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*Desalination and Water Treatment*
www.deswater.com
doi: 10.1080/19443994.2016.1180642

XX (2016) XX–XX
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# Forward osmosis process for supply of fertilizer solutions from seawater using a mixture of draw solutions

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Received 8 January 2016; Accepted 15 April 2016

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## ABSTRACT

Novel desalination approaches are required to provide both drinking and agricultural water as there is ever increasing stress upon precious freshwater resources. It was our hypothesis that a modified Forward Osmosis (FO) process had the potential for production of irrigation water comprising of appropriate concentrations of fertilizers from a seawater feed. Four agents, $KNO_3$, $Na_2SO_4$, $CaNO_3$, and $MgCl_2$, plus 35 g/L seawater were used as the draw and feed solutions of the FO process. Net Driving Pressure in the FO process was manipulated either by increasing the concentration of draw solution (FO process) or by increasing feed pressure (Pressure Assisted FO (PAFO) process). A series of nanofiltration (NF) and reverse osmosis (RO) membranes were used for the regeneration of draw solution. The results suggested that a PAFO process was more energy efficient than simple FO, provided the energy relating to the brine flow from the NF/RO membrane for pressurizing the feed solution of PAFO process was used. Furthermore, this study suggested using a mixture of a primary draw solution, $MgCl_2$, and a secondary draw solution, $KNO_3$, for $NO_3$ supply into the irrigation water was preferable. As such, $MgCl_2$ provided the driving force for fresh water extraction while $KNO_3$ was the source of fertilizer in the irrigation water. Results showed that water quality provided by application of a $MgCl_2 + KNO_3$ draw solution was better than that from $KNO_3$ or $Ca(NO_3)_2$. The concentrations of $NO_3$ and $SO_4$ in irrigation water were within recommended levels when the diluted draw solution was regenerated by a dual stage low-pressure RO process.

*Keywords:* Forward osmosis; Irrigation water; Draw solution; Fertigation; Regeneration

## 1. Introduction

The general shortage of water globally has the potential to negatively impact farming and agricultural activities [1–3]. Compounding the issue of lack of water resources is the problem of groundwater contamination which further exacerbates the availability for irrigation purposes [4–6]. Several countries have resorted to tertiary treated wastewater effluent as an alternative to fresh water for irrigation [7,8]. Unfortunately, there have been a number of concerns raised against wastewater applications in agriculture such as:

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detrimental impact upon chemical and physical properties of soil; inhibition of plant growth and yield; groundwater contamination; and, microbial contamination of the receiving soil [9,10]. Desalination of seawater has been proposed for freshwater supply in arid and semi arid regions which suffer from water shortage. Seawater desalination has also been proposed for irrigation water supply using Reverse Osmosis (RO) and thermal evaporator systems such as multi-stage flash (MSF) and multi-effect distillation (MED) [11–13]. Despite the lower desalination cost involved with the RO process, it suffers from a number of drawbacks such as production of a brine discharge and relatively high power consumption [7,8].

In recent years, there has been a growing interest in Forward Osmosis (FO) processes as a method for seawater desalination [9,10]. The main issues to solve are the quality of the membrane and the type and regeneration process of the draw solution employed to drive the separation mechanism [11,12]. Thermal (MED and MSF) and membrane processes (RO, Nanofiltration (NF), and Membrane Distillation (MD)) have been suggested for the regeneration of draw solution [13]. RO was demonstrated for high purity recovery and regeneration of NaCl and $MgCl_2$ draw solutions used for seawater desalination [14,15]. For brackish water desalination, NF membrane was used for freshwater extraction and $MgSO_4$ draw solution regeneration [14–16]. Furthermore, MD membranes were suggested for the regeneration of thermolytic draw solution such as ammonium-based compounds [17]. Potential advantages of the membrane distillation process relate to low power consumption, reduced susceptibility to fouling and less intensive feed pretreatment technologies. However, membrane distillation exhibits limited water recovery rates and the energy requirement for recovery of the draw solution may negate other benefits [18–20].

FO has been suggested for irrigation water supply using a suitable fertilizer draw agent and saline water as the draw and feed solutions, respectively [21–23]. The latter approach has not only been proposed to reduce the cost of seawater desalination, but also to produce high-quality irrigation water. A custom-designed draw solution which is a concentrated fertilizer solution to extract fresh water from seawater has the advantage of removing the requirement for costly recovery of the draw solution [21,23]. After FO treatment, the draw solution would be less concentrated but still sufficient for direct irrigation use. A source of freshwater, therefore, should be available for adjusting the concentration of the fertilizer draw solution before application on the field (Fig. 1). In water scarcity regions, a RO desalination plant, therefore, is required to provide fresh water for the dilution of fertilizing water. Unfortunately, this increases the cost of seawater treatment with fertilizing water supply. For low salinity brackish water and low quality wastewater, the diluted draw solution can be further treated by NF for draw solution regeneration and fertilizing water production [24].

Sahebi et al. [23] investigated the feasibility of a pressure-assisted FO (PAFO) process for irrigation water supply. A net hydraulic pressure between 1 and 10 bar was applied on the feed side of the FO membrane to promote membrane flux beyond the osmotic equilibrium. Different draw and feed concentrations were evaluated and the membrane flux was measured at variable feed pressures. The higher membrane fluxes recorded were attributed to the increased net driving pressure (NDP) across the FO membrane. The outlined study suggested that no further membrane treatment process was required for the fertilizer draw solution. However, the desalination strategy was only feasible with low salinity feed waters such as brackish waters. In such cases, the fertilizer draw solution would probably be suitable for direct field application. At higher feed solution concentrations, freshwater flux across the membrane had a limited dilution effect on the draw solution and further treatment was required before use. PAFO is not suitable for seawater feed solutions in its current state of development due to the high draw solution concentrations required for seawater treatment.

