replenished after 4.25 hour of operation (Figure 5a). This suggests that membrane fouling by SGDF was insignificant during the FO process and the decrease in water flux could be largely attributed to the concentration of feed SGDF solution and the dilution of draw KCl solution.

Different approaches were applied to enhance the water flux in VMD process, including sweeping air, elevated feed solution temperature and enhanced vacuum pressure (Figure 5b). Unfavourable water condensation happened in the VMD membrane module and distillation side tubings (designate as “a” in Figure 5b), which resulted in unstable water flux in VMD process. To enhance the water flux, a sweeping air was used in the distillate side at a flow rate of 6 L/min (designate as “b” in Figure 5b). The sweeping air significantly enhanced the water flux from 12 to 16 L/m²h. In addition, elevated feed solution temperature from 59 to 65 °C led to a substantial increase in water flux from 16 to 24 L/m²h (designate as “c” in Figure 5b). Furthermore, water flux increased from 16 to 19 L/m²h when the vacuum pressure increased from -40 to -58 kPa (designate as “d” in Figure 5b).

[Figure 5]

Product water quality from FO-VMD hybrid process was indicated by its gradual conductivity decline from 7.5 to 3 μS/cm (Figure 5b). More importantly, there was negligible difference between product water and retail bottle drinking water in terms of basic water quality parameters and inorganic substances (Table 1). [Such high product](#)

water quality by the FO-VMD process was largely attributed to near complete rejection of non-volatile compounds by the VMD process, despite variation in feed SGDF water quality (e.g., pH (Xie *et al.* 2012), TDS, temperature (Xie *et al.* 2013d)) affecting water flux and contaminant rejection of the FO process. In addition, it was noteworthy that the FO process achieved significant rejection of inorganic contaminants and sparingly soluble inorganic salts (Table 1). Particularly, boron rejection was 78% by the FO process, which was similar to previous studies (Jin *et al.* 2011; Kim *et al.* 2012). Sparingly soluble CaSO_4 was completely rejected whereas rejection of silica was only 33%. Poorly rejected contaminants (e.g., silica) by the FO process could be accumulated in the draw solution because the VMD process offers near complete rejection for non-volatile compounds. Such detrimental accumulation could hamper the sustainability of the FO-VMD system in long-term operation (Xie *et al.* 2013a). In addition, an appropriate SGDF concentrate management should be considered because the conductivity and TDS of the SGDF concentrate increased 7 and 4.2 times, respectively, after FO-VMD hybrid process (Table 1). More importantly, the Langelier Saturation Index (*LSI*) of the concentrated SGDF after FO-VMD system was 0.53, which indicated the tendency of scaling formation.

High water recovery and exceptional product water quality reported here have significant implications in the SGDF-related wastewater management. This near zero-liquid-discharge FO-VMD hybrid system could effectively reclaim freshwater from SGDF, which could be beneficial to reservoir augmentation and agricultural or industrial applications.

4 Conclusions

Results reported here demonstrated the feasibility of a novel hybrid forward osmosis (FO) – vacuum membrane distillation (VMD) system for water reclamation from shale gas drilling flow-back fluid (SGDF). Key operating parameters were optimized in the FO process. KCl was identified as a suitable draw solution that can offer a high water flux and an acceptable reverse solute flux. Water recovery of up to 90% was achieved from real SGDF using a laboratory scale hybrid FO-VMD system. A notable advantage of this hybrid system was that the partial draw solution over-flow that could substantially reduce the energy consumption in VMD. Quality of the product water by the FO-VMD process was comparable to that of bottled water.

