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Abstract

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**Evaluation of fertilizer-drawn forward osmosis for coal seam gas reverse osmosis
brine treatment and sustainable agricultural reuse**

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Abstract

The fertilizer-drawn forward osmosis (FDFO) was investigated for treating coal seam gas (CSG) produced water to generate nutrient rich solution for irrigation. Its performance was evaluated and compared with reverse osmosis (RO) in terms of specific energy consumption (SEC) and nutrient concentrations in the final product water. The RO-FDFO hybrid process was developed to further improve FDFO. The results showed that FDFO has the lowest SEC followed by the RO-FDFO and RO processes. The final nutrient concentration simulation demonstrated that the RO-FDFO hybrid process has lower final concentration, higher maximum recovery and lower nutrient loss than the stand alone FDFO process. Therefore, it was suggested that the RO-FDFO is the most effective treatment option for CSG RO brine as well as favorable nutrient supply. Lastly, membrane fouling mechanism was examined in CSG RO brine treatment by FDFO, and the strategies for controlling fouling were critically evaluated. KNO_3 exhibited the highest flux decline corresponding to the highest reverse salt flux, while the most severe membrane scaling was observed with calcium nitrate, primarily due to the reverse transport of calcium ions. To control membrane fouling in FDFO process, both physical flushing and chemical cleaning were examined. Membrane cleaning with citric acid of 5% resulted in a complete flux recovery.

Keywords: CSG produced water, Fertilizer-drawn forward osmosis, Specific energy consumption, FDFO simulation, Membrane cleaning.

45 **Nomenclature**

46

47 A Water permeability coefficient

48 B Salt permeability coefficient

49 $C_{D,i}$ Maximum DS concentration

50 $C_{D,f}$ Final DS concentration having equal osmotic pressure with the initial

51 FS concentration

52 $C_{nut,f}$ Nutrient concentration in the final produced water

53 J_s Reverse salt flux

54 J_w Water flux

55 $Loss_{Draw}$ Draw solute loss at the maximum recovery rate in FDFO

56 M_w Molecular weight of DS

57 n Number of species

58 P_D Draw pressure (bar)

59 P_F Feed pressure (bar)

60 Q_D Draw flow rate (m³/h)

61 Q_F Feed flow rate (m³/h)

62 $Q_{P,FDFO}$ Permeate flow rate (m³/h) in FDFO

63 $Q_{P,RO}$ Permeate flow rate (m³/h) in RO

64 $Q_{P,total}$ Total permeate flow rate (m³/h)

65 $Ratio_{nut}$ Ratio of each nutrient component

66	R_{max}	Maximum recovery rate in FDFO
67	R_g	Universal gas constant
68	S	Structure parameter of the support layer
69	SEC_{FDFO}	Specific energy consumption of FDFO
70	SEC_{RO}	Specific energy consumption of RO
71	$SEC_{RO+FDFO}$	Specific energy consumption of the RO-FDFO hybrid process
72	$SRSF$	Specific reverse salt flux
73	T	Temperature
74	$V_{D,i}$	Initial DS volume
75	$V_{D,f}$	Final DS volume
76	V_{ext}	Water extraction capacity
77		
78	Greek symbol	
79		
80	η	Pump efficiency
81		
82	Abbreviation	
83		
84	CAN	Calcium nitrate
85	CSG	Coal seam gas
86	DAP	Di-ammonium phosphate

87	DI	Deionized
88	DS	Draw solution
89	EDTA	Ethylenediaminetetraacetic acid
90	EDX	Energy dispersive x-ray spectroscopy
91	FDFO	Fertilizer-drawn forward osmosis
92	FO	Forward osmosis
93	FS	Feed solution
94	FSF	Forward salt flux
95	ICP	Internal concentration polarization
96	NF	Nanofiltration
97	OMBR	Osmotic membrane bioreactor
98	PA	Polyamide
99	RO	Reverse osmosis
100	SEM	Scanning electron microscopy
101	SOA	Ammonium sulphate
102	RSF	Reverse salt flux
103	SEC	Specific energy consumption
104	SRSF	Specific reverse salt flux
105	TFC	Thin-film composite
106	XRD	X-Ray diffraction
107		

108. Introduction

109 Coal seam gas (CSG), which is also known as coal-bed methane, has been widely
110 explored in United States, Australia, Canada, United Kingdom, and other nations since the
111 1970s [1]. During CSG extraction, underground water in the coal seam is pumped to the
112 surface together with methane gas. This is often called CSG produced water, which is
113 dominantly composed of sodium, chloride and bicarbonate [2]. In Australia, the salinity of
114 CSG produced water is relatively low, typically in the range of up to 6,000 mg/L [3]. Thus,
115 CSG produced water can be treated and utilized for a variety of application including
116 irrigation [4]. Since CSG produced water has a high sodium content (i.e. a high sodium
117 adsorption ratio), utilization of untreated CSG produced water for irrigation can lead to a
118 gradual decrease in the permeability of soil, eventually causing infiltration problems and
119 other form of soil degradation [5]. Therefore, it is necessary to remove sodium to enable
120 reuse of CSG produced water for irrigation.

