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ABSTRACT

In this study, we propose a novel module design to integrate forward osmosis (FO) and membrane distillation (MD). The two processes are sealed in one module and operated simultaneously, making the system compact and suitable for a wide range of applications. To evaluate the system under large-scale module operating conditions, FO and MD experiments were performed separately. The effect of draw solution (DS) temperature on the FO performance was first assessed in terms of flux, reverse salt flux (RSF), and specific RSF (SRSF). While a higher DS temperature resulted in an increased RSF, a higher FO flux was achieved, with a lower SRSF. The influence of DS concentration on the MD performance was then investigated in terms of flux and salt rejection. High DS concentration had a slightly negative impact on MD water vapor flux, but the MD membrane was a complete barrier for DS salts. The FO-MD integrated module was simulated based on mass balance equations. Results indicated that initial DS (MD feed) flow rate and concentration are the most important factors for stable operation of the integrated module. Higher initial DS flow rate and lower initial DS concentration can achieve a higher permeate rate of the FO-MD module.

INTRODUCTION

The continuous increase in fresh water demand together with the high energy requirements and investment costs of conventional desalination technologies drive the need to diversify water resources (e.g., wastewater reuse) in order to secure a more sustainable water supply for the future.¹ Emerging membrane-based desalination treatment technologies such as forward osmosis (FO) and membrane distillation (MD), which have several advantages over conventional desalination processes, are facing several challenges for their scale-up.²⁻⁴

Significant progress has been achieved in the development of such emerging technologies which consume less electrical energy and may use low-grade thermal energy, such as waste heat, low enthalpy geothermal energy, or solar-thermal energy ⁵, and may be substituted for conventional processes or have potential niche applications such as water extraction and valuable mineral recovery from desalination brines or treatment of hypersaline wastewater.⁶⁻⁸ Moreover, these non-pressure driven processes potentially require inexpensive polymeric membranes, inexpensive (non-pressurized) module materials, and reduced amounts of chemicals for their operation and cleaning compared to conventional processes.⁹

FO is an osmotically driven membrane-based separation process. The driving force in FO is an osmotic gradient created by the osmotic pressure of a high concentration stream or higher ionic strength solution (draw solution, DS) and a low concentration feed water flowing on both sides of the membrane in a counter or co-current mode.¹⁰ Among a variety of possible applications, FO can be used in a direct or indirect desalination mode, i.e., to directly treat seawater (where a higher-concentration solution is used as DS while seawater is FS) or to indirectly desalinate seawater where wastewater or any other impaired-quality water source with a lower-salinity functions as feed solution (FS) while seawater is DS.⁶ However, in either mode, FO is considered as a pretreatment process because fresh water recovery is not completed in one-step (i.e., not a stand-alone process). After the FO step, the DS needs to be regenerated and separated from the diluted DS, which is one of the main drawbacks of FO. DS regeneration is a costly and energy-intensive process, especially in direct FO where a high energy process (e.g., thermal) is required ¹¹ while in the indirect mode, a low-pressure reverse osmosis (LPRO) system can be used to treat the diluted seawater which makes it a more effective and economical process.¹² FO membranes can achieve very high rejection of salts, natural organic matter (NOM)

including biopolymers and humic substances, but they are not a total barrier for all contaminants (e.g., FO can achieve 100% rejection of trace metals, up to 99% rejection of COD and phosphate, and 60–70% rejection of ammonium and total nitrogen).¹³

On the other hand, MD is a thermally driven membrane-based separation process. The driving force for MD is the partial vapor pressure difference created by the temperature difference across the membrane to drive the water vapor from the hot stream to the other side of the microporous hydrophobic membrane through dry pores so that it condenses on the permeate side. MD yields product water with high quality, with 99.99% salt rejection achieved for different seawater qualities.¹⁴ Furthermore, MD is less significantly affected by very high feed water salinity than other membrane technologies, proven for desalination brines, produced water, and hypersaline waters ^{11, 15, 16}, while producing high quality distillate, with a conductivity below 10 $\mu\text{S}/\text{cm}$, without observing severe fouling and scaling.^{16, 17} Therefore, MD has a great potential to be integrated with FO, especially to regenerate the FO DS. In addition, even though MD is considered a high thermal energy-consuming process, the utilization of low grade waste heat can enable a low energy desalting process.¹⁸

