Environmental and economic assessment of hybrid FO-RO/NF system with selected inorganic draw solutes for the treatment of mine impaired water

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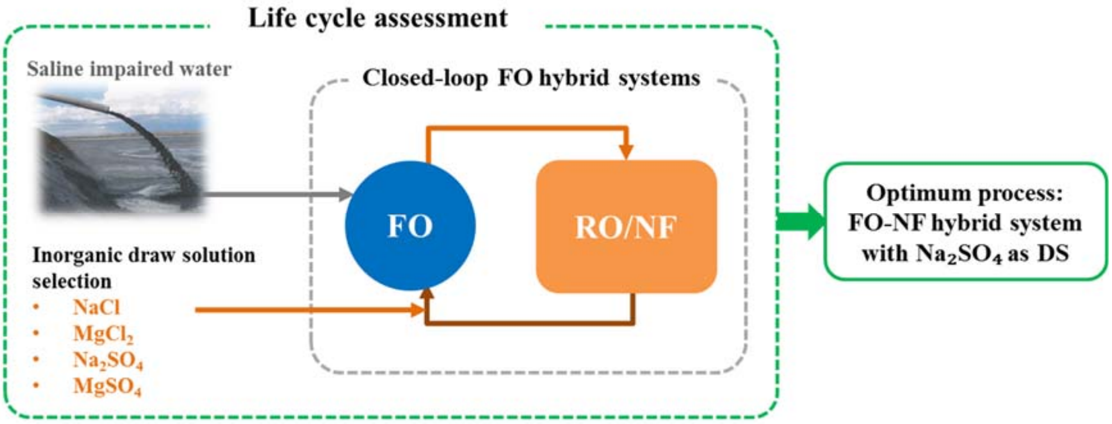
Graphical Abstract



Abstract

A hybrid forward osmosis (FO) and reverse osmosis (RO)/nanofiltration (NF) system in a closed-loop operation with selected draw solutes was evaluated to treat coal mine impaired water. This study provides an insight of selecting the most suitable draw solution (DS) by conducting environmental and economic life cycle assessment (LCA). Baseline environmental LCA showed that the dominant components to energy use and global warming are the DS recovery processes (i.e. RO or NF processes) and FO membrane materials, respectively. When considering the DS replenishment in FO, the contribution of chemical use to the overall global warming impact was significant for all hybrid systems. Furthermore, from an environmental perspective, the FO-NF hybrid system with Na_2SO_4 shows the lowest energy consumption and global warming with additional considerations of final product water quality and FO brine disposal. From an economic perspective, the FO-NF with Na_2SO_4 showed the lowest total operating cost due to its lower DS loss and relatively low solute cost. In a closed-loop system, FO-NF with NaCl and Na_2SO_4 had the lowest total water cost at optimum NF recovery rates of 90 and 95%, respectively. FO-NF with Na_2SO_4 had the lowest environmental and economic impacts. Overall, draw solute performances and cost in FO and recovery rate in RO/NF play a crucial role in determining the total water cost and environmental impact of FO hybrid systems in a closed-loop operation.

Keywords: Life cycle assessment; Forward osmosis; Reverse osmosis; Nanofiltration; Draw solution; Specific reverse salt flux.

1. Introduction

In Australia, extracting and washing coal are becoming of greater concern as it produces massive volumes of saline wastewater. For example, one of the coal mine sites located in the Hunter Valley, New South Wales (NSW), Australia produces approximately 2.5 ML/day of contaminated mine saline water with a broad range of concentration with total dissolved solids (TDS) ranging from 320 to 21,000 mg/L (Thiruvenkatachari et al., 2011). Therefore, impaired water produced during mining activities needs to be treated before being discharged to the receiving environment or used as an alternative water resource to augment water supplies.

Recently, forward osmosis (FO) has emerged as a novel technology for treating contaminated water produced during the hydraulic fracturing of wells (Hickenbottom et al., 2013, McGinnis et al., 2012, Yun et al., 2015). Hickenbottom et al., (2013) demonstrated the feasibility of an osmotic dilution operation for treating oil and gas waste streams from shale gas wells. This study aimed at evaluating and optimizing process performances under different operating conditions using cellulose tri acetate (CTA) FO membranes. McGinnis et al., (2013) also investigated an FO membrane brine concentrator (FO-MBC, Oasys Water) in a pilot-scale level and used spiral wound polyamide thin film composite (TFC) FO membrane modules. This study conducted FO pilot experiments using NH_3/CO_2 as a draw solution (DS) to treat raw drilling wastewater and low salinity water from the Marcellus shale formation. More recently, Yun et al., (2015) investigated pressure assisted FO, which is a relatively new technology, for shale gas wastewater treatment. From all these studies, it seems that FO is a promising technology to treat mine impaired water to reach an acceptable level before discharging to the environment.

However, in FO, selecting the most suitable draw solute is a top priority because its performance and reconcentration are ultimately related to net benefits in terms of total capital and operating costs of an FO process (Chekli et al., 2012). DS for FO applications has to meet main criteria: high solubility, high osmotic pressure, low viscosity, environmental-friendly and cost-effective recovery/reconcentration process (Bai et al., 2011, Chekli et al., 2012, Cornelissen et al., 2011, Hancock et al., 2009).

One of the biggest challenges in FO is the loss of draw solutes through reverse salt diffusion (RSF, J_s) across a semi-permeable FO membrane (Bowden et al., 2012, Cath et al., 2006, Ge et al., 2013). The RSF is an economic loss as it adds to the replenishment cost. In addtion to the replenishment cost associated with the draw solute lost throgh through the RO or NF membranes. The RSF loss could also cause salt accumulation in the feed brine and complicates the brine disposal requiring additional treatment processes especially if the draw solutes contain salts that does not meet the stringent brine discharge regulations (Blandin et al., 2016, Holloway et al., 2015, Phuntsho et al., 2017). It is important that the selection of the most suitable draw solution for FO applications should be conducted based on the specific FO application (i.e. purpose) and membrane types. Achilli et al., (2010) developed a protocol for the selection of the most suitable DS using different inorganic-based DSs for FO applications using a desktop screening process and laboratory and modelling analyses. However, this study did not include an environmental and economic assessment of DSs. In addition, none of studies carried out a direct comparison of overall environmental and economic impacts of hybrid FO systems with different DSs to select the most appropriate DS for mine wastewater treatment application.

There are several studies on the environmental and economic life cycle assessment of an FO hybrid system compared to other conventional water treatment technologies. Valladares Linares et al., (2016) investigated the life cycle cost for a hybrid FO and low-pressure reverse osmosis (LPRO) system for seawater desalination and wastewater recovery. This study reported a detailed economic analysis on capital and operational expenses (CAPEX and OPEX) for the hybrid FO-LPRO process and compared it with seawater RO (SWRO) desalination process and a membrane bioreactor-RO-advanced oxidation process (AOP) for wastewater treatment and reuse. Results showed that the most important variables affecting the economic feasibility of the FO-LPRO system was the FO process due to a large FO membrane area required and FO module cost.

Holloway et al., (2016) further studied two potable reuse technologies: microfiltration/RO/ultraviolet AOP treatment and a hybrid ultrafiltration osmotic membrane bioreactor (UFO-MBR) using an LCA tool and methodology. Results from the LCA showed that overall environmental impact and energy consumption of UFO-MBR treatment were related to a large membrane area in FO and high power consumption in RO. However, by considering the use of RO energy recovery device and higher water permeability FO membranes, results led to the overall reduction of energy use and environmental impacts of the UFO-MBR treatment.