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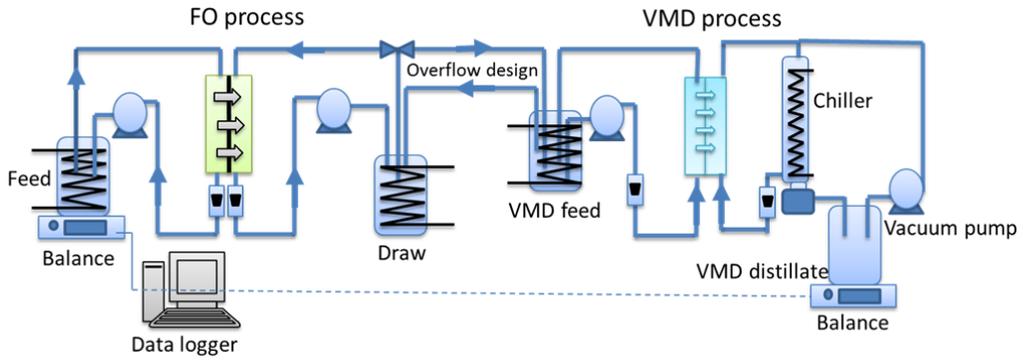
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412 **Tables and Figures**

413 **Table 1:** Water characteristics of raw SGDF, SGDF after different treatment steps, and bottled water from Shanghai (as a reference).

Items	Raw SGDF	Pre-treated SGDF	SGDF concentrate after FO-VMD	Draw solution after FO-VMD	Product water from FO-VMD	Bottled water (as a reference)
Conductivity(μ S/cm)	11290	11300	74400	AUL	5	43.6
Turbidity(NTU)	135	0.18	NA	NA	0.07	0.09
pH	7.4	7.40	8.24	7.89	7.38	7.88
Total hardness as CaCO ₃ (mg/L)	283	260	541	NA	NA	NA
COD (mg/L)	358	259.0	1794.0	NA	0.9	1.1
TDS (mg/L)	6906	6490	27807	NA	NA	NA
B (mg/L)	16.9	15	27	1.1	ND	0.02
Ca (mg/L)	140	102	271	1	ND	3.34
K (mg/L)	393	381	5180	90851	0.50	3.74
Mg (mg/L)	18	24.0	30.9	NA	ND	0.02
Na (mg/L)	2109	2105	4540	92	0.12	0.3
Sr (mg/L)	4.9	3.1	12.4	ND	ND	ND
Si (mg/L)	19.2	15	36.5	10	ND	ND
CO ₃ ²⁻ (mg/L)	149	96	308	9.9	ND	NA
Cl ⁻ (mg/L)	4202	3999	17632.48	91612.7	2.2	10.2
SO ₄ ²⁻ (mg/L)	3.2	3.0	9.1	< 1	<1	NA