Due to the many advantages and the potential applications in hybridizing FO with MD, several groups have proposed to combine these processes or integrate FO with other technologies (multi-hybrid processes) and tested them for different applications.^{19, 20} The first proposed generation of the FO-MD hybrid system consists of two separate loops with separate FO and MD modules, where the FO DS collected in the DS tank is fed to the MD module, as shown in **Fig. S1**.^{11, 21-24} However, such a limited integration of two processes can also lead to high capital cost, potentially limiting its commercialization.¹⁹

A very interesting and more integrated design combining FO and MD sealed in one module, offering additional advantages such as more compact, smaller foot print, and low-cost system, has been proposed in a patent by Cath et al.²⁵ (**Fig. 1**) and investigated by others.²⁶⁻²⁸ The integrated module captures the complementary advantages provided by FO and MD in a single step. However, this hybrid system has a serious potential problem associated with the configuration having the FO DS and the MD FS flowing in the same channel simultaneously, i.e., the same stream in contact with the MD and FO membranes, as shown in **Fig. 1**, resulting in a diminished performance of both processes. The temperature of the MD FS can be significantly reduced via the heat transfer to both FO FS and MD permeate, which results in a decrease in MD performance; and the high inlet temperature of the FO DS can potentially damage the FO membrane. Consequently, these processes cannot operate under optimum conditions, as discussed in detail in the next section along with the description of the proposed concept and objective of this study.

Figure 1. Schematic diagram of the FO-MD integrated module patented by Cath et al.²⁵ and investigated by others.²⁶⁻²⁸

THE PROPOSED OSMOTICALLY AND THERMALLY ISOLATED FO-MD INTEGRATED MODULE

A schematic diagram of the novel FO-MD integrated module proposed in this study is presented in **Fig. 2**. As mentioned above, since FO and MD are osmotically and thermally driven processes, respectively, their performances are higher when FO DS concentration and MD feed temperature are higher, respectively.^{9, 10} The newly proposed integrated module has two separated flow channels within the same module, separating the FO DS and MD feed streams using an isolation barrier inserted inside the module with an opening on the top, allowing the MD brine (MD outlet) to flow in the FO DS inlet side, as shown in **Fig. 2**. This feature makes the integrated module osmotically and thermally isolated, leading to a higher efficiency of both processes. Since MD is a thermally driven process, temperature has a significant impact on its performance. However, the loss of heat during MD operation has been a challenge for MD scale-up.²⁹ In the prior FO-MD integrated module (**Fig. 1**), since there is no separation between the FO DS and MD feed streams, the heat of MD feed can be lost via diffusion to the FO FS, and thus lead to a reduction of heat, consequently affecting MD water vapor flux. In the novel conceptual design proposed, the MD feed enters the first channel which is in contact with the MD membrane only, allowing full benefit of the maximum available temperature. Besides the benefit of temperature, the novel module also exhibits a benefit of hydrodynamics: the open channel area of the novel osmotically and thermally isolated FO-MD system is two times smaller than the hybrid system (shown in **Fig. 1**) without an isolation barrier; consequently, considering the same

flow rate, the crossflow velocity of both streams can be two times higher, leading to higher shear forces and fouling/scaling mitigation.³⁰

Figure 2. Schematic diagrams of the osmotically and thermally isolated FO-MD integrated module patented by Ghaffour et al.³¹. Two concepts of MD brine flowing to the FO DS side are possible: (a) internal and (b) external using a water-box typically used in MSF condensers. The isolation barrier could be designed to act as a turbulence promoter in one or both sides as desired, e.g., zigzag, sinusoidal, twisted helical baffles, spacers etc.

Afterwards, the MD brine (outlet of the first chamber) having lower temperature and higher concentration, with values depending on the MD water vapor flux, module length and other operating parameters, enters the second chamber (FO DS side) which is in contact with the FO membrane only, enabling the FO process to run under optimum conditions, i.e., higher salinity (with increase in mass transfer due to higher driving force) and lower temperature but high enough to derive the benefit of higher water flux^{32,33}, as explained above. The FO DS discharge is then recirculated in the MD channel for fresh water recovery and/or blended with