There is compelling empirical evidence that environmental and economic impacts of FO hybrid systems can be reduced by using FO membranes with higher water flux. However, as mentioned earlier, given the system configuration and its application, environmental and economic impact of FO hybrid system with selected DSs should be conducted to ensure that each stage of the process has no or few impacts on the environment and overall process cost to support a full-scale FO hybrid system implementation. The main objective of the current study was to compare the environmental and economic impacts of FO hybrid systems with different DSs. Different DS recovery processes (i.e. RO and NF) were also considered to compare environmental and economic impacts of the closed-loop FO-RO and FO-NF hybrid systems using energy consumption (kWh/m^3) and global warming (GW) impact in carbon dioxide equivalents (kg, CO2-eq) as indicators. The effect of FO brine disposal and DS replenishment cost was also evaluated. The economic analysis results were finally compared with a conventional SWRO hybrid system. Through these environmental and economic evaluations, the most appropriate draw solute was therefore selected for mine impaired wastewater treatment. However, the current study did not include the effect or cost of pre-treatment for mine impaired wastewater and its potential to membrane fouling and the performances of the different FO hybrid systems. The plant lifetime was assumed based on the literature (Wittholz et al., 2008) and membrane replacement time was assumed based on our previous long-term operation of FO and NF membrane modules (Phuntsho et al., 2016).

2. Materials and methods

2.1. Laboratory-scale FO experiments

Four different draw solutes, NaCl, $MgCl_2$, Na_2SO_4 and $MgSO_4$ (Certified ACS-grade), were selected through a desktop screening process based on water flux and RSF results.Mine brackish groundwater (BGW) was employed as feed solution (FS) witha total dissolved solid (TDS) of 5,568 mg/L and osmotic pressure of 3.96 bar. The other compositions of the FS are presented in our previous study (Phuntsho et al., 2016). In FO experiments, each DS was prepared at 1 M concentration which corresponds to different osmotic pressure as presented in Table 1 obtained from OLI Stream Analyser 3.2 (OLI Systems, Inc., Morris Plains, NJ). In order to fairly confirm the performances of the DS recovery processes (i.e. RO and NF), the osmotic pressure of NaCl and Na_2SO_4 (i.e. monovalent and divalent ions). Besides it was assumed that $MgCl_2$ and $MgSO_4$ have the same molar concentration with NaCl and Na_2SO_4 as their osmotic pressure was around two times higher ($MgCl_2$) and lower ($MgSO_4$). It was therefore expected to have further savings in operational costs in terms of FO membrane cost and DS replenishment cost. Fig. S1 of the Supplementary Information (SI) presents the osmotic pressure, viscosity, electrical conductivity (EC) and diffusivity as a function of the concentration of the draw solutes.

A flat sheet TFC FO membrane manufactured by Toray Chemical Korea (TCK) Inc. was used for all experiments. The pure water permeability coefficient (A) and salt rejection (R) were determined under RO mode using DI water and 2 g/L sodium chloride as feed, respectively. The pressure was varied from 4 to 10 bar. The A and R values were 5.53 $Lm^{-2}h^{-1}bar^{-1}$nd 95%. All the input parameters used for FO process simulation including water and salt fluxes (J_w and J_s), rejection (R), salt permeability (B), diffusivity (D), solute resistance coefficient (K) and structural parameter (S) values for each solution are shown in Table S1 in the SI.

The effective membrane area of an acrylic FO cell was 20.02 cm^2 (7.7 cm in length, 2.6 cm in width, and 0.3 cm in depth). The dense active layer of the FO membrane was facing with the feed solution (AL-FS mode), and all the experiments were conducted under counter-current flow mode due to better flux stability with a lower fouling tendency (Tang et al., 2010). All FO experiments were carried out at a constant temperature of 25°C with a flow rate of 400 mL/min for 10 hrs operation time.

The performance of each DS was evaluated for water flux (J_w) and RSF (J_s). J_w was determined by measuring the change in mass of the DS tank (placed on a digital scale connected to a computer) for the duration of each experiment. The first 30 min of data was disregarded in the flux calculation to account for transport equilibration. Two different methods were used to measure RSF of draw solutes. When DI water was used as FS, the EC in the FS tank was measured at the beginning and end of each experiment. When BGW was used as FS, ion compositions in the collected samples at the beginning and end of each experiment were measured using a Perkin Elmer Elan DRC-e Inductively Coupled Plasma Mass Spectrometer.

Table 1. Characterization of DSs used for FO experiments and this data obtained from Fig. S1 in the SI.

Chemicals	Osmotic pressure π@1M(bar)	Viscosity@1M (cP)	Hydrated diameter, 10^{-12} (m) (Achilli et al., 2010)
NaCl	46.77	0.97	Cl^- : 300
$MgCl_2$	92.55	1.27	SO_4^{2-} : 400
Na_2SO_4	46.01	1.26	Na^+ : 450
$MgSO_4$	23.31	1.71	Mg^{2+} : 800

2.2. Full-scale simulation of FO, RO and NF processes

A full-scale simulation of FO process was conducted based on a simple mass balance relationship (Liyanaarachchi et al., 2016, Phuntsho et al., 2017) and a module-scale approach (Deshmukh et al., 2015) under a closed-loop FO hybrid system since there is no commercial FO simulation software available. An 8” spiral wound TFC FO membrane module with a total membrane area of 15.3 m^2 (Toray Industries, Korea) was used. Mass balance equations to calculate the key solution concentrations, flow rates, water flux and salt flux are described in Table S2 of the SI.

It must be clarified here that, implications of forward diffusion of feed solutes towards the DS during the FO process has not been accounted in this study. The forward diffusion of feed solutes could have a significant impact on the quality of the DS in a closed loop FO-RO or NF hybrid system due to accumulation of feed solutes with time potentially requiring draw solute replacement from time to time which can add to the cost (Phuntsho et al., 2017, Phuntsho et al., 2016). While the rate of forward diffusion of feed solutes could depend on the rejection of the FO membrane however the types of ions and co-ions present on each side of the membrane would significantly affect their dynamics. This consideration requires more detail characterisation and analytical studies and hence is not included within the scope of this study.

The Reverse Osmosis System Analysis (ROSA, Dow Filmtec, Mildland, MI) software was used to simulate the performance of full-scale RO and NF processes. An 8” spiral wound polyamide RO and NF membrane modules were utilized in the RO and NF processes (i.e. DS recovery process). Membrane module details are presented in Tables S3 and S4 of the SI. The RO and NF system design parameters including number of stages, pressure vessels, and membrane modules were incorporated into ROSA as input parameters to meet a fixed RO and NF permeate flow rate of 100,000 m^3/day. Using the OLI Stream Analyser 3.2, the final diluted DS concentrations were assumed to be equal to the osmotic pressure of BGW FS based on the principle of osmotic equilibrium. It has to be noted that only three DSs (NaCl, $MgCl_2$, and Na_2SO_4) were used to conduct a full-scale simulation of RO and NF processes. This will be discussed in Section 3.1.

2.3. Environmental and economic life cycle assessment

2.3.1. Environmental impact assessment

Life cycle assessment (LCA) is a method to identify potential environmental impacts of selected wastewater treatment and desalination technologies and determine factors that can be reduced (Coday et al., 2015, Hancock et al., 2012, Holloway et al., 2016, Valladares Linares et al., 2016). LCA consists of four phases, including goal and scope definition, life cycle inventory analysis (LCI), life cycle impact assessment (LCIA), and interpretation (Pryshlakivsky et al., 2013). The first two phases define the detailed objectives and input data collection from experimental and simulation results. Finally, the LCIA and its interpretation are discussed in the results and discussion section.

The system boundaries of the current study are shown in Fig. 1. Material surveys including construction, maintenance and operational phases were undertaken by utilising the currently available data published in the literature (Coday et al., 2015, Hancock et al., 2012, Holloway et al., 2016, Valladares Linares et al., 2016) and Ecoinvent LCA database v. 3.0 and Australian LCA database in Simapro software v. 8.1.1. The detailed and calculated data are shown in Table S5 in the SI. Based on the LCI analysis, the LCIA was carried out using the

Australian indicator set v.3.0 and thus an environmental impact was then evaluated using global warming indicator (GW, kg CO_2-eq) (PRé-Consultants 1998). However, the current study did not include the effect of pre-treatment for mine impaired wastewater and membrane fouling on the performances of the different FO hybrid systems. It has to be noted here that the plant lifetime was assumed based on the literature (Wittholz et al., 2008) and membrane replacement time was assumed based on our previous long-term operation of FO and NF membrane modules (Phuntsho et al., 2016).