The application of FO process for fertilizer solution supply was demonstrated in previous studies [22]. However, a source of fresh water was required for the dilution of concentrated draw solution before the field application. Unfortunately, this is not always feasible in water stressed regions, which makes the process more complicated. This study investigated the feasibility of using a novel FO-membrane hybrid system for irrigation water supply from seawater. A series of membrane processes were applied for the regeneration of FO draw solution and fertigation water supply. Depending on the type of draw solution, high rejection and water permeability NF/Brackish Water RO (BWRO) membrane systems were used for draw solution regeneration and reuse. A number of draw solutions consisting of single or multiple compounds were evaluated for seawater desalination by the FO process. For ionic species that have low rejection rate by NF and BWRO membrane such as $NO_3^-$, a mixture of two chemical agents was suggested as the draw solution. The mixture consisted of (i) a primary draw solution, such as $MgCl_2$, of high osmotic pressure to provide the osmotic driving force for the FO process (ii) low concentration secondary additive, such as $KNO_3$, to

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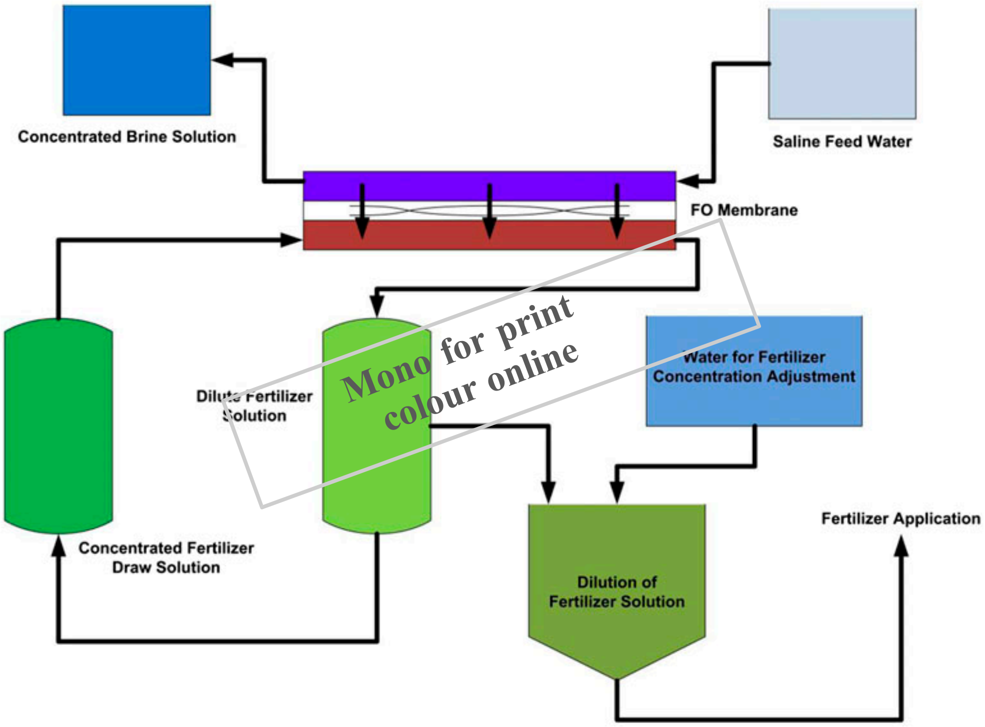

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Fig. 1. Conceptual design of fertilizer draw solution FO process.

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provide nutrients in the irrigation water. The primary draw solution represented the majority of draw solution concentration while the secondary additive forms a small percentage (less than 3%) of the total draw solution concentration. A series of NF and BWRO membranes of different permeabilities and rejection rates were selected for the regeneration process; these membranes have: (i) high rejection rate to the ionic species of the primary draw solution; (ii) low rejection rate to the ionic species of the secondary draw solution. Therefore, careful attention should be paid to the process of selecting the primary and secondary draw solutions. For example, $NO_3^-$ and $K^-$ ions have lower rejection rate by the membrane than $Mg^{2+}$ and $Cl^-$ ions; when $NO_3^-$ ions cross the membrane, K ions follow because of their low rejection rate by the membrane whereas $Mg^{2+}$ ions are rejected by the membrane. It should be mentioned that the positive charges should balance the negative charges in solution to maintain the electroneutrality of the solution.

A comparison between the PAFO and FO processes was carried out to underline the advantages and disadvantages of each method. Reverse Osmosis System Analysis (ROSA) and pre-developed FO software were used to estimate the performance of NF/BWRO and FO membranes, respectively [14]. ROSA software can reliably estimate the performance of a membrane system and be applied for system design [17,25]. $KNO_3$, $Na_2SO_4$, $CaNO_3$, and $MgCl_2$ were evaluated as potential draw agents of the FO process. However, not all of these chemical agents are suitable for FO seawater treatment and subsequent regeneration of membrane processes. Therefore, the present study evaluated the feasibility of using not only single draw agents, but also mixtures for fertilizer water supply based on the TDS and composition of product water. The concentrations of $NO_3^-$, $K^+$, $SO_4^{2-}$, $Ca^{2+}$, and $Mg^{2+}$ ions in treated water were estimated by ROSA software. It should be noted that ROSA was applied to demonstrate the initial performance of membranes and more experimental work is required in the future to confirm the applicability of this system.