121 Reverse osmosis (RO) is currently the most widely used technology for CSG
122 produced water treatment (**Fig. 1a**) due to its several merits such as small footprint, ease of
123 automation, and modular design [6]. However, RO generally exhibits high energy
124 consumption (i.e., typically above 4-5 kWh/m³ for a seawater desalination plant) due to the
125 high hydraulic pressure as a driving force [7]. Moreover, RO is often hampered by high
126 fouling potential and inherent limitations such as low recovery [8, 9]. To overcome these
127 issues, forward osmosis (FO) was proposed since it can provide high rejection of
128 contaminants, low fouling propensity, high fouling reversibility and low energy
129 requirement [10, 11]. However, FO has several limitations including the need to extract

pure water from the diluted draw solution (DS), requiring the additional desalting processes (e.g., nanofiltration (NF), RO or membrane distillation) [12, 13].

Figure 1. Conceptual process layout for integrating RO-FDFO hybrid process: (a) 2 stage RO system, (b) FDFO alone system and (c) RO-FDFO hybrid system.

Recently, fertilizer-drawn forward osmosis (FDFO) has received increased attention since the diluted fertilizer solution can be utilized directly for irrigation purpose and thus the diluted DS separation and recovery process is not required [14-16]. However the diluted fertilizer solution still required substantial dilution since the final nutrient concentration can exceed the standard nutrient requirements for irrigation especially using feed water sources

with high salinity [15, 16]. Thus, NF can be employed as a post-treatment process for further dilution and in meeting the water quality requirements for fertigation [14]. However, FDFO is seen to be more suitable for the treatment of low salinity impaired water sources (e.g., CSG produced water, wastewater and so on) as shown in **Fig. 1b** so that desired fertilizer dilution can be achieved without the need of a NF post-treatment process [17].

Since FDFO utilizes highly concentrated fertilizer DS, FDFO has serious problems regarding the reverse solute flux of the draw solute induced by the large concentration differences between the feed solution (FS) and DS across FO membrane. The reverse diffusion of draw solutes to FS in the FDFO process can reduce the recovery rate and lose the valuable fertilizers in DS. In addition, [reverse salt flux \(RSF\), which is reversely diffused draw solute through FO membrane from DS to FS](#), can alter the feed chemistry and accelerate membrane fouling or scaling [18-20], and inhibit the biological processes in osmotic membrane bioreactor (OMBR) which is one of the potential applications [17, 21]. Moreover, because of an increase in FS concentration caused by RSF, direct discharge of FS may entail negative impacts to the environment [22], which requires further treatment of FS concentrate.

In order to solve or mitigate these problems (i.e., high energy consumption in RO and valuable fertilizer draw solute loss by RSF in FDFO), a RO-FDFO hybrid process was proposed for simultaneous CSG produced water treatment for the agricultural application based on the concept described in **Fig. 1c**. This hybrid system consists of two parts (i.e., RO and FDFO). The 1st stage RO will concentrate CSG produced water by up to 75% and produce clean water. Then, the 2nd stage FDFO will treat CSG RO brine from the 1st stage

RO and also produce nutrient solution. The diluted fertilizer DS from the FDFO process will be mixed with RO permeate and supplied for fertigation. In this system, CSG produced water will be utilized as an influent and a highly concentrated fertilizer solution will be used as DS for the RO-FDFO hybrid process. The diluted fertilizer solution can then be obtained and supplied to fertigation.

Therefore, this study aims to evaluate the feasibility of the RO-FDFO hybrid system for the treatment of CSG produced water and production of nutrient solution by comparing with RO alone and FDFO alone. Comparisons are made based on the specific energy consumptions (SEC) and nutrient concentrations in the final FDFO product water. Finally, membrane scaling and fouling in FDFO during CSG RO brine treatment was evaluated and the cleaning strategies were further investigated using both physical cleaning and chemical cleaning.

2. Materials and methods

2.1 FO membrane and draw solutions

FO membrane used in this study was provided by Toray Chemical Korea (South Korea). This membrane was a thin-film composite (TFC) polyamide (PA) FO membrane with an embedded woven mesh for mechanical strength as shown in **Fig. S1**. The total membrane thickness was approximately 60 μm . The intrinsic FO membrane characteristics (i.e., the water permeability coefficient (A) and the salt permeability coefficient (B) of the active layer, and the structure parameter (S) of the support layer) were determined based on

the mathematical method [23] and shown in **Table S1**. For storage, the membranes were immersed in deionized (DI) water at 4 °C and the water was replaced regularly.

Four different reagent grade chemical fertilizers (i.e., ammonium sulphate (SOA), calcium nitrate (CAN), di-ammonium phosphate (DAP), potassium nitrate (KNO₃)) (Sigma Aldrich, Australia) were used as draw solutes. DS was prepared by dissolving fertilizer chemicals in DI water. Detailed information of fertilizer chemicals is provided in **Table S2**. Osmotic pressure and diffusivity of four fertilizers were obtained by OLI Stream Analyzer 3.2 (OLI System Inc., Morris Plains, NJ, USA).

2.2 Coal seam gas reverse osmosis brine

CSG RO brine used in this study was from a RO pilot plant treating CSG produced water from Gloucester Basin in the Upper Hunter, New South Wales, Australia. Operation conditions of the pilot plant were as follows: ultrafiltration pre-treatment, 5 mg/L antiscalant (Osmotreat, Osmoflo, Adelaide, South Australia, Australia), and RO recovery of 75% [2]. Detail information of CSG RO brine used as FS in this study is provided in **Table 1**.

Table 1. Water quality of CSG RO brine used in this study. CSG RO brine was collected from a pilot-scale RO system for treating CSG produced water from the Gloucester gas field [24].