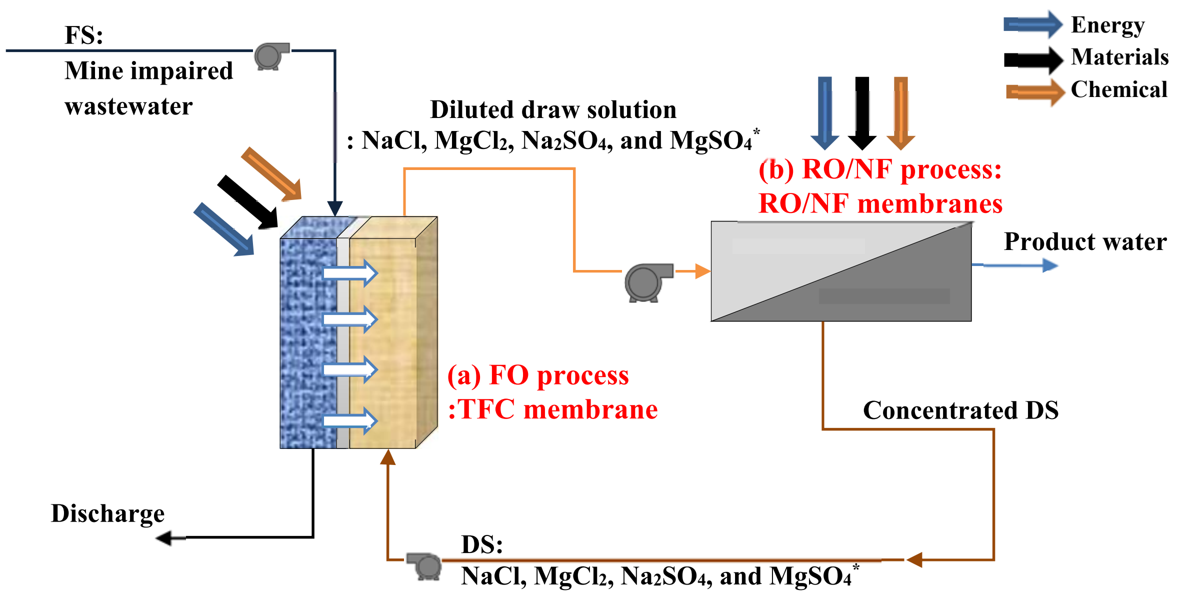


Fig.1. A schematic diagram of a closed-loop FO and RO/NF hybrid system operation. *$MgSO_4$ was excluded for a simulation of the post-treatment processes due to its poor performance in the FO process (see Section 3.1).

2.3.2. Economic impact assessment

An economic analysis on CAPEX and OPEX of three different hybrid systems: FO-RO, FO-NF90 and FO-NF270 (90 and 270 refer to two different types of commercial NF membranes, Filmtech Dow Chemicals), was conducted. The total water cost ($/$m^3$) of each hybrid system was compared based on a production capacity of 100,000 m^3/day. The results of the FO hybrid systems were compared with the results of a conventional brackish water RO (BWRO) hybrid system.

The capital construction costs may vary, if considering the logistics and impacts of transporting chemicals and materials to the site. Thus, the CAPEX cost analysis was conducted without considering a specific site. This study used literature information with approximations based on global trends and real data from the commercially available products in the market (e.g. cost of membrane modules and chemicals). The unit cost of each FO, RO, and NF membrane module was found in the literature as presented in Table 2 (Bigbrandwater 2016, Coday et al., 2015).

The cleaning strategies for RO and NF were considered to be periodic chemical cleaning (four times per year). FO membrane cleaning strategies were considered to be periodic hydraulic cleaning and eventual chemical cleaning (once a year) although recent studies demonstrated that physical cleaning was very efficient and easy to apply for FO process (Lotfi et al., 2017, Phuntsho et al., 2016). The amount of chemical required for cleaning process was calculated based on the manufacturer's recommendation (DowChemical 2017). From the process performance simulation, the number of elements and pressure vessels was obtained. Then, a size of a cleaning tank (i.e. cleaning solution volume) was roughly calculated using the empty pressure vessels volume. The chemical cost was therefore evaluated based on the amount of the cleaning chemical during the cleaning process, and this study considered NaOH and HCl as cleaning chemicals for hybrid systems. It must be acknowledged that cleaning strategies for the FO process should be determined by its applications as it affects the environmental and economic assessment of the whole process. In addition, DS replenishment cost was calculated using a specific RSF value (SRSF, J_s/J_w, g/L), which is directly related to the process efficiency and sustainability. The specific cost of each draw solute was determined based on the mass of solute needed to produce one litre of diluted DS with an initial concentration of 1 M. An illustrative summary of the cost parameters considered for the economic analysis is shown in Fig. 2, and specific economic values are presented in Table 2.

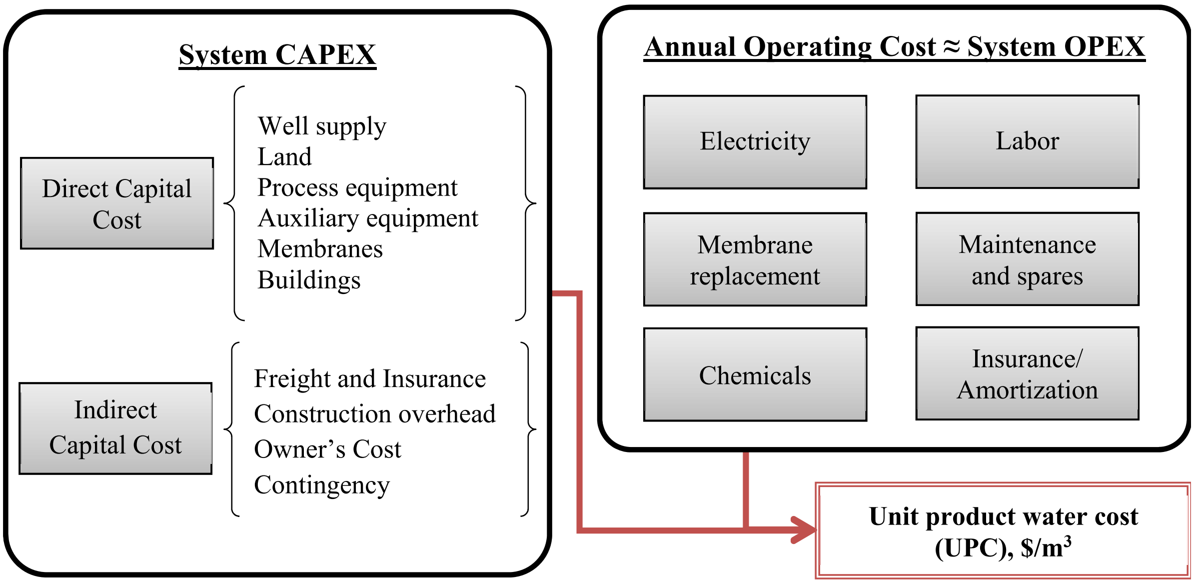


Fig.2. Specific parameters for cost estimation for hybrid desalination processes.

Table 2. Economic values used in cost analysis for hybrid desalination processes (Australian dollar).