MD feed/FO DS to increase the overall recovery of the system depending on the application used. Similarly, MD could be operated in either a closed loop for recovery and reuse of FO DS or an open loop with optional water supply, i.e., make-up water (not shown in the figure for simplicity). It should be noted that the proposed FO-MD integrated module is different from an MD module and an FO module connected in series. The absence of the outer connection between FO and MD modules is not only beneficial to eliminate the additional pumping and piping but also to eliminate the heat loss and pressure drop through pipes, thereby reducing the overall cost and enhancing energy efficiency. Furthermore, all of the suggested FO-MD hybrid systems connected in series in a separate loop use an intermediate tank, which could be an environment conducive to bacterial growth.³⁴

Therefore, the introduced isolation barrier provides a synergistic advantage to not only prevent mixing of FO permeate, minimizing dilution and cooling of the MD feed but also maintaining the driving forces of both FO and MD processes as maximized, leading to an increase in the production capacity and efficiency of the whole system. Another advantage is to design the isolation barrier with different geometries to act as a turbulence promoter, e.g. zigzag, sinusoidal, twisted helical baffle types, in one or both sides (MD, FO, or both as required), to enhance the process performance by decreasing the concentration polarization and temperature polarization phenomena.³⁵ Turbulence inside the module can also be created using spacers in any channel of both processes.

Together, the FO and MD membranes act as a double barrier to reject contaminants, organics and inorganics from the impaired-quality water (FO feed), and guarantee a high-quality product water. MD has a constraint in the rejection of volatile compounds and the presence of surfactants can accelerate deterioration of MD performance.^{23, 36} However, the FO-MD hybrid

can compensate for the individual weakness of FO and MD membranes and hence enhances the rejection of all contaminants.^{23, 37}

The proposed FO-MD integrated module (**Fig. 2**) is expected to exhibit lower capital and operational costs than the two-loop FO-MD hybrid system (**Fig. S1**) and the typical FO-MD integrated module (**Fig. 1**). The FO-MD integrated module does not need additional pumps, pipes, an intermediate tank and other relevant equipment to assure the flow circulation in both modules.²⁵ In addition, the FO-MD integrated module requires one vessel while the two-loop hybrid system requires the installation of the FO and MD membranes in separate vessels. The higher performance of the proposed integrated module can also reduce the required membrane surface area compared to the typical integrated module.

This study aims to design and optimize a novel osmotically and thermally isolated FO-MD integrated module based on experiments and simulation. For this objective, the effect of DS temperature and concentration on the FO performance was investigated in terms of water flux, reverse salt flux (RSF), and specific RSF (SRSF). In conjunction, the MD performance was evaluated in terms of water vapor flux and salt rejection. Operational parameters (e.g., FO and MD recovery rates, initial DS flow rate, and initial DS concentration) were evaluated via simulation based on mass balance equations in order to optimize the design of the FO-MD integrated module. These parameters were selected because they are important operational parameters for FO and MD processes.³⁸ In order to evaluate the performance of this concept under large-scale operating conditions (i.e., enough variation of concentration and temperature along both FO and MD channels, which cannot be obtained using a small scale integrated module) and obtain necessary data for the simulation, FO and MD experiments were conducted separately using lab-scale modules in which inlet conditions were varied.

MATERIALS AND METHODS

FO and MD membranes. A cellulose triacetate (CTA) FO membrane embedded in a woven polyester mesh, provided by Hydration Technology Innovations (USA), was used in this study. A hydrophobic polytetrafluoroethylene (PTFE) membrane with 0.22 μm average pore diameter was purchased from Millipore (Germany) and utilized for MD experiments. The detailed characteristics of these commercial membranes can be found elsewhere.^{39, 40}

FO experiments. All FO experiments were carried out using a lab-scale FO system similar to the one described elsewhere.³⁹ The FO cell had two symmetric channels; 100 mm long, 20 mm wide, and 3 mm deep; on both sides of the membrane for each FS and DS. Variable speed gear pumps (Cole-Parmer, USA) were used to provide cross-flows under counter-current directions at a cross-flow velocity of 8.5 cm/s. DS temperatures were set at 20 °C, 30 °C, 40 °C, and 50 °C with a fixed FS temperature of 20 °C. FO operations were carried out using 1 M MgCl_2 as DS and DI water as the FS under the AL-FS (i.e., active layer facing FS) mode of membrane orientation. Despite a variety of novel draw solutes proposed in other studies^{41, 42}, inorganic draw solutes are still advantageous due to their high water flux and low cost. In this study, MgCl_2 was selected as the DS owing to its relatively low RSF, low fouling and scaling potential, and its amenability to re-concentration by MD.⁴³ 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 weight changes were recorded by a computer in real time at 3-minute intervals to determine the water flux. At the end of each experiment, the FS and DS solutions were sampled and then concentrations of Mg^{2+} and Cl^- ions were analyzed by inductively coupled plasma – mass spectrometry (ICP-MS, Agilent Technology 7500 series, USA) and ion

chromatography (ICS-1600, DIONEX, USA), respectively. Equations for the calculation of water flux, RSF, and SRSF are presented in the Supporting Information (SI).