General	Values	Ion concentration	Values
---------	--------	-------------------	--------

characteristics			
pH	9.07	SO ₄ ²⁻ (mg/L)	23.3 ± 3.1
Conductivity (mS/cm)	22.58 ± 0.02	PO ₄ ³⁻ (mg/L)	5.21 ± 0.17
Total dissolved solids, TDS (mg/L)	15,354 ± 12	Cl ⁻ (mg/L)	4,793 ± 87
Alkalinity (mg/L CaCO ₃ equivalent)	6,467 ± 58	Na ⁺ (mg/L)	6,089 ± 48
Water hardness (mg/L CaCO ₃ equivalent)	151 ± 1	K ⁺ (mg/L)	28.7 ± 0.6
Sodium absorption ratio (SAR)	215.3 ± 1.2	Ca ²⁺ (mg/L)	36.3 ± 0.6
Turbidity (NTU)	1	Mg ²⁺ (mg/L)	14.7 ± 0.6
		Si (mg/L)	23.5 ± 0.9

2.3 Fertilizer-drawn forward osmosis experiments

2.3.1 Fertilizer-drawn forward osmosis experiments

All FDFO experiments were carried out using a lab-scale FO system similar to the one described in our previous studies [25]. The FO cell had two symmetric channels consisting of 77 mm long, 26 mm wide and 3 mm deep on both sides of the membrane each for each FS and DS. Variable speed gear pumps (Cole-Parmer, USA) were used to provide crossflows under counter-current directions at a crossflow rate of 8.5 cm/s and solution temperature of 25 ± 1 °C. All FDFO operations were carried out using 1 M fertilizers as DS and CSG RO brine as FS under the AL-FS (i.e., active layer facing FS) mode of membrane orientation. Both solutions were recirculated in a closed-loop system resulting in a batch mode process operation. The DS tank was placed on a digital weighing scale and the weight changes were recorded by a computer in real time every 3 minutes interval to determine the water flux. Conductivity and pH meters (HACH, Germany) were connected to a computer to monitor concentration and pH changes in the feed tank.

2.3.2 Physical cleaning

In order to investigate the effect of physical cleaning on water flux recovery of the FO membrane after fouling, two different physical cleaning methods (i.e., [hydraulic washing](#) and osmotic backwashing) were adopted for all FDFO experiments. [Hydraulic washing](#) consisted of flushing DI water inside the DS and FS channels at 3 times higher crossflow velocity (25.5 cm/s) for 30 minutes. Osmotic backwashing was conducted for 30 minutes by flushing 1M NaCl DS solution on the active layer side of the membrane and DI water on the support layer side (both at 8.5 cm/s crossflow velocity) (AL-DS mode of

membrane orientation) in order to provide water flux in reverse direction to the fouling experiments. Water recovery rate was determined by comparing the baseline water flux of the virgin FO membrane conducted before the CSG RO brine treatment and after the physical cleaning using 1M NaCl as DS and DI as FS.

2.3.3 Chemical cleaning

To investigate the effect of chemical cleaning on water flux recovery, three different chemical cleaning agents (1 mM ethylenediaminetetraacetic acid (EDTA) [26], 1 mM sodium hydroxide (NaOH) [27] and 1-5% citric acid [28]) were adopted. Chemical cleaning consisted of flushing a cleaning agent inside the FS channel and DI water inside the DS channel at the same crossflow velocity (8.5 cm/s) for 30 minutes. Water recovery rate was determined by comparing the baseline water fluxes of the virgin FO membrane and membrane after chemical cleaning using 1M NaCl as DS and DI as FS.

2.4 Membrane surface characterization

The surfaces of FO membranes were observed and analysed by scanning electron microscopy (SEM, Zeiss Supra 55VP, Carl Zeiss AG, Germany) and energy dispersive X-ray spectroscopy (EDX) following the procedures described in a previous study [29]. Samples taken from each membrane were first lightly coated with Au/Pd. The SEM imaging was carried out at an accelerating voltage of 10 kV and multiple image magnifications at various areas were taken for each sample.

X-Ray diffraction (XRD) (Siemens D5000, USA) analysis was also performed over Bragg angles ranging from 10° to 60° (Cu K α , $\lambda=1.54059$ Å) to investigate the dominant species responsible for scaling formed on the membrane surface. Membrane samples

collected after experiments were first soaked in DI water for a few minutes to remove any feed or draw solutes and then dried in a desiccator for 1 day before SEM imaging was measured.

2.5 Specific energy consumption (SEC) estimation

Energy consumptions of the three processes (i.e., RO, FDFO and RO-FDFO hybrid process) were estimated in terms of SEC. ROSA 9.1 software (DOW FILMTEC, USA) was used to estimate SEC of RO alone. SEC of the FDFO standalone process was estimated based on the following equation [30]:

$$SEC_{FDFO} = \frac{P_F Q_F + P_D Q_D}{36 \times \eta \times Q_P} \quad (1)$$

where, P_F is the feed pressure (bar), P_D is the draw pressure (bar), Q_F is the feed flow rate (m^3/h), Q_D is the draw flow rate (m^3/h), Q_P is the permeate flow rate (m^3/h) and η is the pump efficiency. The total SEC in the RO-FDFO hybrid process is the sum of the energy consumption as shown in **Eq. (2)**.

$$SEC_{RO+FDFO} = \frac{SEC_{RO} Q_{P,RO} + SEC_{FDFO} Q_{P,FDFO}}{Q_{P,total}} \quad (2)$$

where, $Q_{P,total}$, $Q_{P,RO}$ and $Q_{P,FDFO}$ are the total permeate flow rate (m^3/h), the permeate flow rate (m^3/h) in RO and the permeate flow rate (m^3/h) in FDFO, respectively. It should be noted here that, for SEC estimation of both RO and FDFO, RO membrane, FS, the pump efficiency and the feed and draw pressure in FDFO alone were assumed to be BW30-4040 (Dow Filmtec, USA), CSG produced water [2], 80% and 1 bar, respectively. BW30-4040 is a brackish water RO membrane with high salt rejection. [If CSG produced water contains](#)

high concentration of organics, the viscosity will be seriously increased as the CSG produced water is concentrated, which can result in a significant reduction in the pump efficiency. However, since CSG produced water has quite low concentration of organics (e.g., 1.7 mg/L TOC) [2], the pump efficiency can be assumed to be constant as 80%.