Parameters	Unit	Values
Plant		
Plant capacity	m^3/day	100,000
Plant availability (Wittholz et al., 2008)		0.95
Plant lifetime (Wittholz et al., 2008)	year	20
[a] Electricity price (Mountain 2012)	$/kWh	0.29
Membranes		
RO membrane element cost (Filter 2016)	$	1,161
NF 90 membrane element cost (Filter 2016)	$	1,092
NF 270 membrane element cost (Americanro 2016)	$	987
[b] FO membrane element cost	$	1,161
Pressure vessel (7elements/PV) (Moch et al., 2008, Valladares Linares et al., 2016)	$	1,690
Draw solution (Achilli et al., 2010)	Unit cost[c], $/kg	Specific cost, $/L
NaCl	19	1.11
$MgCl_2$	37	3.52
Na_2SO_4	11	1.56
$MgSO_4$	68	8.19

[a] Electricity price in Australia.
[b] FO membrane cost was assumed to be the same as the cost of RO module.
[c] USD 1$ = AUD 1.3$: August. 2016

The CAPEX cost for FO process was calculated using the specific cost of economic parameters of FO process reported in the recent studies (Coday et al., 2015, Valladares Linares et al., 2016). In addition, the CAPEX cost for RO and NF processes was estimated using a capacity and capital cost correlation used in engineering practice was utilised. This is called the power law rule as followed:

$$\left(\frac{\text{Capital cost}_{\text{plant 1}}}{\text{Capital cost}_{\text{plant 2}}}\right) = \left(\frac{\text{Plant capacity}_{\text{plant 1}}}{\text{Plant capacity}_{\text{plant 2}}}\right)^{m}$$

where the power law exponent, m, is usually 0.8 and 0.74 for SWRO and BWRO, respectively. Those values were determined from the cost database analysis conducted elsewhere (Chilton 1950, Wittholz et al., 2008). In the present study, 0.74 was therefore used for RO and NF processes. Mathematical formulations used to calculate the annualised capital cost ($\$/m^3$) are shown as follow (Poullikkas 2001, Valladares Linares et al., 2016):

Capital amortization (α) $= \frac{i(1+i)^n}{(1+i)^n - 1}$

Capital recovery (C_R), \$ = $\alpha \times$ Total capital cost (C_T)

Annual capital recovery cost (C_A), $\$/m^3 = \frac{C_R}{365 \times \text{Plant capacity}\left(\frac{m^3}{d}\right) \times \text{Plant availability}}$

where the total cost is the sum of the direct and indirect capital costs in Fig. 2., *i* is the interest rate of 6%, n is the number of years of the project fixed at 20 years, 365 corresponds to the number of days in a year and 0.95 is plant availability due to downtime.

The OPEX costs including membranes, chemicals and electricity were calculated based on the results of a full-scale simulation and ROSA software and the values in Table 2. Labour and maintenance were calculated based on the reported percentages in the literature

(Valladares Linares et al., 2016). Finally, the OPEX cost was calculated based on a yearly basis cost. The total cost per m^3 of water is the sum of unit CAPEX and OPEX costs. All the calculated data are presented in Table S6 in the SI.

3. Results and discussion

3.1. DS performances

Table 3 shows the water flux, RSF and SRSF in the FO process using four different DSs with FS concentration of around 5.6 g/L BGW. At similar DS concentration of 1 M, the water flux and RSF values followed the order of NaCl > $MgCl_2$ > Na_2SO_4 > $MgSO_4$, corresponding to the specific osmotic water fluxes of 0.311, 0.097, 0.153, and 0.171 LMH/bar. Although the osmotic pressure of $MgCl_2$ shows the highest at 1 M, the water flux was significantly lower compared to NaCl (around 38% lower). However, in terms of their specific osmotic water flux, the order was different NaCl > $MgSO_4$ > Na_2SO_4 > $MgCl_2$ although NaCl still showed the highest specific osmotic water flux. This is mainly due to the diffusion coefficient of the NaCl (1.41E-09 m^2/s) which is highest compared to $MgCl_2$ (9.36E-10 m^2/s), Na_2SO_4 (8.72E-10 m^2/s) and $MgSO_4$ (5.19E-10 m^2/s). Higher diffusion coefficient of the draw solutes enhances the diffusivity of the solute through the membrane support layer thereby lowering the ICP effects. The other reason for highest water flux for NaCl is also due to lower viscosity of NaCl (0.97 cP), $MgCl_2$ (1.27 cP), Na_2SO_4 (1.26 cP), and $MgSO_4$ (1.71 cP) at 1M concentrations which enhances the permeability of the DS through the membrane support layer thereby decreasing the ICP effects (Achilli et al., 2010, Johnson et al., 2017, Li et al., 2014, Phuntsho et al., 2013). This result underscores the importance of having with higher diffusion coefficient and lower viscosity to have a higher FO water flux. The lowest water flux and RSF for $MgSO_4$ DS is not surprising given that it has the lowest osmotic pressure, lowest diffusion coefficient, and the highest viscosity. In addition, the DSs containing larger-sized hydrated anions (i.e. $MgSO_4$ and Na_2SO_4) showed the lowest RSF values, regardless of their paired cations and this is consistent with a previous study (Achilli et al., 2010). Based on this experimental evaluation, $MgSO_4$ was excluded for further investigations due to its poor performance results.

Table 3. FO experimental reuslts in terms of water flux (J_w), RSF (J_s), and SRSF (J_s/J_w) using 1 M DSs with BGW as FS in the FO process.

FS	DS	J_w, LMH	Specific J_w, LMH/bar	J_s, gMH	J_s/J_w, g/L
5.6 g/L BGW	NaCl	14.54	0.0311	9.49	0.65
	$MgCl_2$	9.00	0.0972	2.61	0.29
	Na_2SO_4	7.02	0.1526	1.98	0.28
	$MgSO_4$	3.99	0.1711	0.84	0.21

*LMH: $Lm^{-2}h^{-1}$, gMH: $gm^{-2}h^{-1}$

3.2. Evaluation of the DS reconcentration in RO and NF processes

Table 4 shows the performance results of RO and NF processes obtained from the ROSA software. The RO process shows the highest removal efficiency of Na_2SO_4, which is around 99.9% followed by $MgCl_2$ and NaCl (99.9 and 99.6%, respectively). Therefore, when Na_2SO_4 is used as DS in the FO process, utilising the RO process as a DS recovery process would be more beneficial to obtain high quality of product water.

However, the NF processes with two different NF membrane modules of NF90 and NF270 show poor rejection rate of NaCl (87.1% for NF90 and 48.1% for NF270). This indicates that utilizing NaCl as DS in the FO process would result in poor rejection rates of the NF processes. Nevertheless, the NF processes show much higher rejection rates with Na_2SO_4, 96.5% for NF90 and 76.8% for NF270. These results indicate that the use of divalent ions in an FO hybrid system could be more advantageous as it shows lower DS loss in FO and higher rejection in RO/NF (Johnson et al., 2017). This confirms that the physio-chemical properties of the draw solutes including a high osmotic pressure, a low viscosity and a high diffusion coefficient are of paramount importance. The ROSA simulation input and output data are summarised in Table S7 in the SI.

Table 4. ROSA software simulation results of the RO and NF processes using different RO and NF membrane modules (Version 9.1, Filmtech Dow Chemicals, USA).

Membrane	Feed solution[a]	Rejection, %	Permeate, mg/L TDS
SW30HR-380	NaCl	99.6	23
	$MgCl_2$	99.9	10
	Na_2SO_4	99.9	8
NF 90-400/34i	NaCl	87.1	755
	$MgCl_2$	94.0	443
	Na_2SO_4	96.5	245
NF 270-400/34i[b]	NaCl[b]	48.1	3,024
	$MgCl_2$	46.8	3,947
	Na_2SO_4[b]	76.8	1,577

[a] The concentrations of the feed solution in RO and NF processes corresponded to the osmotic pressure of feed water in FO process under the osmotic equilibrium condition (≈ 3.96 bar).
[b] The ROSA was not able to conduct on NF270 with NaCl and Na_2SO_4 thus the RO experiments were conducted under the conditions of flow rate of 400 mL/min, temperature of 25˚C, membrane cell area of 0.0068 m^2 and operating pressure of 25 bar.

3.3. Environmental impact assessment of FO hybrid systems

3.3.1. Baseline environmental life cycle assessment

The environmental impact of FO-hybrid systems in terms of global warming (GW, kg CO_2-eq) was evaluated for the production of 100,000 m^3/day of reusable water. Fig. 3 shows the relative contribution analysis of the FO hybrid systems to GW impact without (Fig. 3 (a)) and with (Fig. 3 (b)) DS replenishment in the FO process.

Fig. 3 (a) clearly shows that the predominant contribution to the GW impact comes from FO membrane material required and RO and NF energy use for all hybrid systems. These results are similar to previous research conducted by other research groups (Coday et al., 2015, Hancock et al., 2012, Raluy et al., 2005).

However, in a closed-loop hybrid system, the draw solute loss during the system operation must be replenished to maintain the same initial DS concentration in the FO process

(Achilli et al., 2010, Holloway et al., 2015). Using a simple mass balance relationship in the FO process, the mass of the total draw solute replenishment ($m_{D,R}$, kg/d) was estimated using equations described in Table S2 in the SI. Fig. 3 (b) therefore shows that when considering the DS replacement for each hybrid system, the contribution of chemical use to the GW impact becomes significant compared to the results presented in Fig. 3 (a).