MD experiments. The MD experiments were performed with a lab-scale direct contact MD (DCMD) system used in our previous study.³⁰ The MD module had two symmetric channels; 77 mm long, 26 mm wide, and 3 mm deep; on both sides of the membrane. Variable speed gear pumps (Cole-Parmer, USA) were used to provide cross-flows under counter-current directions at a cross-flow velocity of 8.5 cm/s. Transmembrane temperatures were set at 20 °C, 40 °C, and 60 °C with a fixed coolant temperature of 20 °C. MD operations were carried out using MgCl₂ having different concentrations (35 g/L, 60 g/L and 140 g/L, equivalent to 0.37 M/L, 0.62 M/L and 1.44 M/L, respectively) as feed and DI water at 20 °C was used as coolant. Different low concentrations of MgCl₂ were selected to investigate the effect of FS concentration on MD performance since low concentration is preferred in the MD inlet (especially at high range of concentration, see **Fig. 5**) and the solution is further concentrated along the MD feed channel. Both solutions were recirculated in a closed-loop system resulting in a batch-mode process operation. The permeate tank was placed on a digital balance and weight changes were recorded by a computer in real time at 3-minute intervals to determine the water vapor flux. A conductivity meter (HACH, Germany), connected to a computer, was used to monitor the conductivity in the permeate tank.

Mass balance simulations. The novel osmotically and thermally isolated FO-MD integrated module consists of MD and FO membranes, an isolation barrier, and flow channels for the FS, DS and MD permeate. DS flows from the inlet of the MD feed channel to the outlet and proceeds to the FO DS flow of the FO-MD module while the FS and the permeate flow are designed to occur in a counter-current mode. Thus, the DS before entering into the module and

the DS at the end of the MD membrane can be considered as MD FS and MD brine, respectively. The loss of draw solutes caused by RSF through the FO membrane is replenished by adding draw solutes. Simulations are entirely based on an ideal mass balance model in a closed FO-MD module by assuming FO and MD membranes as a black box. A steady-state flow with net build-up of volume was also assumed, making FO and MD permeates the same as the module capacity. A schematic diagram of the mass balance of the hybrid system and expected concentration and temperature profiles in both channels is presented in **Fig. 3**. Only rejection rates and recovery rates of both FO and MD membranes are used as membrane properties for the simulations. In the present study, the flow of feed solutes is neglected since FO has a high rejection rate due to the hindrance effect of RSF on the transport of feed solutes.⁴⁴ A 100% salt rejection by MD is considered, which is confirmed from our experimental results. Rejection properties can be assumed to be constant even though they may vary slightly in reality. Details of the mass balance simulations are presented in the Supporting Information and the simulation conditions are summarized in **Table S1**. Simulation were conducted according to the following algorithm (**Fig. S2**) using Microsoft Excel software.

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pressure and (ii) an increase in diffusivity. High temperature induces an increase in osmotic pressure according to the modified van't Hoff equation, resulting in an increase in the driving force of FO. The diffusivity of draw solutes can also be influenced by an increase in DS temperature according to the Stokes-Einstein equation; this can reduce the mass transfer resistance and thus decrease the internal concentration polarization (ICP), enhancing the effective concentration gradient across the active layer of the FO membrane. As a result, water flux increased as DS temperature increased.

$$J_w = A[\pi_{D,b} \exp(-J_w K) - \pi_{F,b} \exp(J_w/k)] \quad (1)$$

$$K = S/D \quad (2)$$

where $\pi_{D,b}$ and $\pi_{F,b}$ are the osmotic pressure of DS and FS, respectively, K is the mass transfer resistance of the support layer, S is the structural parameter of the support layer, and D is the diffusivity of DS. **Fig. 4b** also shows that RSF increased from 86.9 mg/m²/h to 117 mg/m²/h with an increase in DS temperature from 20 °C to 50 °C. RSF is theoretically governed by the DS concentration as well as the membrane structural and solute rejection properties. An increase in DS temperature can raise the diffusivity of draw solutes, thereby mitigating the ICP phenomenon and thus enhancing the effective concentration gradient across the active layer. Consequently, an increase in DS temperature results in more reverse diffusion of draw solutes to the FS side.