## 2. Methodology

Previous work suggested that a dual stage NF-BWRO membrane system may be more energy efficient than a conventional RO system [25]. Fig. 2(A) and (B) show the proposed FO-membrane hybrid system for irrigation water supply. NF and BWRO membranes of high water permeability were proposed for the regeneration of draw solution. The impact of: draw solution concentration; draw solution type; and

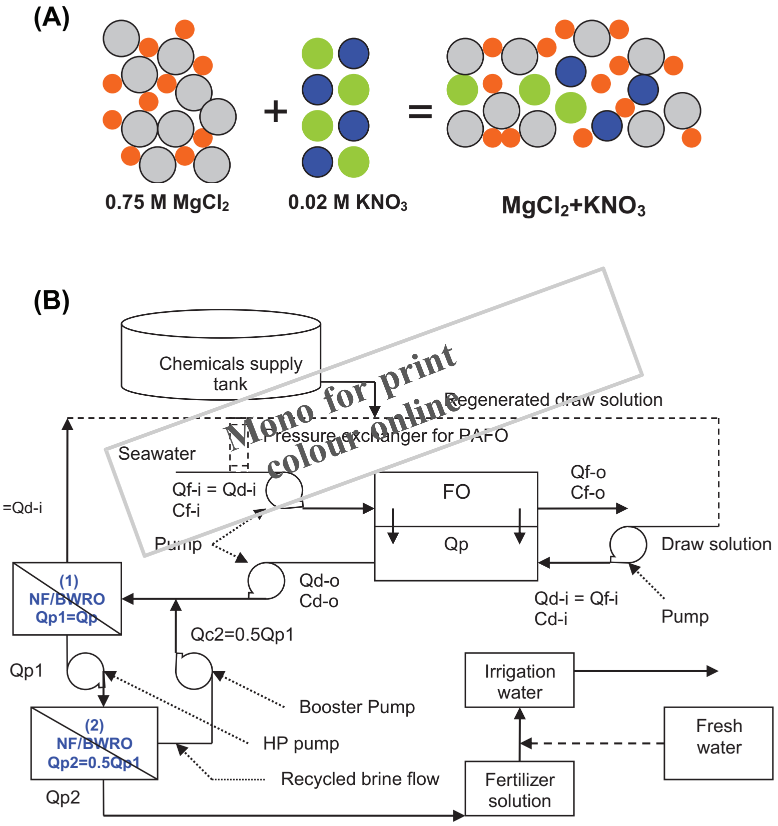

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Fig. 2. Proposed FO system for supply of fertilizer solutions.

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identity of the NF/RO membranes in the regeneration system, upon the quality of irrigation water was investigated. Seawater, TDS 35 g/L, was used as the feed for the FO process. Furthermore, the net hydraulic pressure was in the range 0–16 bar, and was applied on the feed side of the FO membrane to promote freshwater flux. A pressure-assisted FO (PAFO) process has been previously suggested for enhancing the process performance [23].

### *2.1. Process modeling*

The purpose of the FO-membrane hybrid system was to provide nutrient rich irrigation water which could be either directly applied onto a field to accelerate crop growth or used with minimal treatment. Salts such as $KNO_3$, $Na_2SO_4$, $Ca(NO_3)_2$, and $MgCl_2$ were used as the draw solution in the FO process as they not only are highly water soluble, but also necessary for stimulating plant development [22,23]. As shown in Fig. 2, the draw solution entered the FO membrane for freshwater extraction from seawater feed solution. Water flux induced by osmotic pressure across the membrane diluted the draw solution which was then introduced to a series of membrane treatment stages for regeneration and irrigation water extraction. To keep the system balanced, it was assumed that the FO recovery rate was equal to that of the regeneration unit. Depending on the type of draw solution, two-stage membrane treatment could be applied for draw solution regeneration using high permeability and water flux membranes (Fig. 2). The concentrated brine from the first NF/BWRO membrane treatment was recycled back to the FO as the draw solution whereas the permeate flow went to a second membrane system for further treatment. Permeate from the second NF/BWRO membrane system forms the irrigation water while concentrated brine was recycled to the first stage membrane treatment unit. This approach will reduce the power consumption required for feed solution treatment in the regeneration stage. As a matter of fact, first stage membrane treatment is more energy intensive and it is designed for re-concentrating the draw solution, while the second stage is less power intensive than stage one and it is mainly designed for permeate polishing. Two different methods were adopted to promote water flux in the FO process: (i) using different draw solution concentrations (FO process); and (ii) applying hydraulic pressure on the feed side to promote water permeation across the FO membrane (PAFO process). In the first method, draw solution concentrations between 0.75 and 0.95 M (osmotic pressure between 53 and 68 bar) were used to increase freshwater permeation across the FO membrane (Table 1). Consequently, the power consumption of the regeneration process was expected to increase with increasing concentration of the draw solution.

In the second regeneration method, a positive hydraulic pressure, PAFO process, was applied on the feed solution to enhance water permeation across the FO membrane. Based on this method, the concentrated brine from the first regeneration membrane treatment stage returned to the FO membrane to exchange pressure with the FO feed solution. The range of hydraulic pressure applied on the feed side of the PAFO process was between 0 and 16 bar. Water flux, $J_w$ (L/m$^2$ h), in the FO process was estimated from Eq. (1) [26]:

$$J_w = A_w \left( \frac{\pi_{Db} e^{\left(\frac{-J_w}{k}\right)} - \pi_{Fb} e^{(J_w K)}}{1 + \frac{B}{J_w}\left(e^{(J_w K)} - e^{\left(\frac{-J_w}{k}\right)}\right)} \right) \tag{1}$$

In Eq. (1): $A_w$ is the membrane permeability coefficient (L/m$^2$ h bar), $\pi_{Db}$ and $\pi_{Fb}$ are the osmotic pressures of the bulk draw and feed solution, respectively (bar); $k$ is the mass transfer coefficient (m/s); $B$ is the solute permeability coefficient (kg/m$^2$ h); $K$ is the solute resistivity for diffusion within the porous support layer (s/m) defined as the ratio of the membrane structure parameter, $S$ (μm), to the solute diffusion coefficient, $D$ (m$^2$/s) (Eq. (2)):

$$K = \frac{S}{D} \tag{2}$$

For a PAFO process, the relevant equation should include the hydraulic pressure, $P$ (bar), on the feed side of the membrane as shown in Eq. (3):

$$J_w = A_w \left( \frac{\pi_{Db} e^{\left(\frac{-J_w}{k}\right)} - \pi_{Fb} e^{(J_w K)}}{1 + \frac{B}{J_w}\left(e^{(J_w K)} - e^{\left(\frac{-J_w}{k}\right)}\right)} + \Delta P \right) \tag{3}$$