Specifically, the contribution of the total DS replenishment in FO-RO hybrid system with all DSs shows the lowest mainly because of the higher salt rejection in the RO process (i.e. the lowest draw solute loss via RO permeate). However, FO-NF hybrid systems with all DSs show the greatest increase in the total chemical contribution (FO and NF) to the GW impact. For example, the contribution of the chemical use in the FO-NF90 is around 30% while that in the FO-NF270 is around 55%. This is because the draw solute loss through NF permeate is more significant than RO permeate. Interestingly, Na_2SO_4 shows a slightly higher contribution to the GW impact despite its lower SRSF in FO and higher rejection rates in RO and NF. These results indicate that the manufacturing process required to produce Na_2SO_4 could have more negative impacts on the environment. Thus, the FO hybrid system with Na_2SO_4 does not appear environmentally favourable. Although the results suggest that the overall environmental impacts of all three hybrid systems would be attributed to the amount of DS replenishment needed, the DS replenishment cost in each hybrid process has to be considered as one of the main OPEX cost parameters (Achilli et al., 2010). Hence, a cost analysis of each hybrid system with different DSs will be discussed in the following Section 3.4.

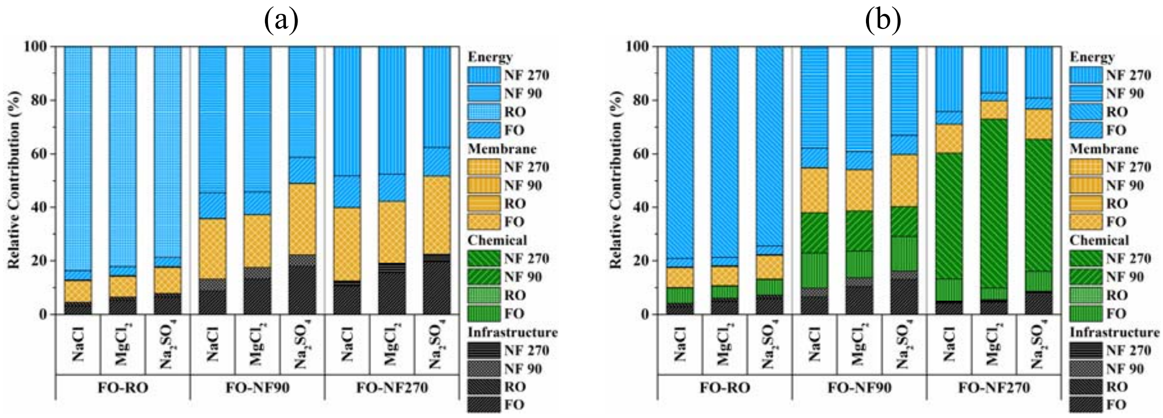


Fig. 3. Relative contribution analysis of various components of the FO-RO and FO-NF hybrid systems with different DSs to global warming impact (a) without DS replenishment and (b) with DS replenishment in FO hybrid systems.

3.3.2. Impact of operational adjustment of FO-NF hybrid systems

The required potable water quality targeted in this study was a TDS concentration of less than 500 mg/L (NHMRC 2011) whereas the required non-potable water quality was a TDS concentration of less than 1,000 mg/L, which can be applied for most turf grass irrigation (Holloway et al., 2016, Phuntsho et al., 2012 a). Although energy requirement of the FO-RO hybrid systems was higher than other hybrid systems, the final water quality was much lower than 500 mg/L TDS (data are shown in Table 4). Thus, this indicates that the final product water from the FO-RO hybrid system is reusable water (potable and/or non-potable). In this section, the initial performance of NF process with NF90 and NF270 membrane modules was therefore adjusted to achieve NF permeate quality as good as RO permeate (around 100 mg/L). Power consumptions for each FO-NF hybrid system were therefore estimated based on the final permeate target concentration of 100 mg/L TDS. There is a slight difference between the SEC of the FO hybrid systems due to the fact that the osmotic pressure of DSs is different under the similar TDS concentrations (as shown in Fig. S1 in the SI).

Fig. 4 (a) and (b) shows that the highest energy use and GW for the FO-NF hybrid systems with NaCl and $MgCl_2$ were calculated for a system operation with a final concentration of 100 mg/L and 0.6 M NaCl brine concentration. Whereas, the lowest energy use and GW impact were Na_2SO_4 before and after adjusting the process, and FO-NF hybrid systems are still lower than FO-RO hybrid systems. These results clearly show that NF membrane application in FO hybrid systems would be more promising to reconcentrate the draw solute at relatively lower energy consumption and with less environmental impacts.

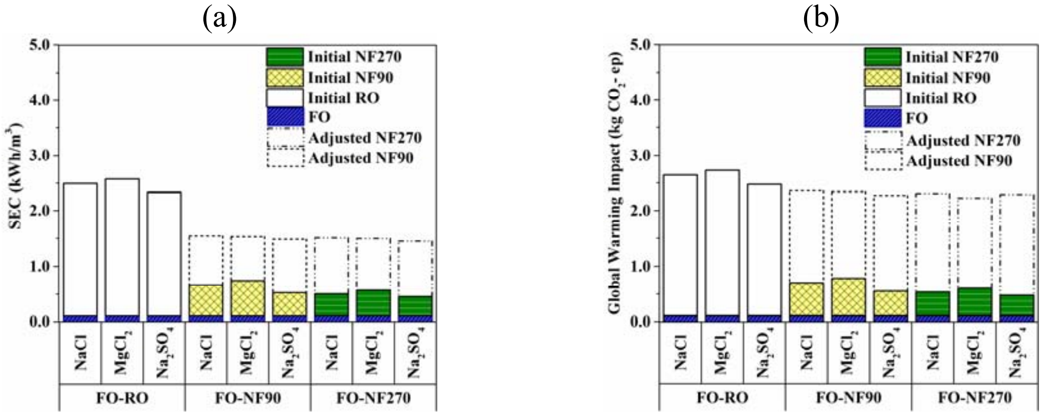


Fig. 4 Initial and adjusted (a) energy use and (b) global warming impact for FO-NF hybrid systems with different DSs. Target data: final product concentration of 100 mg/L TDS and brine concentration of 0.6 M NaCl (i.e. seawater osmotic pressure).

3.3.3. Impact of FO brine disposal on environmental potential

Energy and GW impacts were evaluated for FO hybrid systems by considering a direct discharge of brine into the oceans and using brine injection wells. The direct discharge to the sea was assumed to be a disposal at a pressure of almost 0 bar (referred to without FO brine disposal in Fig. 5) while the disposal pressure of deep well injections was assumed to be the one of FO brine concentrate at FO recovery rate of 50% in the FO process. The FO brine concentration was calculated using solute mass balance relationships described in Table S3 in the SI.

Fig. 5 shows the impact of FO brine disposal pressure on energy use and GW for all FO hybrid systems using different DSs. FO hybrid systems with NaCl showed the highest increase of the brine pressure on energy use and GW (6, 10, and 10% with RO, NF 90 and 270, respectively). In a closed-loop system, feed stream concentration increases over operation time due to increasing FO feed recovery and diffusing draw solutes from the draw side of membrane modules (Phuntsho et al., 2016). Such accumulated draw solute in the feed stream can be reduced by controlling the FO feed recovery rate (lower than 80% recovery rate) and using FO membranes with a high reverse flux selectivity such as a TFC FO membranes (Achilli et al., 2010, Phuntsho et al., 2016). It has to be acknowledged that a specific composition of FO brine is not considered in the current study due to the lack of real sample analysis and background data. Based on this study, further research needs to be conducted on the management of FO brine depending on its specific composition to prevent any additional environmental issues.