414 Notes: ND - not detected; NA - not applicable; AUL: Above Upper Limit.



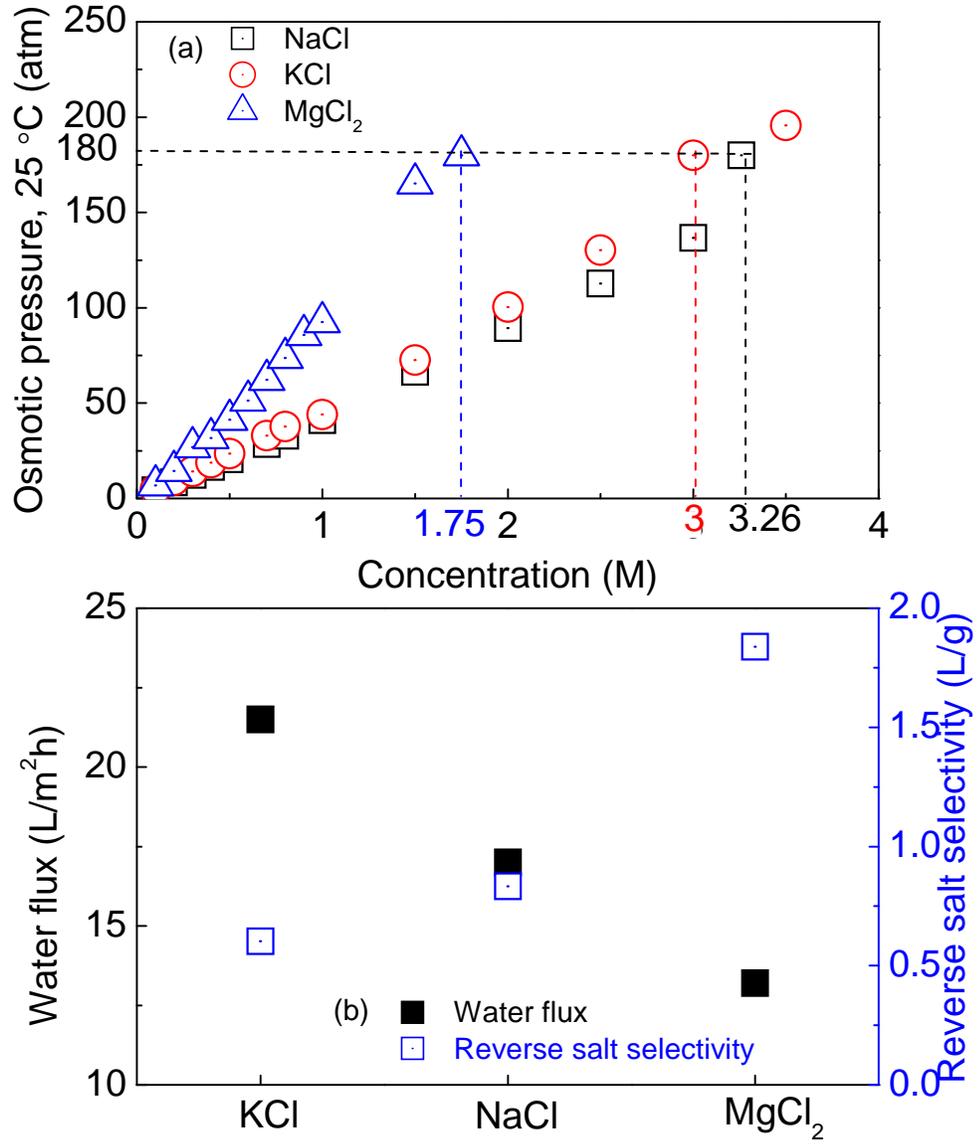
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417 **Figure 1:** (A) schematic diagram and (B) photo of the forward osmosis (FO) – vacuum
 418 membranedistillation (VMD) hybrid system.