In order to further examine the relative transport of water and draw solutes under varying DS temperatures, SRSF, defined as the ratio of RSF to water flux in **Eq. (S3)**, was calculated experimentally using the measured values of water flux and RSF, and results are presented in **Fig. 4b**. Although both RSF and water flux increased as shown in **Fig. 4a**, SRSF decreased by

290 14.12% with increasing DS temperature up to 40 °C, where the lowest SRSF (8.29 mg/L) was
291 observed, indicating higher pure water extraction compared to the loss of draw solutes. SRSF is
292 influenced by operating temperature based on the theoretical equation, as given by **Eq. (S3)**.
293 When varying DS temperature with fixed FS temperature, the temperature of the active layer
294 under the AL-FS mode is minimally changed, thereby inducing no/low change in the intrinsic
295 properties (i.e., water and salt permeabilities) of the active layer.³² Nevertheless, as this equation
296 is also governed by DS temperature ⁴⁶, SRSF can be decreased with an increase in DS
297 temperature, consistent with our results. However, when DS temperature was further increased
298 up to 50 °C, draw solutes more readily diffused to the FS side than water flux, likely because of
299 the increased permeability of the draw solutes at higher temperature, thereby leading to a slight
300 increase (2.99%) in SRSF. In addition, a high standard deviation of SRSF at 50 °C indicates
301 instability of the FO membrane. Other studies have observed a decrease in solute rejection for
302 RO ⁴⁷ and an increase in RSF in FO at higher temperature.³³ From these results, we can conclude
303 that FO should be operated at 40 °C to achieve favorable water flux and reasonable RSF as well
304 as high stability. This brine temperature range is considered to be reasonably achievable in large-
305 scale MD modules due to heat loss through MD membrane even though MD FS has a higher
306 temperature than optimum FO FS (40 °C).

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Figure 4. Effect of FO DS temperature on (a) water flux and RSF, and (b) SRSF. Experimental conditions for FO experiments: DI water as FS; 1 M MgCl_2 as DS; cross-flow velocity of 8.5 cm/s; and variable DS temperatures (20 °C – 50 °C) with fixed feed temperature (20 °C).

From these results, it can be inferred that the flow direction can also be an important factor for the FO-MD integrated module. If DS with low temperature is fed into the FO channel, it should be heated before the MD inlet, which is challenging to achieve inside the FO-MD module (a configuration with a water-box could be possible). Moreover, a condition with low water flux and high SRSF at low DS temperature requires a larger module size and a larger amount of solute for DS replenishment. In order to resolve this issue, DS temperature should be high enough to obtain high water flux and low SRSF for FO. Furthermore, DS temperature should be higher to operate MD, considering heat loss through the FO membrane. This can also cause an unstable FO operation by exceeding the recommended maximum working temperature of the CTA FO membrane (45 °C) as well as significant loss of draw solutes by higher SRSF. This issue can be resolved by simply operating with proper flow direction, as presented in **Figs. 2** and **3**. High MD feed temperature helps to produce high water vapor flux and effectively concentrate DS for better FO operation. Along the MD module channel, DS temperature will

decrease due to the heat loss and then the desired DS temperature (less than 45 °C) will be fed into FO channel. Moreover, high MD feed temperature can result in a low specific thermal energy consumption (STEC) due to high water vapor flux and high water recovery rate.⁴⁸

MD performance: Effect of feed temperature and concentration on water vapor flux and salt rejection. To evaluate the MD performance in the FO-MD integrated module, MD experiments were carried out by varying feed temperature and concentration. As has been widely reported for different applications, **Fig. 5** shows that when feed temperature increased, water vapor flux exponentially increased from 16.6 L/m²/h at a transmembrane temperature difference (ΔT) of 20 °C to 102 L/m²/h at $\Delta T = 60$ °C, as per the effect of salt concentration on vapor pressure theory (see **Fig. S1**).⁴⁹ The increment of water flux (513%) was smaller than that of the partial vapor pressure difference (1,040%), likely due to temperature polarization caused by heat transfer from the feed to the permeate.⁵⁰