(a)

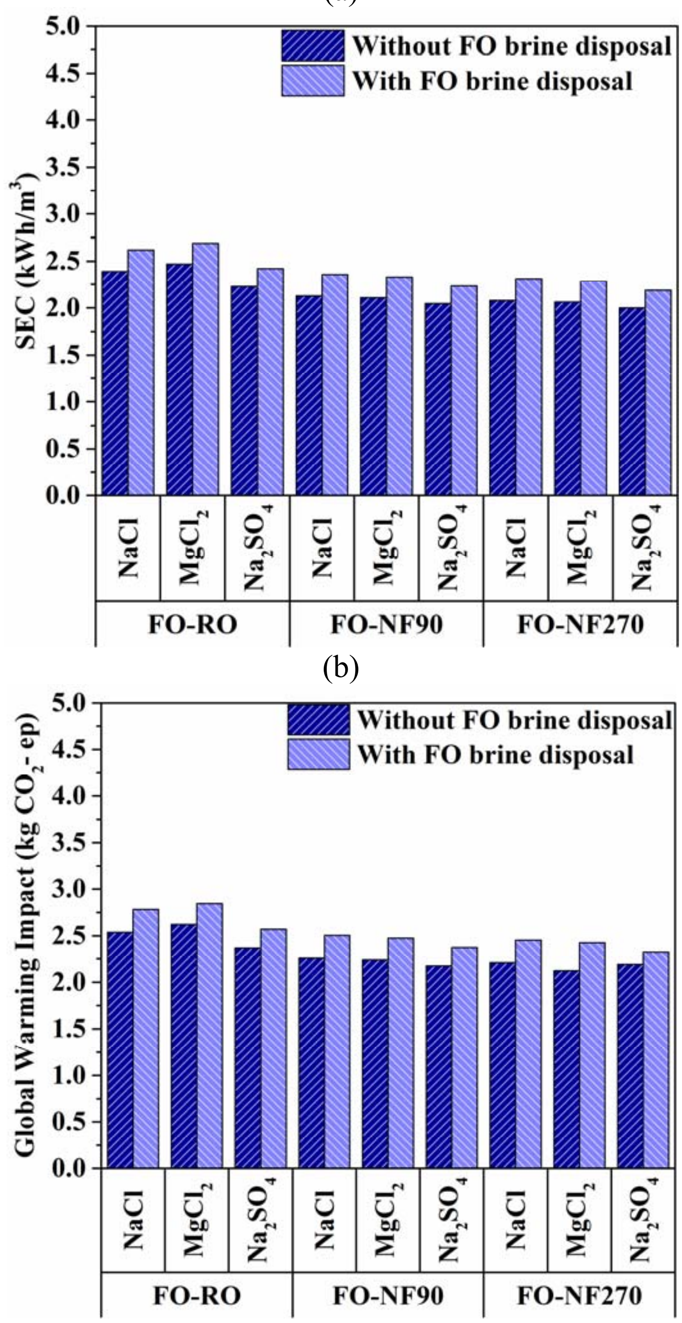


Fig. 5. The impact of FO brine disposal on (a) energy and (b) global warming per unit of water produced for each hybrid system with different DSs. FO brine disposal energy was calculated based on the optimised conditions of FO hybrid system: final product concentration of 100 mg/L TDS and brine concentration of 0.6 M NaCl (i.e. seawater osmotic pressure).

3.4. CAPEX and OPEX cost evaluation

The contribution of various components to the total water cost of each hybrid system was evaluated by assuming the whole hybrid process recovery of 50%. Detailed calculations on the CAPEX and OPEX can be found in Table S6 in the SI. Overall, Fig. 6 (a) shows that the CAPEX cost of FO hybrid systems was around 37.5% higher on average than that of SWRO due to the larger number of FO membrane modules required. However, the OPEX cost of FO hybrid systems was around 62% lower on average than that of SWRO due to lower operating energy requirement (no hydraulic pressure required).

More specifically, FO hybrid systems with $MgCl_2$ showed the highest OPEX cost and thus the highest total water cost (Fig. 6 (a)). As shown in Table 3, $MgCl_2$ had around 55% lower SRSF in the FO process and hence it can be clearly seen that the amount of $MgCl_2$ replenishment is considerably lower than that of NaCl. However, the FO hybrid systems with NaCl show the lowest total water cost. This is because the specific cost of $MgCl_2$ draw solute is around 67.0% higher than that of NaCl, thus leading to a significant cost for replenishing $MgCl_2$ in FO hybrid systems in the closed-loop operation.

In addition, although NaCl has the highest SRSF, FO hybrid systems with NaCl show the lowest total water cost. This is because NaCl produces higher water flux, resulting in the lowest contribution of FO membrane modules required to the total water cost. These results indicate that a DS with low initial cost and high water flux can provide a potential for further reducing the total water cost of an FO hybrid system.

Fig. 6 (b) shows the impact of SRSF on the OPEX cost of each hybrid system. SRSF values used for the baseline are shown in Table 3. It was assumed that the SRSF for each DS can be further reduced by using an FO membrane with higher selectivity and hence the SRSF was assumed to be 0.1 g/L for all DSs. It has to be noted that the additional energy cost to achieve the target product water (100 mg/L) was not considered to clearly see the benefit of having a low SRSF in the system. The result clearly indicates that the OPEX cost decreases with the reduction in the SRSF value at similar water flux with the baseline. For example, for NaCl, when the SRSF is down to 0.1 g/L, the OPEX cost of FO-RO hybrid system decreases from $0.22/m^3 to $0.16/m^3, which is around 30% reduction. In addition, for Na_2SO_4, which has the lowest SRSF value of 0.28 g/L, when the SRSF decreases from 0.28 to 0.1 g/L, the OPEX cost of FO-RO hybrid system decreases from $0.19/m^3 to $0.17/m^3 (i.e., 10% reduction). These results clearly show that decreasing the SRSF in the FO process can reduce the DS replenishment cost and thus the overall OPEX costs. From an economic aspect, this confirms that the specific DS cost plays a significant role in the OPEX cost in terms of the total chemical cost required. Therefore, these results suggest the need for draw solutes with lower SRSF, FO membranes with higher selectivity, and lower solute price for further reducing environmental and economic impacts of FO hybrid systems. However, it may be noted that when a similar rejection rate for FO, RO and NF membrane modules is considered, the loss of salt in the FO, RO and NF process is expected to be similar.