2.6 Final nutrient concentration simulation

Nutrient concentrations in the final product water can be simulated using the water extraction capacity (V_{ext}) of 1 kg DS [15, 31]. This equation was derived under counter – current crossflow mode with an assumption of no forward salt flux (FSF) and no RSF.

$$V_{ext} = \frac{1000}{M_w} \left[\frac{1}{C_{D,i}} - \frac{1}{C_{D,f}} \right] \quad (3)$$

where, M_w is molecular weight of DS, $C_{D,i}$ is the maximum DS concentration (solubility) and $C_{D,f}$ is the final DS concentration having equal osmotic pressure with the initial FS concentration. In the FO process, RSF could have a significant impact on the FO process by increasing the FS concentration and decreasing the DS concentration, resulting in lower effective osmotic driving force. However, the effect of RSF on the FDFO process was not considered for **Eq. (3)** and thus, the water extraction capacity by **Eq. (3)** is likely to be over-estimated. In this study, therefore, **Eq. (3)** was modified by adopting the definition of specific reverse salt flux (SRSF) as follows.

$$V_{ext} = \frac{1 - \left(\frac{C_{D,f}}{C_{D,i}} \right)}{\left(\frac{C_{D,f} M_w}{1000} \right) + SRSF} \quad (4)$$

where SRSF is defined as the ratio of RSF to water flux in the FO process as presented in **Eq. (5)**. The SRSF is independent of membrane support layer properties and

can quantitatively elucidate FO membrane performance [25]. Here, we assumed that SRSF is constant without any change even though membrane fouling occurs during operation.

$$\frac{J_s}{J_w} = \frac{B}{A} \frac{1}{nR_gT} \quad (5)$$

where, n is the number of species that the draw solute dissociates into, A is the water permeable coefficient, B is the salt permeable coefficient, R_g is the gas constant, and T is the temperature. Nutrient concentrations in the final produced water can be obtained by using **Eq. (6)**. This equation was derived from mass balance for draw solute.

$$C_{nut,f} = \frac{1-SRSF \times V_{ext}}{V_{D,f}} \times Ratio_{nut} \quad (6)$$

where, $Ratio_{nut}$ is the ratio of each nutrient component and $V_{D,f}$ is the final DS volume. Based on **Eq. (4)**, the draw solute loss and the maximum recovery rate of FDFO can be also obtained as **Eq. (7)** and **Eq. (8)**, respectively.

$$Loss_{Draw} = \frac{SRSF \times V_{ext}}{C_{D,i} V_{D,i}} \times 100\% \quad (7)$$

$$R_{max} = \frac{Q_F - V_{ext}}{Q_F} \quad (8)$$

where, $Loss_{Draw}$ is the draw solute loss at the maximum recovery rate in FDFO, $V_{D,i}$ is the initial DS volume and R_{max} is the maximum recovery rate in FDFO.

3. Results and discussion

3.1 Specific energy consumption simulation of reverse osmosis, fertilizer-drawn forward osmosis and reverse osmosis – fertilizer-drawn forward osmosis hybrid processes for coal seam gas produced water treatment

The simulated SECs of the three processes (i.e., RO, FDFO and RO-FDFO hybrid processes) for treating CSG produced water and the supplying nutrient solution for irrigation are presented as a function of feed recovery rates (%) in **Fig. 2**. The efficiency of the high pressure pump for RO and the circulation pump for FDFO was assumed at 80% and the applied pressure for circulating FS and DS in FDFO was set at 1 bar [30].

Figure 2. SEC evaluation of RO alone, FDFO alone and RO-FDFO hybrid processes as a function of recovery rate (%). The estimated SEC results are defined as overall energy consumption (kWh) per produced water (m³). The flow rate in FS for all processes and the working pressure for FDFO operation were assumed to be 20 m³/d and 1 bar, respectively.

The pump efficiency was assumed to be 80%. Osmotic pressures of CSG produced water and RO brine at 75% recovery were 2.46 bar and 11.64 bar, respectively.

In RO alone, the SEC significantly reduced from 3.5 kWh/m³ to 0.7 kWh/m³ by increasing the feed recovery rate of up to 75% beyond which the SEC started to increase rapidly. This is due to the significant increase in hydraulic pressure needed to overcome the increased osmotic pressure of the feed concentrate along the fee channel. For example, osmotic pressure increases 4 times when recovery rate reaches up to 75% against 2 times increase at 50% recovery rate. The reults in **Fig 2** indicates that, the osmotic pressure of feed concentrate increases exponentially with the recovery rates above 75% thereby significantly increasing the hydraulic pressure needed to overcome this enhanced osmotic pressure.

The SEC of the FDFO process alone shows that, the SEC continuously reduced with increasing recovery rate. In the RO process, the hydraulic driving force incresed with the recovery rates due to increase in the the osmotic pressure of the feed and its concentrate thereby incresaing the SEC. However, in the FDFO process, the driving force and the feed recovery rates can be simply increased by increasing the initial DS concentration without impacting the hydraulic pressure and SEC of the process [32]. Consequently, FDFO has much lower SEC than RO due to its lower hydraulic operatiing pressure, consistent with other studies [30, 33].