Table 1
Concentration and osmotic pressure of draw agents

| | | | | | |
|---|---|---|---|---|---|
| $MgCl_2 + KNO_3$ | | | | | |
| Concentration (mol/L) | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 |
| Osmotic pressure (bar) | 54.21 | 57.76 | 61.30 | 64.85 | 68.40 |
| $Na_2SO_4$ | | | | | |
| Concentration (mol/L) | 0.75 | 0.80 | 0.85 | 0.90 | 0.95 |
| Osmotic pressure (bar) | 53.23 | 56.79 | 60.34 | 63.88 | 67.44 |

In Eq. (3), $P$ is the hydraulic pressure on the feed side (bar). It should be mentioned that Eqs. (1) and (3) were used to estimate water flux in the FO and PAFO, respectively, using a flat sheet plate and frame testing unit. In contrast to the FO process, the driving force in the RO system is the hydraulic pressure on the feed side (Eq. (4)):

$$J_w = A_w \times (\Delta P - o \times \Delta\pi) \tag{4}$$

where $\sigma$ is the membrane reflection coefficient. Eq. (4) was used to predict the performance of NF/RO membrane in the regeneration unit using ROSA software. Reverse salt diffusion, $J_{s-r}$ (kg/m$^2$ h), from the draw to the feed solution side was estimated from Eq. (5):

$$J_{s-r} = B \left( \frac{C_{Db} e^{\left(\frac{-J_w}{k}\right)} - C_{Fb} e^{(J_w K)}}{1 + \frac{B}{J_w}\left(e^{(J_w K)} - e^{\left(\frac{-J_w}{k}\right)}\right)} \right) \tag{5}$$

where $C_{Db}$ and $C_{Fb}$ are the bulk concentrations of the draw and feed solutions, respectively (mg/L). Van't Hoff's equation was applied for prediction of the osmotic pressure of the draw solution (Eq. (6)):

$$\pi = \eta i C R T \tag{6}$$

where $\eta$ is the osmotic coefficient; $i$ number of ions; $C$ is solute concentration in mol/L; $R$ is the gas constant (L atm K$^{-1}$ mol$^{-1}$) and $T$ is temperature in Kelvin (273 + °C). The recovery rate (%*Re*) of the FO and RO processes was the ratio of permeate flow rate to feed flow rate (Eq. (7)):

$$Re = \frac{Q_p}{Q_f} \times 100 \tag{7}$$

where $Q_p$ and $Q_f$ are the permeate and feed flow rates (m$^3$/h). It should be mentioned that FO and RO systems in Fig. 2 have the same recovery rates; i.e. $Q_{p1} = Q_p$. The recovery rate of the first regeneration stage was equal to that of the FO system. Permeate from the first regeneration stage went to a second NF/regeneration stage which operated at 50% recovery rate, while the concentrated brine returned to the first regeneration stage for feed flow dilution. Finally, specific power consumption, *Es* (kWh/m$^3$), was estimated for the NF and RO membrane of the regeneration system according to Eq. (8):

$$Es = \frac{P_f}{\eta \times Re} \tag{8}$$

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In Eq. (8), $P_f$ is the feed pressure (bar) and $\eta$ is the pump efficiency (assumed 0.8 here). The types of membranes used for the regeneration of draw solution were entirely selected based on the molecular size of draw solution and membrane rejection rate. A number of chemical compounds which are essential for the plants growth were considered.

The types of membranes used for the regeneration of draw solution were entirely selected based on the molecular size of draw solution and membrane rejection rate. A number of chemical compounds which are essential for the plants growth were considered.

Fig. 3(A), shows a FO process for seawater treatment and draw solution regeneration using a mixed draw solution. $NO_3^-$ has a moderately low rejection rate by NF and BWRO membranes. Therefore, it was introduced through a mixture of high osmotic pressure draw solution, also called a primary or carrier draw agent, and a low concentration $KNO_3^-$ compound was added as a secondary draw agent for $NO_3^-$ supply (Fig. 3(A)). The carrier draw agent was highly rejected by NF/BWRO membrane and it constituted the main solute in the draw solution for freshwater extraction from seawater. As shown in Fig. 3, $MgCl_2$ and $KNO_3$ were introduced to the FO membrane as the primary and secondary draw agents, respectively. High permeability NF membrane was applied in the first regeneration stage for the rejection of $MgCl_2$ while most of the $KNO_3$ was expected to cross the membrane. The concentrate from stage one was the draw solution for the FO process, whereas the permeate went to a second regeneration stage for further treatment. In the second regeneration stage, BWRO membrane was introduced for not only $KNO_3$ rejection but also adjustment of the concentration of irrigation water to an acceptable level.

$Na_2SO_4$ was suggested as the main draw solution for $SO_4^{2-}$ ions supply for irrigation water because of its high osmotic pressure and solubility in water (Fig. 3(B)). Furthermore, $SO_4^{2-}$ compounds were highly rejected by NF membranes, hence a two-stage NF separation process was designed for $Na^-$ and $SO_4^{2-}$ ions separation and recycling. $Na^+$ ions were partially rejected by the first NF membrane stage while most of the $SO_4^{2-}$ species were rejected by the membrane. In the second NF membrane stage, the concentration of $Na^+$ and $SO_4^{2-}$ were further reduced to a desirable level. Using two-stage NF membranes was expected to reduce the power consumption and the regeneration cost of $Na_2SO_4$.

Two-stage BWRO membrane treatment was applied for the regeneration of $Ca(NO_3)_2$ draw solutions (Fig. 3(C)). $Ca(NO_3)_2$ was proposed for $NO_3^-$ ion supply as an alternative to $MgCl_2 + KNO_3$ mixture. High rejection BWRO membrane was used in both stage one and two for draw solution regeneration.