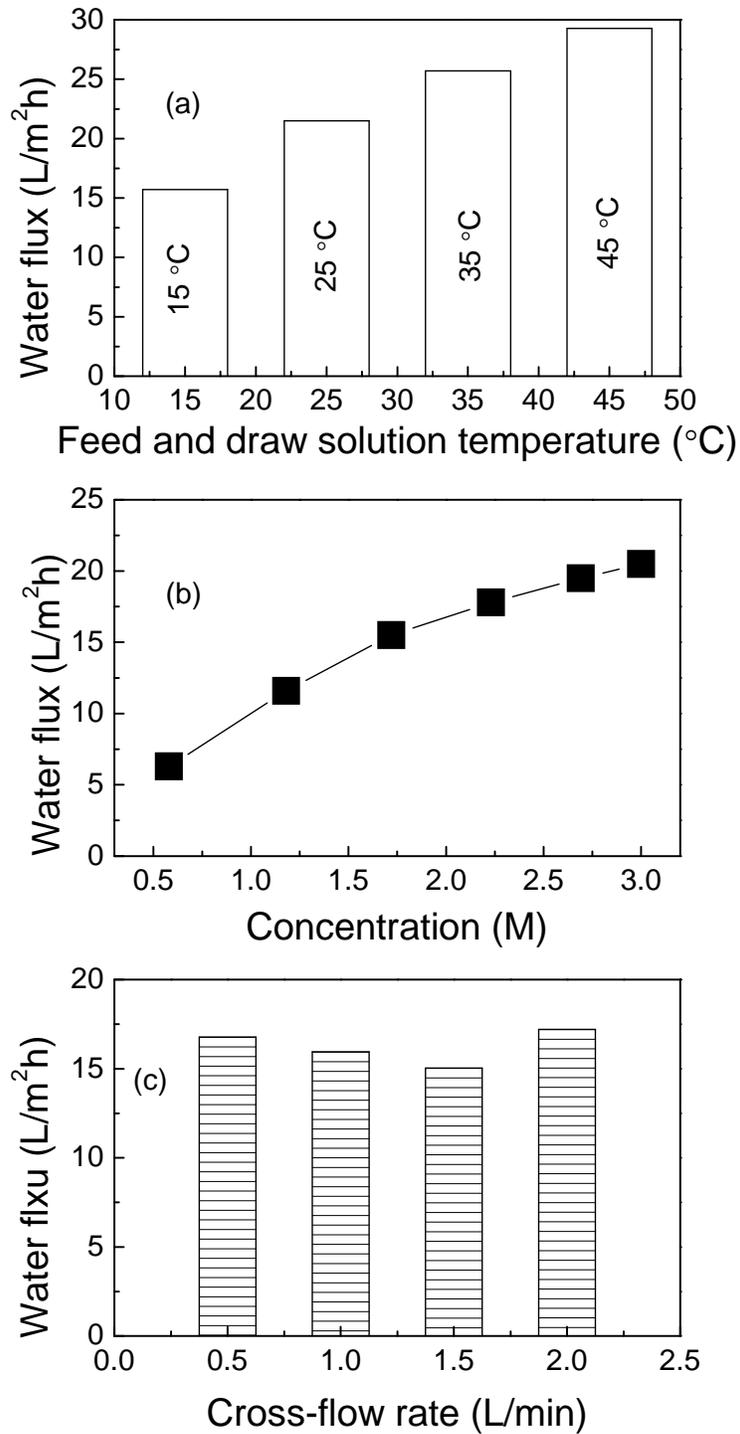
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421 **Figure 2:** Comparison of (a)osmotic pressures,(b) water fluxes and reverse salt

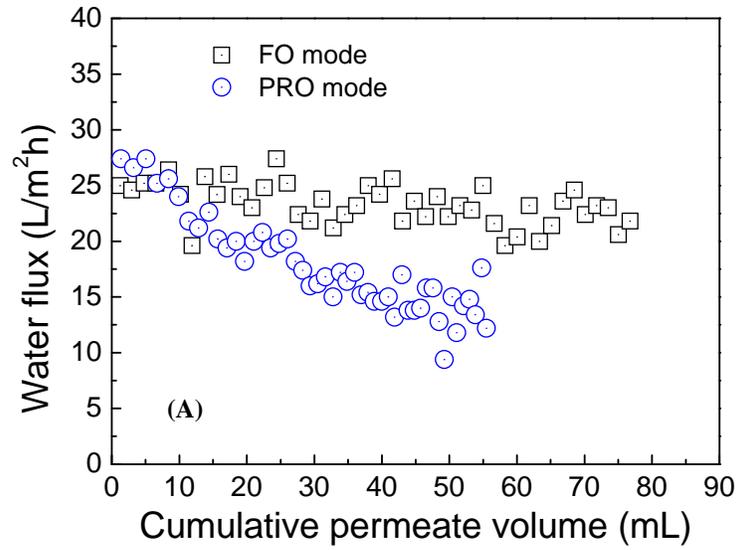
422 selectivitiesusing various concentrations and types of draw solutions.