Lastly, FDFO was combined with RO as shown in **Fig. 1c** to increase the overall feed recovery rate without significantly impacting on the SEC. As discussed above, when

the RO process is used alone, it was found that SEC increased rapidly with feed recovery rates above 75% . When FDFO is combined with RO for the treatment of its brine after 75% recovery rate, the overall recovery rate can be significantly increased without much impact on the total energy consumption or the combined SEC. Simulation results showed that SEC of the RO-FDFO combined process continuously decreased even up to 95% recovery rate. Based on all the SEC simulation results above, it can be concluded that FDFO alone is the most economic process followed by the RO-FDFO hybrid process and RO alone.

3.2 Comparison of final nutrient (N/P/K) concentration between fertilizer-drawn forward osmosis and reverse osmosis – fertilizer-drawn forward osmosis hybrid processes

The RO process alone produces pure water with a quality that is generally suitable for direct irrigation with or without remineralisation. Since the FDFO process alone does not generate pure water, their final water quality must be assessed against key irrigation criteria. For comparison, FDFO alone and the RO-FDFO hybrid process were selected and compared in terms of final nutrient concentration, draw solute loss, and maximum recovery rate.

Before the simulation, SRSF was experimentally measured and presented in **Table S3**. Results show that SOA had the lowest SRSF followed by DAP, CAN and KNO₃. With regards to water flux, KNO₃ showed the highest water flux followed by SOA, CAN and DAP, which is not consistent with osmotic pressures of fertilizers (**Table S2**). This difference in water flux between fertilizers is explained from the variations of the extent of

ICP effects induced by the mass transfer resistance (K) within the membrane support layer. Since mass transfer resistance refers to the ratio between the S parameter and diffusivity of DS, a draw solute with higher diffusivity has low mass transfer resistance and should have high water flux [17, 25]. In terms of RSF, SOA exhibited the lowest RSF followed by DAP, CAN and KNO_3 . Unlike the water flux, the trend for RSF with diffusivity was quite different. This is because RSF is theoretically a function of not only the effective concentration gradient across the active layer of the FO membrane but also the salt rejecting properties of the membrane [17, 34]. As a consequence, SRSF of fertilizer DS was determined by the salt permeable coefficient (B value) which varies with fertilizers. From these results, it can be drawn that SOA is possibly the optimum fertilizer DS in terms of draw solute loss and maximum recovery rate since it has the smallest draw solute loss with the same volume of feed water extraction.

The draw solute loss and the maximum recovery rate of both FDFO and RO-FDFO hybrid processes were firstly simulated using **Eq. (7)** and **Eq. (8)**, respectively and presented in **Fig. 3**. As expected, in FDFO process, KNO_3 exhibited the highest draw solute loss followed by DAP, CAN and SOA (**Fig. 3a**). It is interesting to note that DAP showed higher draw solute loss than CAN in spite of its lower SRSF. This is because the draw solute loss is affected by both the extraction capacity and SRSF as shown in **Eq. (7)**, indicating that higher extraction capacity of DAP also induced higher draw solute loss. Results of **Fig. 3b** indicated that maximum recovery rates of both processes have the totally a different trend with SRSF.

Unlike the draw solute loss (**Fig. 3**), DAP showed the highest maximum recovery followed by SOA, KNO₃ and CAN. This different trend between draw solute loss and maximum recovery rate was originated from their different dominant mechanisms. As we discussed above, draw solute loss was dominantly determined by both SRSF and recovery rate. However, maximum recovery rate was obtained from the extraction capacity of fertilizer DS which is affected by osmotic pressure of fertilizer DS. For example, as shown in **Eq. (4)**, if DS has high osmotic pressure at low concentration, its water extraction capacity will be high based on osmotic equilibrium and thus total recovery rate will be high. Similarly, since DAP has the highest osmotic pressure among fertilizers, DAP exhibited the highest maximum recovery rate in spite of its high SRSF. Results from **Fig. 3** show that, to achieve low draw solute loss and high maximum recovery rate in FDFO, fertilizer DS should have low SRSF and high osmotic pressure.

Figure 3. Comparative performances of FDFO and integrated RO-FDFO processes in terms of (a) draw solute loss and (b) maximum water recovery rate.

Compared to the FDFO process, the RO-FDFO hybrid process exhibited lower draw solute loss and higher maximum recovery rate with all fertilizers. In the RO-FDFO hybrid process, RO produced 75% of the feed as clean water while the FDFO process was used to further extract water only from the concentrate to increase the overall feed recovery rate to 95%. Therefore, the amount of the extracted water from the feed water by FDFO process in the hybrid system was lower than that in FDFO alone. As a result, the draw solute loss in the RO-FDFO hybrid process was much lower than that in FDFO. However, the RO-FDFO hybrid process exhibited higher maximum recovery rate than FDFO alone and this difference is likely induced by the difference of draw solute loss during the FDFO processes. In the FDFO process, the higher amount of draw solute was lost to the FS and thus the concentration of diluted DS could reached faster to its concentration that has equal osmotic pressure as the initial FS, resulting in a lower maximum recovery rate. It is very interesting to note that the trend of the maximum recovery rate between FDFO and the RO-FDFO hybrid process was quite different. Although DAP showed the highest maximum recovery rates for both the processes however, other fertilizers showed a different trend. This is because, besides osmotic pressure, SRSF of the fertilizer DS is also an important factor for determining the maximum recovery rate. For example, as recovery rate increases, the loss of draw solute becomes more significant thereby accelerating the reduction of DS concentration resulting in a decrease in the maximum recovery rates. Therefore, by combining RO with FDFO, draw solute loss can be minimized and total recovery rate can be maximized.