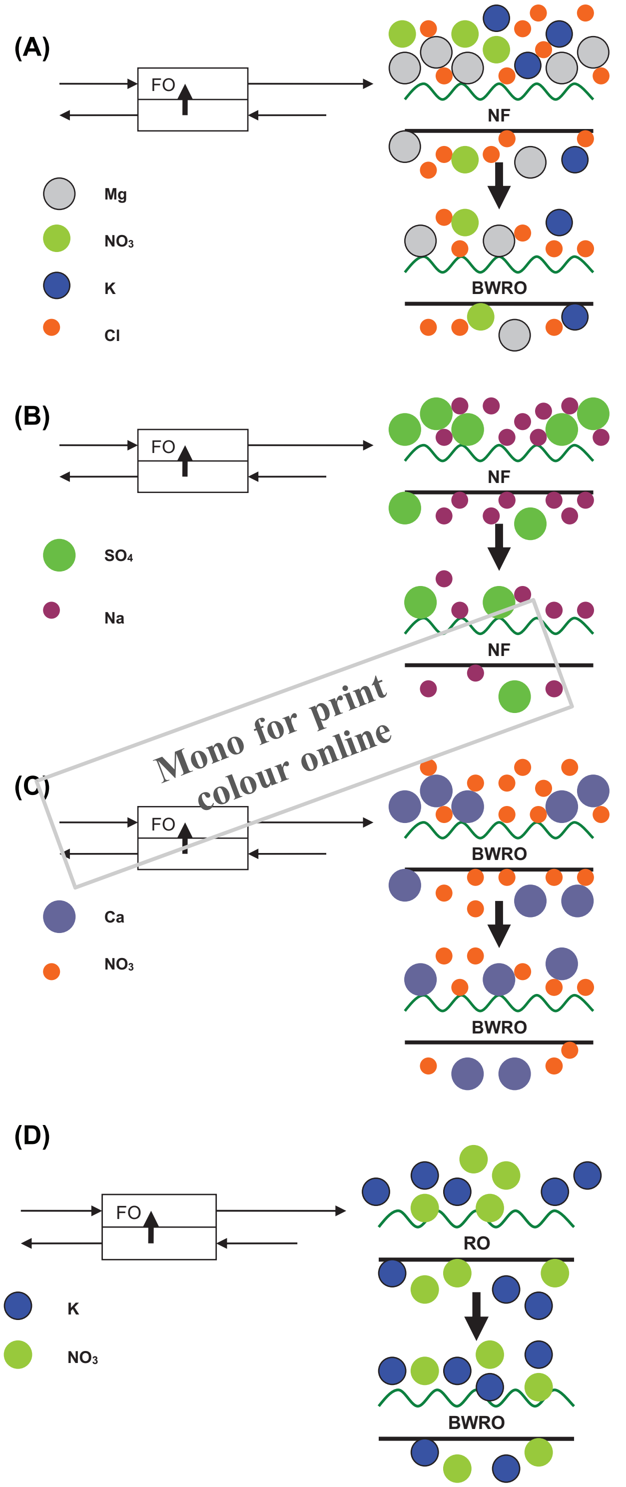

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Fig. 3. Draw solution regeneration and recycling process using two-stage NF/BWRO treatment (A) $MgCl_2$ and $KNO_3$ draw solution, (B) $Na_2SO_4$, (C) $Ca(NO_3)_2$, and (D) $KNO_3$.

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Table 2
Seawater ions composition of total TDS 35,000 mg/L

| | K | Na | Mg | Ca | $HCO_3$ | Cl | $SO_4$ |
|---|---|---|---|---|---|---|---|
| Concentration (mg/L) | 387 | 10,778 | 1,293 | 421 | 142 | 19,406 | 2,710 |

Table 3
The testing parameters for model calibration

| Parameter | $k$ (m/h) | $S$ (m) | $K$ (h/m) | $A$ (m/h bar) | $B$ (m/h) | $D$ ($m^2$/h) |
|---|---|---|---|---|---|---|
| Value | 0.306 | $8 \times 10^{-4}$ | 115–125 | $6.7 \times 10^{-4}$ | $4 \times 10^{-4}$ | $6.1–6.4 \times 10^{-6}$ |

Table 4
Comparison between experimental and model water flux

| Draw concentration (g/L) | Feed concentration (g/L) | Hydraulic pressure (bar) | $J_{w\text{-}exp}$ (L/$m^2$ h) | $J_{w\text{-}mod}$ (L/$m^2$ h) | % Difference |
|---|---|---|---|---|---|
| 35 | 0 | 13 | 7.9 | 8.1 | 2.5 |
| | 2.5 | 12 | 6.8 | 6.3 | 7.3 |
| | 5 | 11 | 6.3 | 5.2 | 17.4 |
| 60 | 0 | 23 | 12.6 | 12.5 | 0.8 |
| | 2.5 | 22.5 | 10.8 | 10 | 7.4 |
| | 5 | 21.8 | 9 | 8.1 | 10 |
| 60 | 0 | 15 | 16.9 | 16.2 | 4 |
| | 2.5 | 15 | 13.3 | 12.2 | 8.2 |
| | 5 | 15 | 10.8 | 9.98 | 7.6 |

In Fig. 3(D), $KNO_3$ was used as a draw solution for $NO_3^-$ and $K^+$ ions supply to irrigation water. Dual stage RO membrane treatment was proposed for $KNO_3$ regeneration and reuse. Due to low rejection rate of $NO_3^-$ by NF membranes, RO was used in stage one for the regeneration of draw solution and permeate from the RO was further treated by BWRO membrane to reduce the concentrations of $NO_3^-$ and $K^+$ ions in BWRO permeate.