The effect of MD feed concentration on water flux was further investigated with varying concentration (i.e., MgCl₂ = 0 g/L, 35 g/L, 60 g/L, and 140 g/L) to investigate the interplay between FO and MD. Results presented in **Fig. 5** show that water vapor flux decreased when increasing the feed concentration at all ranges of feed temperatures (i.e., $\Delta T=20$ °C, 40 °C and 60 °C); the decrease was more pronounced at higher temperatures, which is consistent with other studies⁵¹ because a change in FS concentration can influence partial vapor pressure. Results shown in **Fig. S3** reveal that water vapor pressure slightly decreased with increasing feed concentration (over the indicated range) since higher concentrations decrease vapor pressure, especially at higher temperatures. As a result, increasing the feed concentration results in a significant reduction in water vapor flux. However, during all experiments, no change of the

permeate conductivity was observed, indicating a complete rejection (100%) of draw solutes even at higher concentrations. Results of the present study imply that low feed concentration which is achieved through dilution of the FO DS in the FO channel would be beneficial for the MD performance, thereby enabling a more efficient and compact FO-MD integrated module.

It should be noted that flow direction can significantly influence sustainability of the MD membrane performance. Pore wetting of the MD membrane is governed by the hydraulic pressure represented by the liquid entry pressure (LEP).⁵² If the DS flows from FO membrane to MD membrane, the inlet pressure of MD is determined by the FO performance. However, if the DS flows from the MD membrane to the FO membrane, the inlet pressure can be controlled by adjusting DS flow rate, thereby providing better control of pore wetting.

Transmembrane temperature difference, ΔT (°C)

Figure 5. Effect of feed temperature on water vapor flux in MD. Experimental conditions for MD: MgCl₂ feed solution (i.e., 35 g/L 60 g/L and 140 g/L); cross-flow velocity = 8.5 cm/s; and variable feed temperature (i.e., 40 °C, 60 °C and 80 °C) at constant coolant temperature (20 °C).

Simulation of a closed-loop FO-MD integrated module. To evaluate the novel FO-MD integrated module, simulations were carried out based on mass balance equations varying four different parameters; FO and MD recovery rates, initial DS flow rate, and initial DS concentration; as shown in **Table S1**. Initial FS concentration and flow rate were 10 mM NaCl and 10 m³/d, respectively. SRSF of the FO membrane and salt rejection of the MD membrane were determined as 0.08293 g/L at 40 °C and 100%, respectively, based on results presented in the previous section. It was assumed that the permeate rate in FO is identical to that in MD for no net change in initial DS flow rate, as shown in **Eq. (S4)**. In addition, the ratio of initial DS flow rate to initial FS flow rate, representing the DS/FS ratio, was employed to understand the operation of the FO-MD module. It is important to note that the initial DS flow rate and concentration correspond to initial flow rate and concentration of the MD FS in the module.

In order to evaluate the effect of MD recovery rate on the performance of the FO-MD integrated module, FO recovery rate and achievable permeate rate (same as the module capacity) of the integrated module were first simulated with varying initial DS flow rates (the DS/FS ratio) with results presented in **Fig. 6a**. Both FO recovery rate and permeate rate increased as MD recovery rate increased. It is noteworthy that the DS/FS ratio should be higher than 1.0 to achieve maximum permeate rate. If initial DS flow rate is lower than initial FS flow rate, the MD cannot produce a permeate rate as high as initial FS flow rate since the DS is treated by MD prior to FO, thereby resulting in a low module capacity. The DS concentration (MD brine) in the middle area of the module between FO and MD was then simulated to confirm whether the concentrated DS can be supplied to FO or not. Interestingly, **Fig. 6b** indicates that MD recovery rate should not exceed approximately 0.83 because MgCl₂ crystals can be formed at the end of MD membrane due to MgCl₂ solubility (58.9 g/100 mL water at 40 °C) as shown in **Fig. S4**.

This result implies that the DS/FS ratio should be higher than 1.25 to achieve a high recovery rate (close to 1.0) without the formation of MgCl_2 crystals. The DS loss rate was further simulated for economic evaluation. Results of **Fig. 6b** show that the trend of DS loss rate (same as the replenishment rate) is consistent with that of the permeate rate, as shown in **Fig. 6a**. This is because DS loss rate is a function of SRSF (the ratio of RSF to water flux) and thus the permeate rate determines DS loss rate as depicted in **Eq. (S15)**.