The nutrient concentrations in the final FDFO product water were further simulated in terms of major nutrients (N/P/K) using **Eq. (5)** to find out which process is more suitable for producing favourable nutrient water for irrigation. Results shown in **Table 2** indicate that KNO₃ in the FDFO process exhibited the lowest nitrogen concentration followed by DAP, SOA and CAN since KNO₃ has the lowest nitrogen content (i.e., 13.85%) and the highest draw solute loss (**Fig. 3a**). Although a loss in the draw solute could affect the nutrient concentration however, the final DS concentration is mainly determined by osmotic equilibrium with the initial FS concentration.

Table 2. Comparative performances of FDFO alone and the integrated RO-FDFO processes in terms of N/P/K nutrient concentrations in the final FDFO product water.

Fertilizers	CAN	DAP		SOA	KNO ₃	
Nutrients	N (mg/L)	N (ppm)	P (ppm)	N (ppm)	N (ppm)	K (ppm)
FDFO alone	268.40	201.19	222.45	230.63	114.76	320.33
RO-FDFO hybrid	199.25	186.55	206.26	194.31	93.98	262.34

When considering recommended concentrations (N/P/K) for beneficial plants (e.g., 200/50/300 ppm for a tomato, 170/60/200 ppm for an eggplant and 200/50/200 ppm for a cucumber) [16], **Table 2** indicates that the final product water from the FDFO process

could satisfy the recommended nitrogen concentration, however, still required substantial dilution to reduce the phosphorous and potassium content.

Simulation results show that the RO-FDFO hybrid process has lower final nutrient concentrations than the product water from the FDFO alone, making it more favourable for direct fertigation. This was because, the FDFO process was used for treating only 25% of the feed water in the form of RO brine and the further dilution was achieved by blending the RO permeate and the diluted DS from the FDFO process. Although the RO-FDFO hybrid process could reduce final nutrient concentration significantly and make more favourable for fertigation compared to the FDFO process alone however, substantial dilution is still required to meet the recommended concentration, especially in terms of phosphorous nutrient concentraion. However, by controlling the composition of blended fertilizers, the problem regarding exceeding the recommended concentrations can be solved [16]. For example, if we consider a simple combination for only two different fertilizers (i.e., DAP and KNO_3) with a molar ratio of 1:2.5, the final DS grade can achieve about 120/60/190 mg/L, which is quite suitable for growing an eggplant even though the concentration of nutrients should be slightly adjusted. Based on the simulation results of SEC and final nutrient concentrations, the RO-FDFO hybrid process can be considered as the most suitable process for both CSG produced water treatment and favourable nutrient water supply. Therefore, feasibility of the RO-FDFO hybrid process for treating CSG produced water was further investigated in this study. Since CSG produced water treatment by RO was already studied in the previous study [2], we focused on CSG RO brine

treatment by the 2nd stage FDFO process and assessed its performance in terms of water flux, flux decline and the cleaning requirements.

3.3 Flux decline in fertilizer-drawn forward osmosis during coal seam gas reverse osmosis brine treatment

The FDFO experiments were carried out with CSG RO brine as FS and four different fertilizers as DS under the AL-FS mode and their flux data is presented in the form of normalized water flux in **Fig. 4**. KNO₃ exhibited the highest flux decline during 1 day operation followed by CAN, SOA and DAP. This is because FS conductivity with KNO₃ was rapidly increased from 21.29 mS/cm to 40.9 mS/cm as presented in **Table S4** due to its highest draw solute loss by RSF (**Table S3**) even though KNO₃ exhibited the lowest accumulated permeate volume. The flux decline could also be caused by more severer membrane fouling but based on the SEM images of the membrane surface with KNO₃, it was observed that the membrane surface was only partially covered by foulant deposits as shown in **Fig. 5d**. Thus, it can be concluded that the severest flux decline with KNO₃ is due to significant decrease in the osmotic driving force caused by the loss of draw solutes towards the FS.

Figure 4. Flux-decline curves obtained during FO experiments with four different fertilizer DS. Experimental conditions of all FO experiments: CSG RO brine as FS; four different fertilizers as DS; crossflow velocity of 8.5 cm/s; and temperature of 25 ± 1 °C. All FDFO experiments were conducted repeatedly.

Figure 5. SEM images of (a) virgin membrane and fouled membrane with of (b) CAN DS, (c) DAP DS, (d) KNO_3 DS and (e) SOA DS.

CAN exhibited the second highest flux decline which is likely due to both an increase in salinity in the FS and membrane fouling. **Table S4** showed that FS conductivity with CAN significantly increased from 20.63 mS/cm to 31.6 mS/cm, resulting in a reduction in the concentration gradient between FS and DS. In addition, **Fig. 5b** revealed that the surface of FO membrane with CAN was covered by thick scaling layer, the likely main cause of the severe flux decline. When comparing SOA with DAP, it is interesting to note that DAP exhibited lower flux decline even though severer membrane fouling seems to have occurred on the membrane surface with DAP as shown in **Fig. 5c**. As shown in **Fig. 5e**, no apparent fouling layer was however observed on the membrane surface with SOA as

DS. A lower flux decline with DAP as DS may be due to lower feed recovery rate with DAP as its FS conductivity increased only slightly from 20.84 mS/cm to 26.3 mS/cm while that with SOA increased from 20.58 mS/cm to 28.5 mS/cm.