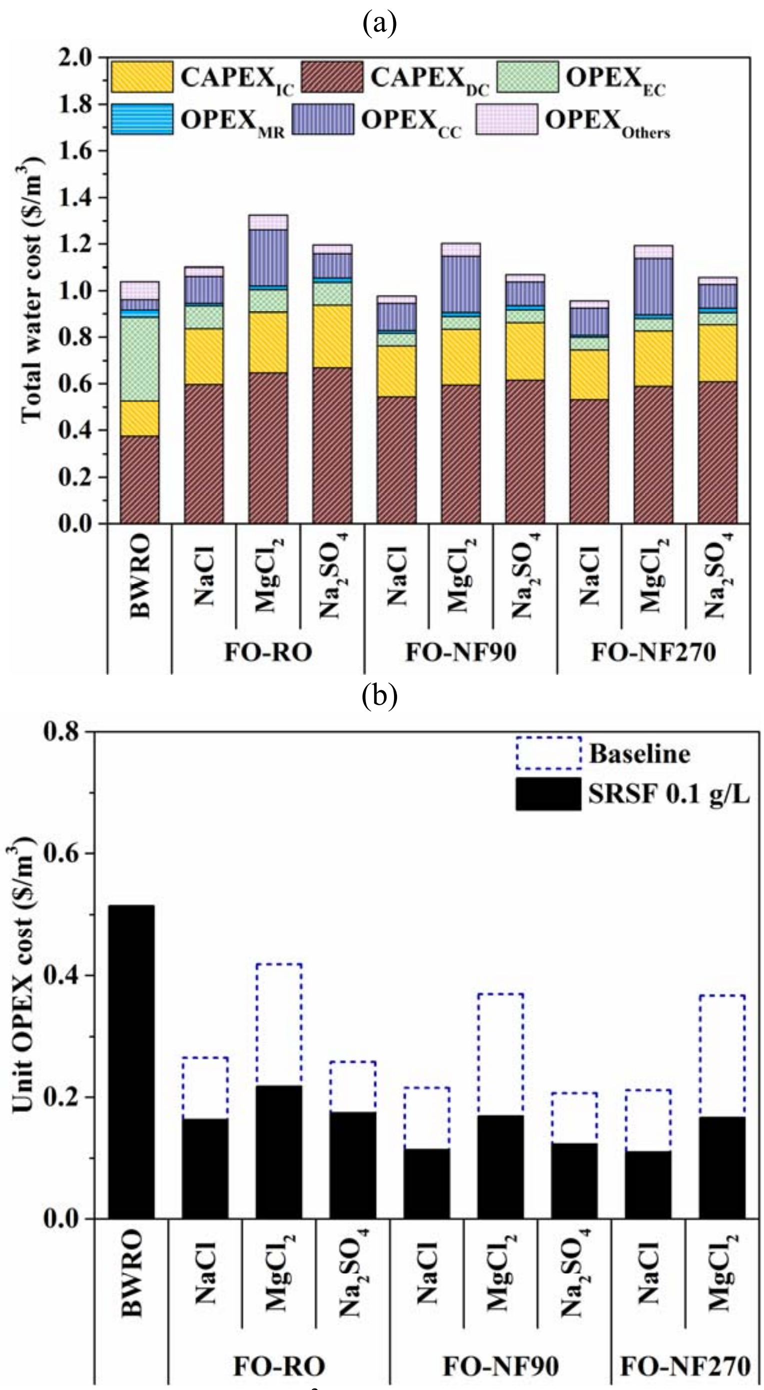


Fig. 6. (a) Life cycle cost analysis ($/m^3 water produced) and (b) impacts of SRSF on the OPEX cost of each hybrid desalination system based on a plant capacity of 100,000 m^3/d. The SRSF was down to 0.1 g/L for all DSs. N.B. IC: indirect capital cost, DC: direct capital cost, EC: energy cost, MR: membrane replacement cost and CC: chemical cost.

3.5. Impact of NF recovery rate on the total water cost of FO-NF hybrid system

RO and NF recovery rates are directly related to the water productivity of the FO process since higher recovery rate in RO and NF leads to higher recycled DS concentration. In

FO hybrid system under closed-loop operation, recovery rate of the DS reconcentration process is also an important factor to optimise to reach a cost effective FO hybrid systems.

Based on the environmental and economic analysis results presented in previous sections, FO-NF 90 has a great potential to be the most sustainable hybrid system for mine impaired water treatment. Fig. 7 shows a comparison of the total water cost for the FO-NF 90 hybrid system amongst the NaCl, $MgCl_2$ and Na_2SO_4 DS at different feed recovery rates 80% to 99%. The total water cost of the FO hybrid system decreased rapidly with an increase in the NF recovery rate however then gradually increased above the feed recovery rates of 90% for NaCl, 93% for $MgCl_2$ and 95% for Na_2SO_4. The optimum NF feed recovery rate was observed to be about 90% with a total water cost of AUD \$0.9/m3 for the FO-NF 90 hybrid system with NaCl. The optimum NF feed recovery rate of the FO-NF 90 hybrid system with Na_2SO_4, however, was observed to be about 95% with a total water cost of AUD \$0.98/m^3. Such high recovery rate would result in a proportionately higher concentration of the recycled DS, which in turn increases the osmotic driving force of the FO process.

As mentioned earlier, although DS loss through RO and NF permeate is not significant, it has to be included when calculating the total DS replenishment costs in the FO hybrid systems. Fig. 7 also shows the impact of NF permeate concentration on the total water cost of the hybrid systems. NF permeate quality was assumed to be 500 and 100 mg/L of TDS. Overall, the total water cost of the FO-NF 90 hybrid system, with all three DSs, increases with the increase in the NF permeate concentration to 500 mg/L. It can be clearly seen that NF membrane performance in terms of salt rejection can be a major contributor responsible for the total DS replenishment cost and thus the total water cost of FO hybrid systems. These results indicate that the DS performance and replenishment cost should be considered to select DS in the design of a real FO hybrid system.

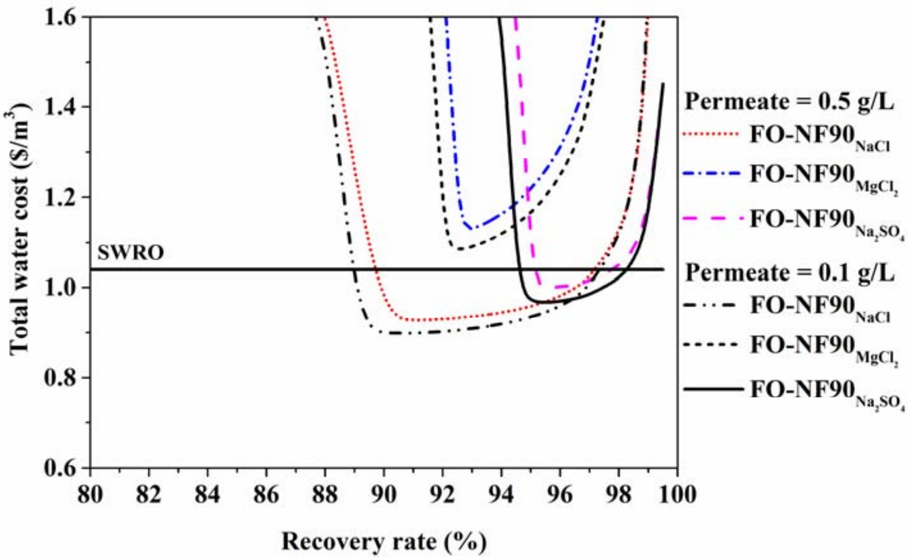


Fig. 7. Total water cost of the FO-NF90 hybrid system with different DSs (NaCl, $MgCl_2$, and Na_2SO_4) to produce 100,000 m^3/d.

4. Conclusions

The following conclusions have been drawn from this particular study:

- DS replenishment cost is one of the most important contributors to chemical and OPEX cost for a continuous closed-loop FO hybrid system which depends significantly on the salt selectivity of the FO and RO/NF membranes. NaCl shows the highest DS replenishment cost while its replenishment cost is lower than Na_2SO_4 and $MgCl_2$ because of its relatively lower loss of DS. Reducing the SRSF can result in further savings in OPEX cost for all hybrid systems and this finding underlines the importance of having a high salt selectivity of the FO membranes. Therefore, this study highlights the importance of improving the selectivity of the FO membrane and optimising the hybrid system for reducing the DS replenishment cost.
- In a closed-loop operation mode, the FO-NF90 hybrid system with Na_2SO_4 was observed to be environmentally and economically favourable for mine impaired water treatment application compared to the other DS options. The lowest OPEX cost including energy use and GW impact was observed for FO-NF90 hybrid system using

Na_2SO_4 as DS when the additional energy consumption in the NF process to achieve a final target concentration (similar to RO permeate) is considered.

- Although the contribution of the FO brine disposal pumping energy to the total energy and the GW impact was not significant, the impact of the FO brine on the economic and environmental impacts of the FO hybrid systems needs to be further investigated.

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References

Achilli, A.,Cath, T. Y. and Childress, A. E., 2010. Selection of inorganic-based draw solutions for forward osmosis applications. Journal of Membrane Science 364(1), 233-241.

Americanro 2016 Membrane cost.

Bai, H.,Liu, Z. and Sun, D. D., 2011. Highly water soluble and recovered dextran coated Fe3O4 magnetic nanoparticles for brackish water desalination. Separation and Purification Technology 81(3), 392-399.

Bigbrandwater 2016 Bigbrandwater.

Blandin, G.,Verliefde, A.,Comas, J.,Rodriguez-Roda, I. and Le-Clech, P., 2016. Efficiently Combining Water Reuse and Desalination through Forward Osmosis—Reverse Osmosis (FO-RO) Hybrids: A Critical Review. Membranes 6(3), 37.

Bowden, K. S.,Achilli, A. and Childress, A. E., 2012. Organic ionic salt draw solutions for osmotic membrane bioreactors. Bioresource technology 122(0), 207-216.

Cath, T.,Childress, A. and Elimelech, M., 2006. Forward osmosis: Principles, applications, and recent developments. Journal of Membrane Science 281(1-2), 70-87.