The DS flow rate in the middle area of the module was also evaluated as presented in **Fig. 6c**. This figure can represent the change of flow rate through FO and MD membranes since the flow rate decreases along the MD membrane and then it increases along the FO membrane when increasing the recovery rate of the module. It should be noted that DS flow rate determines crossflow velocity in the module, which influences concentration and temperature polarization near the membrane surface.⁵³ Therefore, a high DS flow rate can lead to low concentration and temperature polarization. However, **Fig. 6c** shows that high initial DS flow rate (the DS/FS ratio of 2) not only has a maximum MD recovery rate of 50% but also results in a rapid decrease in DS flow rate. This implies a potential rapid change of the MD performance via increased concentration and temperature polarization.⁵⁰ Also, the pressure on the draw side of FO membrane can be increased by increased flow rate, thereby resulting in a decrease in water flux due to the decrease of the driving force.²⁰ In addition, a high flow rate requires high electric energy consumption. On the other hand, a low initial DS flow rate can have not only low recovery rates of both FO and MD (**Fig. 6c**) but also low performance due to serious concentration and temperature polarization.^{53, 54} Consequently, it can be concluded that the DS/FS ratio should be ranged approximately from 1 to 1.5 to achieve high MD recovery rate and high flow rate at the same time.

Figure 6. Effect of MD recovery rate on (a) FO recovery rate (left axis, colored lines) and permeate rate (right axis, colored dotted-lines), (b) DS concentration in the middle area of the module (left axis, dotted-line) and DS loss rate (right axis, colored lines), and (c) DS flow rate in the middle area. Simulation conditions: initial FS concentration of 10 mM NaCl, initial FS flow rate of 10 m³/d, initial DS concentration of 1 M MgCl₂ (95.2 g/L), and SRSF of 0.08293 g/L at 40 °C DS. The permeate rates of both FO and MD were assumed to be same.

To further investigate the effect of FO recovery rate, MD recovery rate and the final permeate rate (same as the module capacity) were also simulated with different DS/FS ratios.

Fig. 7a show that the permeate rate is linearly related with FO recovery rate, which is consistent with **Fig. 6a**. Thus, the balance of permeate rate between FO and MD is one of the key factors for the FO-MD integrated module. The results of **Fig. 7a** also indicate that a high DS/FS ratio is beneficial to achieve high MD recovery rate as well as high permeate rate. To determine the maximum FO recovery rate in terms of MgCl_2 solubility, DS concentration in the middle area of the module was simulated as presented in **Fig. 7b**. The result suggests that initial DS flow rate should be high enough for high FO recovery rate. DS loss rate was also simulated as a function of FO recovery rate. As discussed above, since the permeate rate of both FO and MD is directly related to FO recovery rate, DS loss rate linearly increases as FO recovery increases. However, since DS loss rate is inevitable in FO, a method to further reduce SRSF should be developed.

Fig. 7c presents the effect of FO recovery rate on DS flow rate in the middle area of the module. As discussed above, high DS flow rate is desired to enhance both FO and MD performances. However, high DS flow rate requires high energy consumption for the circulation.⁵⁵ Therefore, the DS flow rate needs to be optimized by considering electric energy consumption and the performance of both FO and MD.

Figure 7. Effect of FO recovery rate on (a) MD recovery rate (left axis, colored lines) and permeate rate (right axis, dotted-line) of the integrated module, (b) DS concentration in the middle area of the module (left axis, colored lines) and DS loss rate (right axis, dotted-line), and (c) DS flow rate in the middle area. Simulation conditions: initial FS concentration of 10 mM NaCl, initial FS flow rate of 10 m³/d, initial DS concentration of 1 M MgCl₂ (95.2 g/L) and SRSF of 0.08293 g/L at 40 °C DS.