A Cellulose Triacetate (CTA) FO membrane (Hydration Technology Innovation (HTI), USA) was used for simulation of the water flux in the FO unit. The rejection rate was >90%, for monovalent ions. Seawater, normal TDS 35 g/L, was the feed for the FO unit (Table 2). Filmtech NF90-400 and BW30LE-440 membranes were used in the regeneration process. NF90-400 was selected because of its high water permeability and rejection rate to nitrate [27]. Additionally, its rejection rate to divalent ions was >97%. On the other hand, BW30LE-440 exhibited >99% rejection to monovalent ions and operated at low feed pressure, which made it a good candidate for the regeneration process. It was also assumed here that no Energy Recovery Instrument (ERI) was applied in the regeneration process. Finally, salt diffusion coefficients of $KNO_3$, $Na_2SO_4$, $Ca(NO_3)_2$, and $MgCl_2$, were taken to be between $0.657 \times 10^{-9}$ and $1.98 \times 10^{-9}$ $m^2$/s [27–30].

### 2.2. FO model testing

A pre-developed FO model was tested against experimental data generated from a laboratory scale study [14,26,31]. Table 3 shows the testing parameters for a CTA flat sheet HTI FO membrane and used for the model calibration. It should be noted here that Aw, B, S, and D parameters were experimentally determined in the previous studies [30]. Membrane flux, $J_w$, was calculated using Eq. (1) and results were compared with data from the experimental work. It should be noted that Eq. (1) was developed for estimating membrane flux in a bench scale FO unit hence the performance of a full-scale membrane would be different. However, since there is no model developed for a full-scale FO membrane, Eq. (1) used for water flux prediction in FO system [32].

The results displayed in Table 4 illustrate the experimental and model flux values, $J_{w\text{-}exp}$, and

$J_{w\text{-mod}}$, respectively, for 35 and 60 g/L draw solution concentrations and feed solution concentrations ranging from 0 to 5 g/L. The difference between experimental and model water flux values was calculated as a percentage value and shown in column 5 of Table 4. The difference between the experimental and model values was between 0.8 and 17.4%, which suggested good agreement between $J_{w\text{-exp}}$ and $J_{w\text{-mod}}$.

### 2.3. Fertilizer water quality

Common fertilizers are inorganic compounds which deliver the essential macro and micro elements required for plant growth [33]. Examples of macro elements include N, P, K, Ca, Mg, and S whereas micro elements include Fe, Mn, B, Zn, Cu, Mo, and Cl. Required fertilizer solution compositions vary depending on many factors such as type of crops, cropping seasons, and soil nutrient amounts (Appendix A, Table A1)( [34]. The recommended concentration for “N” nutrient in irrigation water is between 50 and 200 mg/L, whereas for “K” nutrient it is between 15 and 250 mg/L [35]. For Mg, the recommended concentration is between 48 and 65 mg/L [33] and for $SO_4^{2-}$ it is approximately 321 mg/L [36]. In the current study, fertilizer water quality was evaluated based primarily on the concentrations of $K^+$, $NO_3^-$, and $SO_4^{2-}$ elements albeit $Mg^{2-}$ was considered in some cases.

## 3. Results and discussion

### 3.1. Performance of an FO membrane system

$MgCl_2$, $KNO_3$, $Na_2SO_4$, and $Ca(NO_3)_2$, were the draw solutions for the FO and PAFO process for seawater desalination and provision of irrigation water. Feed pressures between 0 and 16 bar were used in the PAFO process; different concentrations of draw solutions were applied to give 54 bar osmotic pressure. Five draw solution concentrations between 0.75 and 0.95 mol/L (with 0.05 mol/L concentration interval) were used in the FO process. The impact of feed pressure, $P_f$ (bar), and concentration of feed solution, $C_{DS}$ (mol/L), on the performance of the FO process is illustrated in Fig. 4(A). $J_w$ was calculated for the FO process and results compared with $J_w$ for the PAFO process (Fig. 4(A)). The results indicated that $J_w$ in the FO and PAFO process increased with increasing concentration of the draw solution and the feed pressure, respectively. For $MgCl_2 + KNO_3$ draw solution, there was a 56% increase in the value of $J_w$ as the feed pressure increased from 0 to 16 bar in the PAFO process (Fig. 4(A)). While in the FO process, $J_w$ increased by 44% when the concentration of $MgCl_2$ in the $MgCl_2 + KNO_3$ solution increased from 0.75 to 0.95 mol/L. In general, for $MgCl_2 + KNO_3$ draw solution, $J_w$ was 15 L/m$^2$ h at 16 bar feed pressure in the PAFO process and 14.1 L/m$^2$ h at 0.95 mol/L draw solution concentration in the FO process.

$J_w$ was higher in the PAFO system than in the FO process for all draw solutions presumably because of the higher NDP across the membrane (Fig. 4(B)). It should be mentioned that feed flow in the PAFO process was pressurized by exchanging pressure with the concentrated brine of the first stage NF/RO membrane system (Fig. 2). Applying higher NDP increased the recovery rate of PAFO and FO processes as shown in Fig. 4(C). The recovery rate of PAFO and FO increased with increasing feed pressure and draw solution concentration in the PAFO and FO process, respectively. It was noted that 41 and 39% recovery rates were achieved in the PAFO and FO processes, respectively, at 16 bar feed pressure and 0.95 mol/L draw solution concentration. However, there were limitations to use of elevated feed pressures or draw solution concentrations in the PAFO and FO processes. For instance, RO brine from the first stage NF/RO membrane treatment exchanges pressure with the feed solution of the PAFO process. This pressure should be less than the maximum feed pressure tolerated by the FO membrane. On the other hand, NDP in the FO process was directly dependent upon the concentration of draw solution assuming the salinity of feed solution was fixed at 35 g/L (seawater feed).