Chekli, L.,Phuntsho, S.,Shon, H. K.,Vigneswaran, S.,Kandasamy, J. and Chanan, A., 2012. A review of draw solutes in forward osmosis process and their use in modern applications. Desalination and Water Treatment 43(1-3), 167-184.

Chilton, C. H., 1950. Six-tenths factor applies to complete plant costs. Chemical Engineering 57(4), 112-114.

Coday, B. D.,Miller-Robbie, L.,Beaudry, E. G.,Munakata-Marr, J. and Cath, T. Y., 2015. Life cycle and economic assessments of engineered osmosis and osmotic dilution for desalination of Haynesville shale pit water. Desalination 369, 188-200.

Cornelissen, E. R.,Harmsen, D. J. H.,Beerendonk, E. F.,Qin, J. J. and Kappelhof, J. W. M. N., 2011. Effect of draw solution type and operational mode of forward osmosis with laboratory-scale membranes and a spiral wound membrane module. Journal of Water Reuse and Desalination 1(3), 133.

Deshmukh, A.,Yip, N. Y.,Lin, S. and Elimelech, M., 2015. Desalination by forward osmosis: Identifying performance limiting Parameters through module-scale modeling. Journal of Membrane Science 491, 159-167.

DowChemical 2017 FILMTEC Membranes - The Dow Chemical Company.

Filter, B. B. W. 2016 Membrane cost.

Ge, Q.,Ling, M. and Chung, T.-S., 2013. Draw solutions for forward osmosis processes: Developments, challenges, and prospects for the future. Journal of Membrane Science 442(0), 225-237.

Hancock, N. T.,Black, N. D. and Cath, T. Y., 2012. A comparative life cycle assessment of hybrid osmotic dilution desalination and established seawater desalination and wastewater reclamation processes. Water Research 46(4), 1145-1154.

Hancock, N. T. and Cath, T. Y., 2009. Solute coupled diffusion in osmotically driven membrane processes. Environmental science & technology 43(17), 6769-6775.

Hickenbottom, K. L.,Hancock, N. T.,Hutchings, N. R.,Appleton, E. W.,Beaudry, E. G.,Xu, P. and Cath, T. Y., 2013. Forward osmosis treatment of drilling mud and fracturing wastewater from oil and gas operations. Desalination 312, 60-66.

Holloway, R. W.,Maltos, R.,Vanneste, J. and Cath, T. Y., 2015. Mixed draw solutions for improved forward osmosis performance. Journal of Membrane Science 491, 121-131.

Holloway, R. W.,Miller-Robbie, L.,Patel, M.,Stokes, J. R.,Munakata-Marr, J.,Dadakis, J. and Cath, T. Y., 2016. Life-cycle assessment of two potable water reuse technologies: MF/RO/UV–AOP treatment and hybrid osmotic membrane bioreactors. Journal of Membrane Science 507, 165-178.

Johnson, D. J.,Suwaileh, W. A.,Mohammed, A. W. and Hilal, N., 2017. Osmotic's potential: An overview of draw solutes for forward osmosis. Desalination.

Li, X.-M.,Zhao, B.,Wang, Z.,Xie, M.,Song, J.,Nghiem, L. D.,He, T.,Yang, C.,Li, C. and Chen, G., 2014. Water reclamation from shale gas drilling flow-back fluid using a novel forward osmosis–vacuum membrane distillation hybrid system. Water Science & Technology 69(5), 1036-1044.

Liyanaarachchi, S.,Jegatheesan, V.,Muthukumaran, S.,Gray, S. and Shu, L., 2016. Mass balance for a novel RO/FO hybrid system in seawater desalination. Journal of Membrane Science 501, 199-208.

Lotfi, F.,Chekli, L.,Phuntsho, S.,Hong, S.,Choi, J. Y. and Shon, H. K., 2017. Understanding the possible underlying mechanisms for low fouling tendency of the forward osmosis and pressure assisted osmosis processes. Desalination In Press.

McGinnis, R. L.,Hancock, N. T.,Nowosielski-Slepowron, M. S. and McGurgan, G. D., 2012. Pilot demonstration of the NH_3/CO_2 forward osmosis desalination process on high salinity brines. Desalination 312, 67-74.

McGinnis, R. L.,Hancock, N. T.,Nowosielski-Slepowron, M. S. and McGurgan, G. D., 2013. Pilot demonstration of the NH3/CO2 forward osmosis desalination process on high salinity brines. Desalination 312(0), 67-74.

Moch, I.,Querns, W. R.,Steward, D.,Environmental Resources, T.,Water Treatment Engineering Research, T.,Water Desalination, R. and Development, P. 2008 WT Cost II modeling the capital and operating costs of thermal desalination processes utilizing a recently developed computer program that evaluates membrane desalting, electrodialysis, and ion exchange plants : case study for a seawater 20-million-gallon-per-day (MGD) hybrid system involving 10-MGD multistage flash distillation plus 10-MGD reverse osmosis, U.S. Dept. of the Interior, Bureau of Reclamation, Technical Service Center, Water and Environmental Services Division, Water Treatment Engineering Research Team ; Available through the National Technical Information Service, Denver, Colo.; Springfield, Va.

Mountain, B., 2012. Electricity prices in Australia: An International Comparison. A report commissioned by the Energy Users Association of Australia.

Phuntsho, S.,Kim, J. E.,Hong, S.,Ghaffour, N.,Leiknes, T.,Choi, J. Y. and Shon, H. K., 2017. A closed-loop forward osmosis-nanofiltration hybrid system: Understanding process implications through full-scale simulation. Desalination 421(Supplement C), 169-178.

Phuntsho, S.,Kim, J. E.,Johir, M. A. H.,Hong, S.,Li, Z.,Ghaffour, N.,Leiknes, T. and Shon, H. K., 2016. Fertiliser drawn forward osmosis process: Pilot-scale desalination of mine impaired water for fertigation. Journal of Membrane Science 508, 22-31.

Phuntsho, S.,Sahebi, S.,Majeed, T.,Lotfi, F.,Kim, J. E. and Shon, H. K., 2013. Assessing the major factors affecting the performances of forward osmosis and its implications on the desalination process. Chemical Engineering Journal 231(0), 484-496.

Phuntsho, S.,Shon, H. K.,Hong, S.,Lee, S.,Vigneswaran, S. and Kandasamy, J., 2012 a. Fertiliser drawn forward osmosis desalination: The concept, performance and limitations for fertigation. Reviews in Environmental Science and Bio/Technology.

Poullikkas, A., 2001. Optimization algorithm for reverse osmosis desalination economics. Desalination 133(1), 75-81.

PRé-Consultants, S., 1998. LCA software. The Netherlands (www. pre. nl/simapro/default. htm).

Pryshlakivsky, J. and Searcy, C., 2013. Fifteen years of ISO 14040: a review. Journal of Cleaner Production 57(0), 115-123.

Raluy, R. G.,Serra, L.,Uche, J. and Valero, A., 2005. Life Cycle Assessment of Water Production Technologies-Part 2: Reverse Osmosis Desalination versus the Ebro River Water Transfer (9 pp). The International Journal of Life Cycle Assessment 10(5), 346-354.

Tang, C. Y.,She, Q.,Lay, W. C. L.,Wang, R. and Fane, A. G., 2010. Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration. Journal of Membrane Science 354(1-2), 123-133.

Thiruvenkatachari, R.,Younes, M. and Su, S., 2011. Coal mine site investigation of wastewater quality in Australia. Desalination and Water Treatment 32(1-3), 357-364.

Valladares Linares, R.,Li, Z.,Yangali-Quintanilla, V.,Ghaffour, N.,Amy, G.,Leiknes, T. and Vrouwenvelder, J. S., 2016. Life cycle cost of a hybrid forward osmosis – low pressure reverse osmosis system for seawater desalination and wastewater recovery. Water Research 88, 225-234.

Wittholz, M. K.,O'Neill, B. K.,Colby, C. B. and Lewis, D., 2008. Estimating the cost of desalination plants using a cost database. Desalination 229(1–3), 10-20.

Yun, T.,Koo, J.-W.,Sohn, J. and Lee, S., 2015. Pressure assisted forward osmosis for shale gas wastewater treatment. Desalination and Water Treatment 54(4-5), 829-837.