Lastly, to investigate the effect of initial DS concentration on the FO-MD module, DS concentration at the end of the MD membrane in the module was simulated as a function of recovery rate with fixed initial DS flow rate, the same as initial FS flow rate (i.e., 1.0 DS/FS ratio). **Fig. 8** indicates that initial DS concentration has a significant impact on limitation of the recovery rates for both FO and MD. The results show that lower DS concentration can induce higher recovery rate (higher permeate rate) since it can reach a concentration close to the maximum solubility of MgCl₂ in the DS at high recovery rate as shown in **Fig. 7**. Additionally, it was found that initial DS concentration does not influence DS loss rate because DS loss rate is a function of the permeate rate, as shown in **Eq. (S15)**. The strategies of the DS replenishment warrant further discussion. The DS replenishment consists of two steps: (i) recovery of the DS

loss amount and (ii) recovery of the DS temperature. Because of the linear relationship between DS loss and recovery rate, the specific replenishment cost of the DS loss is constant. The specific cost of the DS temperature recovery may be significantly influenced by the recovery rate because the latter affects the desired inlet temperature. Duong et al.⁵⁶ reported that a 20~50% recovery rate achieved the lowest specific thermal energy consumption for seawater desalination. However, a more accurate evaluation should be carried out via a pilot-scale study.

Figure 8. DS concentration at the end of MD membrane and DS loss rate (dotted-line) with varying initial DS concentration. Simulation conditions: initial FS concentration of 10 mM NaCl, initial FS flow rate of 10 m³/d, initial DS flow rate of 10 m³/d, and SRSF of 0.08293 g/L at 40 °C DS.

From the simulation results, it can be concluded that high DS flow rate is beneficial for high recovery rate in the FO-MD integrated module and has two potential merits: (i) high MD water vapor flux, and (ii) low temperature polarization. In the case of high DS flow rate, an

474 increase in DS concentration will be low even at high MD recovery rate; this induces stable
475 operation of MD due to less impact of high concentration on water flux as discussed in previous
476 sections. Since high DS flow rate induces a high cross-flow velocity, the heat transfer coefficient
477 in the MD feed channel can be enhanced, and hence water vapor flux can be increased. High
478 cross-flow velocity can also mitigate membrane fouling in MD.^{30, 57} The effect of high DS flow
479 rate on FO performance merit further consideration. Since membrane minimal fouling occurs on
480 the DS side due to the permeate flow direction, high DS flow rate is not an important factor for
481 membrane fouling in FO.⁵⁸ On the other hand, high flow rate can enhance water flux by a
482 reduction of ICP.^{54, 59} Also, if DS flow rate is too high, the energy requirement for circulating the
483 solution in the module could be high. Therefore, initial DS flow rate should be optimized for the
484 successful operation of the FO-MD integrated module. The results of the simulations also imply
485 that the FO and MD recovery rates may not be important to operate the FO-MD module since the
486 permeate rate is dominantly governed by initial DS flow rate as well as initial DS temperature
487 fed into MD. In addition to initial DS flow rate, initial DS concentration should be low for high
488 recovery rate. However, this can lead to low water flux in FO and high water flux in MD as
489 discussed in the previous sections, thereby resulting in an imbalance of the permeate rate
490 between FO and MD. Varying membrane surface area of both processes could be used to reach a
491 balance. A more rigorous theoretical model aiming to deeply examine and optimize the
492 performance of a larger-scale integrated module is under development and will be reported in
493 future work. Findings from the present study have significant implications for optimizing the
494 novel FO-MD integrated module proposed. The novel FO-MD integrated module can have
495 relevance for small-scale or mobile water treatment plants for, e.g., the treatment of hypersaline
496 wastewater from shale gas fracking because of the easier control of membrane fouling and high

rejection of volatile compounds and other toxic metals. In addition, waste heat which is often available in industrial areas can reduce the energy consumption.⁶⁰ However, since the simulations were carried out via simple mass balance models, the actual FO-MD integrated module will be further examined, including membrane fouling and cleaning, with the treatment of hypersaline wastewater containing volatile compounds and contaminants in the future. In addition, an economic analysis will be also carried out based on operation of a pilot-scale FO-MD integrated module.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: calculations of experimental water flux, RSF and SRSF; derivation of mass balance equations for simulating the FO-MD integrated module; schematic diagram of a typical FO-MD hybrid system (Figure S1); simulation algorithm of a closed-loop FO-MD integrated module (Figure S2); effect of MgCl_2 concentration on vapor pressure (Figure S3); solubility curve of MgCl_2 (Figure S4); and simulation conditions for the FO-MD integrated module (Table S1) (PDF)

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Notes

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