As shown in Fig. 4(A) and (C), increasing the concentration of the draw solution increased the water flux and recovery rate of the FO process and the concentration of the diluted draw solution, $C_{DS\text{-out}}$, increased with increasing concentration of the draw solution, $C_{DS}$, from 0.75 to 0.95 mol/L (Fig. 4(D)). While in the PAFO process, $C_{DS\text{-out}}$ decreased with increasing pressure of the feed solution.

In the case of $KNO_3$, Fig. 4(E) shows the concentration of $NO_3$ in the diluted draw solution using different draw solutions and feed pressures. Based on the concentration of $NO_3$ in the diluted draw solution, using $MgCl_2 + KNO_3$ draw solution was more relevant than $KNO_3$ for delivering sufficient $NO_3$ concentration to the NF/RO feed solution. Depending on the NDP across the FO membrane, using $MgCl_2 + KNO_3$ as a draw solution resulted in 1.4–1.59 g/L of $KNO_3$ concentration in the diluted draw solution (Fig. 4(E)). This latter value is almost 56 times lower than the concentration of $NO_3$ in the diluted draw solution when $KNO_3$ was used as a draw solution. Increasing the concentration of $MgCl_2$ or feed pressure in the FO and PAFO processes resulted in, respectively, 0.88 and 0.89 g/L of $NO_3$ in the diluted draw solution. It should

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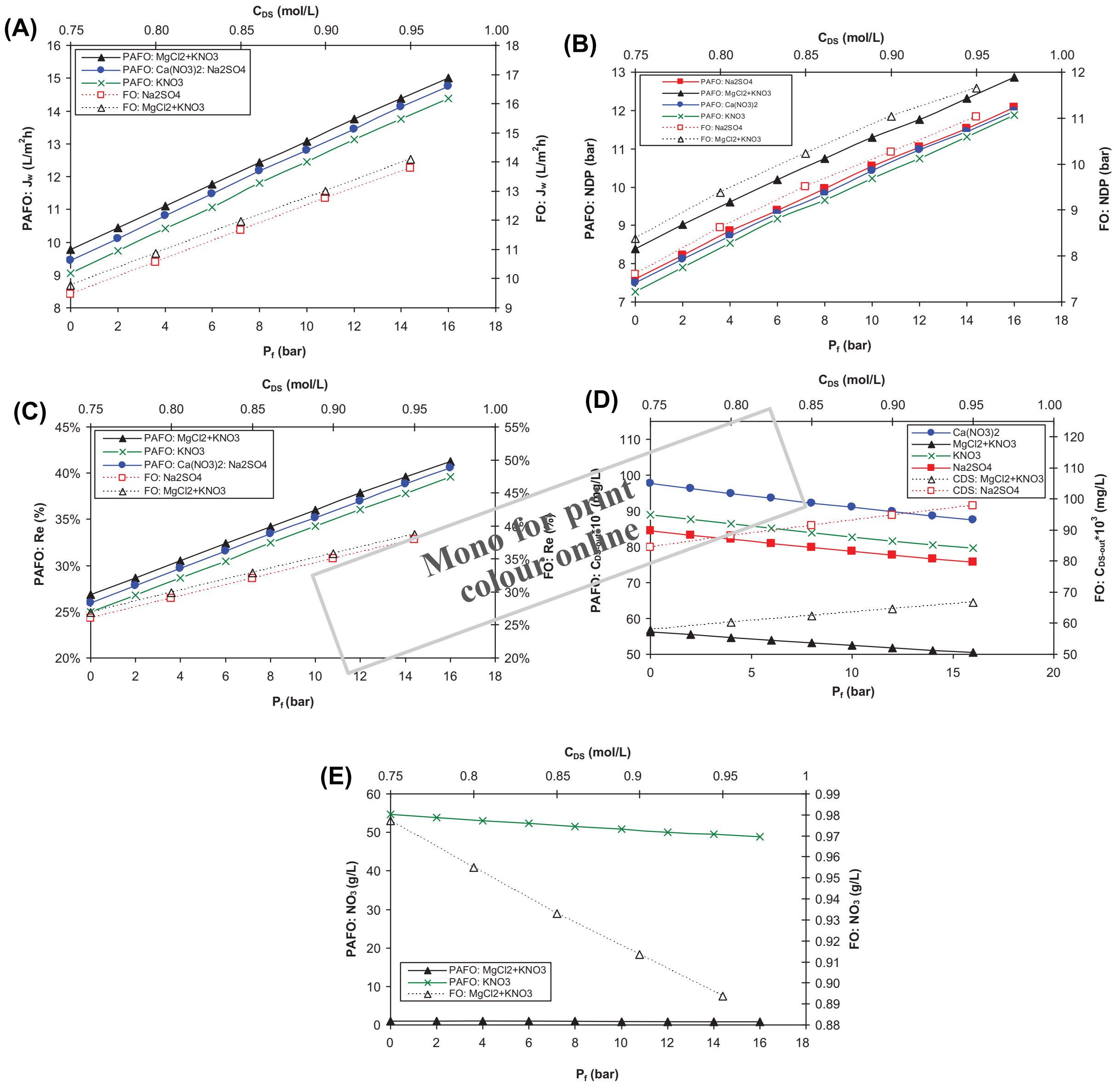

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Fig. 4. Impact of feed pressure and draw solution concentration on the performance of FO process (A) water flux, (B) NDP, (C) %Re, (D) $C_{DS\text{-}out}$, and (e) $NO_3$ concentration.

be noted that high $NO_3$ concentration in the diluted draw solution may result in an undesirable $NO_3$ concentration in the irrigation water.