From these results, it can be concluded that an increase in FS concentration (batch process) and a decrease in DS concentration due to the loss by RSF were the dominant factor affecting the flux decline in the FDFO process even though membrane fouling layer was formed on the membrane surface with some fertilizers. It is interesting to compare experimental SRSF without a fouling layer with the change in the FS conductivity in terms of specific conductivity increment which is defined as a ratio of the difference between initial and final conductivities to accumulated permeate volume. KNO_3 showed the highest specific FS conductivity increment followed by CAN, SOA and DAP, while KNO_3 exhibited the highest SRSF followed by CAN, DAP, SOA. KNO_3 and CAN showed the similar trend since they had very high SRSF while on the other hand, DAP and SOA with quite low SRSF had the different trend, implying that the fouling layer can have an impact on reducing SRSF in FDFO.

To identify the scaling layer formed on the membrane surface with a variety of fertilizer DS, XRD analysis was carried out on the fouled/scaled membrane surface and presented in **Fig. 6a**. Results show that the membrane with KNO_3 and SOA has similar XRD peaks to the virgin membrane, indicating that no scaling layer was formed on the membrane surface, consistent with SEM analysis results (**Fig. 5d and 5e**). As shown in **Table 1**, CSG RO brine is composed of various scaling precursors including calcium, magnesium, phosphate and carbonate ions, indicating that CSG RO brine has high scaling

potential. Thus, membrane scaling can be formed on the membrane surface when CSG RO brine is highly concentrated [35]. Furthermore, since KNO_3 and SOA did not contain any scaling precursor, RSF could not affect membrane scaling formation as depicted in **Fig. 7a**.

Figure 6. XRD patterns of virgin and fouled membranes: (a) comparison of XRD peaks between virgin membrane and fouled membranes with four different fertilizer DS, (b) comparison of XRD peaks between fouled membranes with CAN and CaCO_3 crystal, and (c) comparison of XRD peaks between fouled membranes with DAP, magnesium phosphate, and magnesium ammonium phosphate (struvite).

Figure 7. Schematic description of FO membrane fouling/scaling during CSG RO brine treatment by FDFO: (a) fertilizers (i.e., SOA and KNO₃) without scaling precursors, and (b) fertilizers (i.e., CAN and DAP) with scaling precursors.

On the other hand, the XRD pattern for the membrane surface with DAP and CAN exhibited slightly different peaks compared to the virgin FO membrane. For FO membrane used with CAN, most XRD peaks were identical to virgin membrane but some peaks were not visible and some new peaks appeared suggesting that these XRD peaks likely originated from the membrane scaling layer, not the membrane surface. Since calcium was found from EDX analysis (data not shown), XRD peaks with CAN were compared with reference peaks of calcium carbonate (**Fig. 6b**) which agreed very well indicating the presence of CaCO₃ scaling on the membrane surface. Since magnesium and phosphorous were also found from EDX analysis (data not shown), XRD peaks with DAP were also compared with reference peaks of magnesium phosphate and struvite (**Fig. 6c**). Results

agreed with struvite, indicating that the scaling layer was primarily composed of struvite. These results suggested that the membrane scaling is significantly affected by draw solute containing scaling precursors such as calcium and phosphate as shown in **Fig. 7b**. Due to the high concentration gradient, draw solute with a scaling precursor can pass through FO membrane and accelerate ions concentration on the membrane surface [36]. If this exceeds its solubility limits such as of calcium carbonate, magnesium phosphate and struvite, it results in the formation of scales on the membrane surface contributing to flux decline. Besides, the reversely diffused draw solutes can interact with certain ions in FS and induce the formation of a scaling layer [37]. As a result, calcium carbonate and struvite were dominantly formed on the membrane surface with CAN and DAP, respectively.

It is very interesting to note that struvite was formed on the FO membrane with DAP DS rather than $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$ even though their solubility product constants are much lower than struvite. Ca^{2+} , Mg^{2+} and PO_4^{3-} ions are required for the formation of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Mg}_3(\text{PO}_4)_2$, while HPO_4^{2-} , Mg^{2+} and NH_4^+ ions are required for the struvite formation (MgNH_4PO_4) [20]. However, NH_4^+ and HPO_4^{2-} ions are the dominant species of DAP DS, resulting in their high reverse diffusion to FS. Consequently, struvite is likely formed on the FO membrane with DAP as DS. As well as the effect of RSF on the scaling formation in FS, FSF also can influence the complexation with DS. However, FSF in FDFO is very low compared to other desalting membrane processes (e.g., NF or RO) due to the hindrance effect of RSF on FSF [38]. Thus, the effect of FSF will be very limited. Besides, although the complexation of FS with DS occurs, it can hardly affect the FO performance due to the permeate flow direction from FS to DS.

3.4 Strategy for controlling membrane fouling

The results of membrane physical cleaning show that the water fluxes were fully recovered for FO membrane used with KNO_3 and SOA, which are consistent with SEM results (Fig. 8a). **Fig S2c and S2d** indicated that the membrane fouling layer formed on the active layer could be readily removed by physical or hydraulic washing. This is because, as previously discussed, KNO_3 and SOA have low scaling potential while CAN and DAP exhibited less than 90% water flux recovery. These poor flux recovery rates (i.e., 82.3% and 86.6%, respectively) of FO membrane operated with CAN and DAP show that physical or hydraulic washing was not effective in removing the membrane foulants formed on the active layer. **Fig. S2a and S2b** confirmed that the membrane fouling layer still remained on the active layer with CAN and DAP.