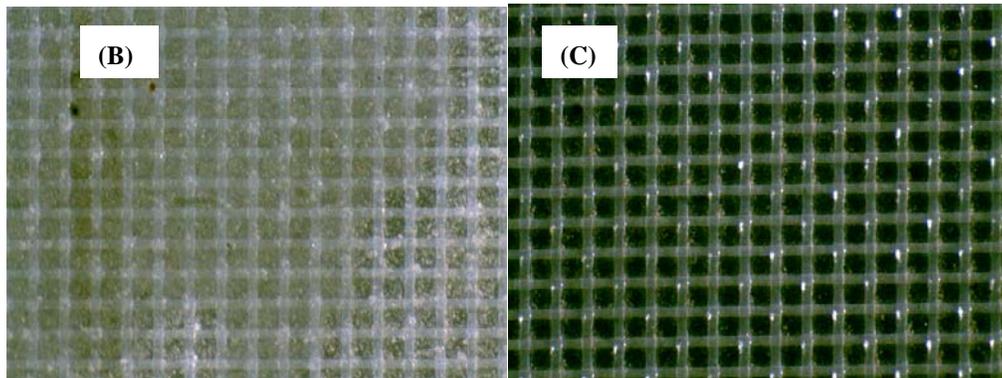
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424 **Figure 3:** Effects of (a) feed and draw solution temperatures, (b) draw solution

425 concentration, and (c) cross-flow rates on water flux.

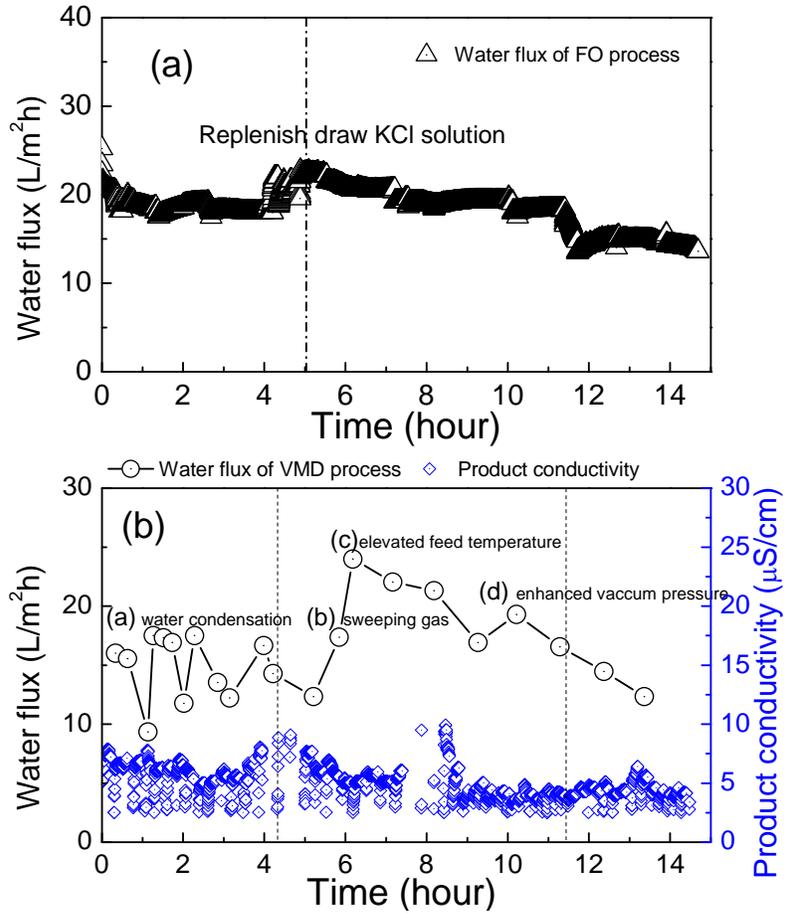


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427

428 **Figure 4:** (A) Water fluxes in FO (active layer facing the feed) and PRO modes (active
 429 layer facing the draw solution) and (B) microscopic observation of foulant deposited on
 430 membrane support layer (compared with the (C) clean membrane).



431

432 **Figure 5:** Bench scale hybrid FO-VMD in treating the shale gas wastewater: (a) water
 433 flux in the FO process; (b) water flux in the VMD process and permeate conductivity of
 434 product water. The initial feed volume was 1 L, and the cumulative permeate volume
 435 was 880 mL after 15-hour treatment by the FO-VMD system, reaching water recovery
 436 of 88%.