Figure 8. Water flux recovery after (a) hydraulic washing and (b) osmotic backwashing. Experimental conditions for hydraulic washing: DI water as FS and DS; crossflow velocity of 25.5 cm/s; cleaning duration of 30 min; and temperature of 25 ± 1 °C. Experimental

conditions for osmotic backwashing: 1M NaCl as FS; DI water as DS; crossflow velocity of 8.5 cm/s; cleaning duration of 30 min; and temperature of 25 ± 1 °C.

In order to further enhance water flux recovery, osmotic backwashing was applied for the fouled FO membrane with CAN and DAP using DI water on the active layer and 1 M NaCl on the support layer side at the same crossflow velocity (i.e., 8.5 cm/s for 30 minutes). **Fig. 8b** shows that water flux recovery was slightly enhanced compared to the hydraulic washing. However, **Fig S2e and S2f** indicate that the fouling layer on the membrane surface could not be completely removed, which is consistent with the water flux recovery results. The results of the osmotic backwashing agreed well with other studies [19]. However, the results of physical cleaning experiments and SEM images showed that FO membranes with CAN and DAP still require further cleaning.

Chemical cleaning was further investigated for the complete removal of the fouling/scaling layer using three different chemicals (EDTA 1mM, NaOH 1mM and citric acid 1%), and the results are presented in **Fig. 9a**. The fouled FO membrane with CAN was utilized for this study since CAN showed the most severe membrane fouling as well as high flux decline. **Fig. 9a** demonstrated that 1% citric acid was more efficient for recovering water flux compared to the other chemicals (i.e., EDTA 1mM and NaOH 1mM). Moreover, SEM images (**Fig. S3d**) showed that the fouling layer structure was slightly changed by exposure to citric acid 1%. Citric acid is a weak acid which can dissolve inorganic minerals and be utilized for removing the scaling layer [39]. In addition, citric acid is widely utilized

as a chelating agent [40]. Therefore, this can lead to complex with Ca^{2+} ions, resulting in a reduction of scaling on the membrane surface.

Figure 9. Water flux recovery of fouled membrane with CAN after chemical cleaning with (a) varying chemical agents (i.e., EDTA 1 mM, NaOH 1 mM and citric acid 3%) and (b) increasing citric acid concentration. Experimental conditions for chemical cleaning: testing chemical agents as FS; DI water as DS; crossflow velocity of 8.5 cm/s; cleaning duration of 30 min; and temperature of 25 ± 1 °C.

Interestingly, 1 mM EDTA and 1 mM NaOH showed better cleaning efficiency than hydraulic washing. EDTA is generally utilized for disrupting the fouling layer structure through a ligand exchange between EDTA and organic-divalent complexes [26]. Therefore, 1 mM EDTA was effective for removing calcium carbonate scaling, resulting in an increase in water flux recovery [19]. However, **Fig. S3b** shows that 1 mM EDTA could not remove the scaling layer. NaOH has been used for dissolving organic foulants in basic solution [27], but it was efficient for recovering water flux even though the major fouling mechanism

was membrane scaling enhanced by RSF. This is because CSG RO brine was a mixture of organics and inorganics as shown in **Table 1**, which can accelerate membrane fouling due to synergistic effects by combined organic–inorganic fouling [41]. Thus, NaOH could enhance water flux recovery by dissolving organics from the combined fouling layer. However, **Fig. S3c** indicates that the effect of NaOH on membrane cleaning efficiency is limited.

To further enhance the cleaning efficiency, chemical cleanings were carried out by increasing the citric acid concentration. By increasing the citric acid concentration from 1 % to 3 %, the water flux recovery was slightly enhanced (**Fig. 9b**) and **Fig. S3e** indicates that there was still some scaling layers on the membrane surface. When the citric acid concentration was further increased to 5%, water flux was perfectly recovered as shown in **Fig. 9b** and this was confirmed in **Fig. S3f** which demonstrates that the fouling layer was completely removed. Since citric acid 5% exhibited the most efficient cleaning efficiency, fouled FO membrane with DAP was also assessed for its cleaning efficiency using 5% citric acid as chemical cleaning agent. As shown in **Fig S3h**, it was observed that the membrane surface was completely cleaned as well as water flux was fully recovered (data not shown) with 5% citric acid chemical cleaning.

6414. Conclusions

In this study, three processes (i.e., RO alone, FDFO alone and the RO-FDFO hybrid process) in terms of SEC and nutrient concentrations in the final FDFO product water were evaluated and compared. Membrane fouling in FDFO during CSG RO brine treatment was

then investigated and the strategies of controlling membrane fouling were also assessed.

The primary findings drawn from this study are summarized as follows:

- SEC analysis showed that FDFO alone has the lowest SEC followed by the RO-FDFO hybrid process and RO alone.
- Simulation of the final nutrient concentration suggested that the RO-FDFO hybrid system can achieve lower final concentration, higher maximum recovery and lower nutrient loss compared to FDFO process alone.
- From both SEC analysis and final nutrient simulation, it can be drawn that the RO-FDFO hybrid process is the most promising process for both CSG RO brine treatment and favorable nutrient supply.
- During CSG RO brine treatment, KNO_3 exhibited the highest flux decline than other fertilizers since FS concentration was highly increased due to high RSF.
- CAN showed the most severe membrane scaling caused by reversely transported calcium ions to FS.
- To control membrane fouling in the FDFO process, citric acid cleaning was the most effective chemical agent for chemical cleaning.

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