Furthermore, reverse salt diffusion, $J_{s\text{-}r}$ (kg/m$^2$ h), required consideration in osmotically driven membrane processes as it potentially exerted an adverse impact upon the process performance. The results indicated that $J_{s\text{-}r}$ decreased with increasing NDP in the PAFO process whereas it increased with increasing NDP in the FO process (Fig. 5(A)). For $Na_2SO_4$, $J_{s\text{-}r}$ was 0.036 kg/m$^2$ h at 7.6 bar in the PAFO and FO process, then increased to 0.0347 kg/m$^2$ h and 0.0437 kg/m$^2$ h at 11 bar NDP in the PAFO and FO processes, respectively. The reason for a lower $J_{s\text{-}r}$ with NDP increase in the PAFO process was attributed to the higher water flux across the membrane at higher NDP. This latter process eventually resulted in a lower draw solution concentration at the membrane surface, $C_{DM}$, and decreased the $J_{s\text{-}r}$ across the membrane (Fig. 5(B)).

On the contrary, $J_{s\text{-}r}$ increased with increasing NDP in the FO process due to the higher initial draw solution concentration at the membrane surface, $C_{DM}$, (Fig. 5(B)). In the FO process, the increase in NDP was

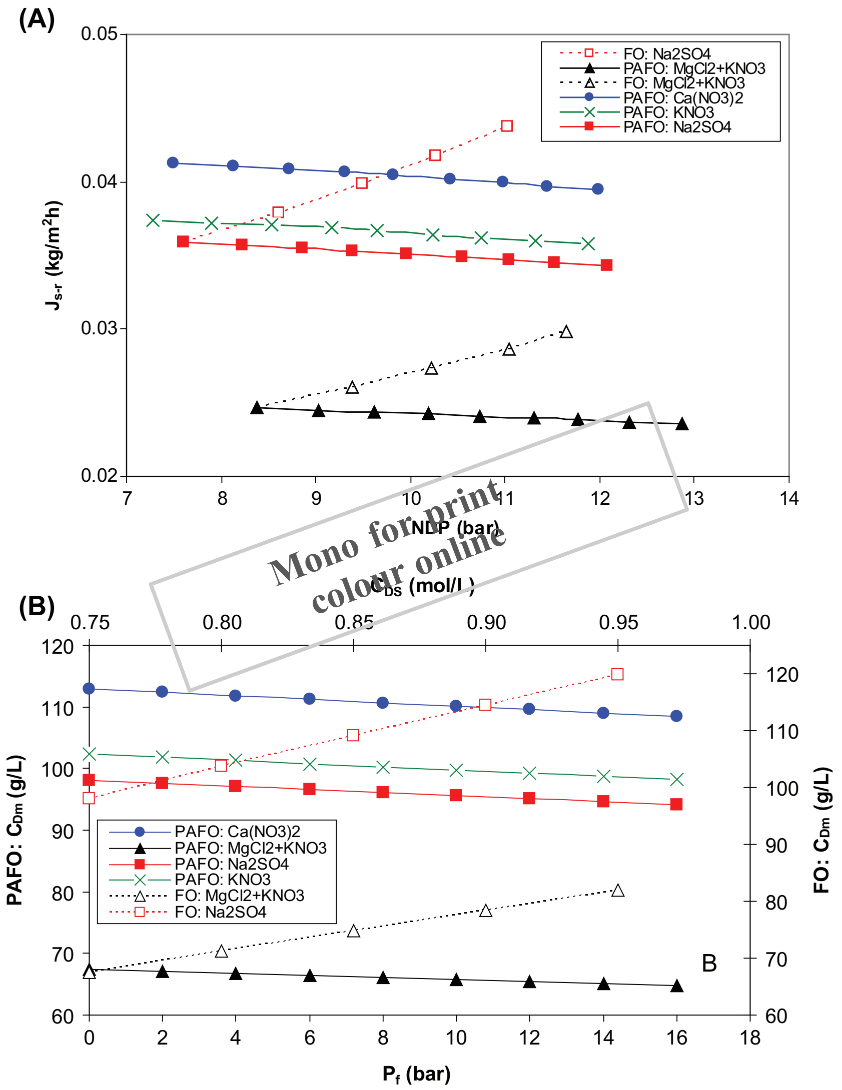

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Fig. 5. Salt diffusion in PAFO and FO process at different feed pressures and draw solution concentrations (A) $J_{s-r}$ in PAFO and FO; (B) $C_{DM}$ in PAFO and FO.

achieved by increasing the concentration of the draw solution. Therefore, $C_{DM}$ increased with the increase of NDP in the FO process. Practically, the higher the $J_{s-r}$ value, the higher draw agent loss was in the FO process. As such, PAFO was more economical than the FO process in terms of chemicals used. Fig. 5(B) shows that increase in the concentrations of diluted draw solution in the PAFO process was in the following order; $Ca(NO_3)_2 > KNO_3 > Na_2SO_4 > MgCl_2 + KNO_3$. In addition to the higher reverse salt diffusion, using $Ca(NO_3)_2$ and $KNO_3$ draw solutions resulted in a relatively high concentration feed solution which may affect the performance of the regeneration process and the related permeate concentration.

### 3.2. Performance of regeneration system

Draw solution regeneration was carried out using dual stage membrane treatment. Table 5 describes the types of membranes used in stage one and two of the regeneration process. $MgCl_2 + KNO_3$, $Na_2SO_4$, $Ca(NO_3)_2$, and $KNO_3$ were the draw solutions for the FO process whereas 35 g/L seawater was the feed solution. The membranes outlined in Table 5 were of the Filmtec™ type. However, alternate membranes with similar properties could also have been used for the regeneration of the draw solution. The regeneration system of $MgCl_2 + KNO_3$ consisted of NF90-400 and BW30LE-440 membranes in stage one and two,

Table 5
Type of membrane used in the regeneration of draw solutions using 35 g/L seawater as the feed solution

| Draw solution | $MgCl_2 + KNO_3$ | $Na_2SO_4$ | $Ca(NO_3)_2$ | $KNO_3$ |
|---|---|---|---|---|
| Stage one membrane | NF90-400 | NF90-400 | BW30LE-440 | SW30HRLE-400i |
| Stage two membrane | BW30LE-440 | NF90-400 | BW30LE-440 | BW30LE-440 |

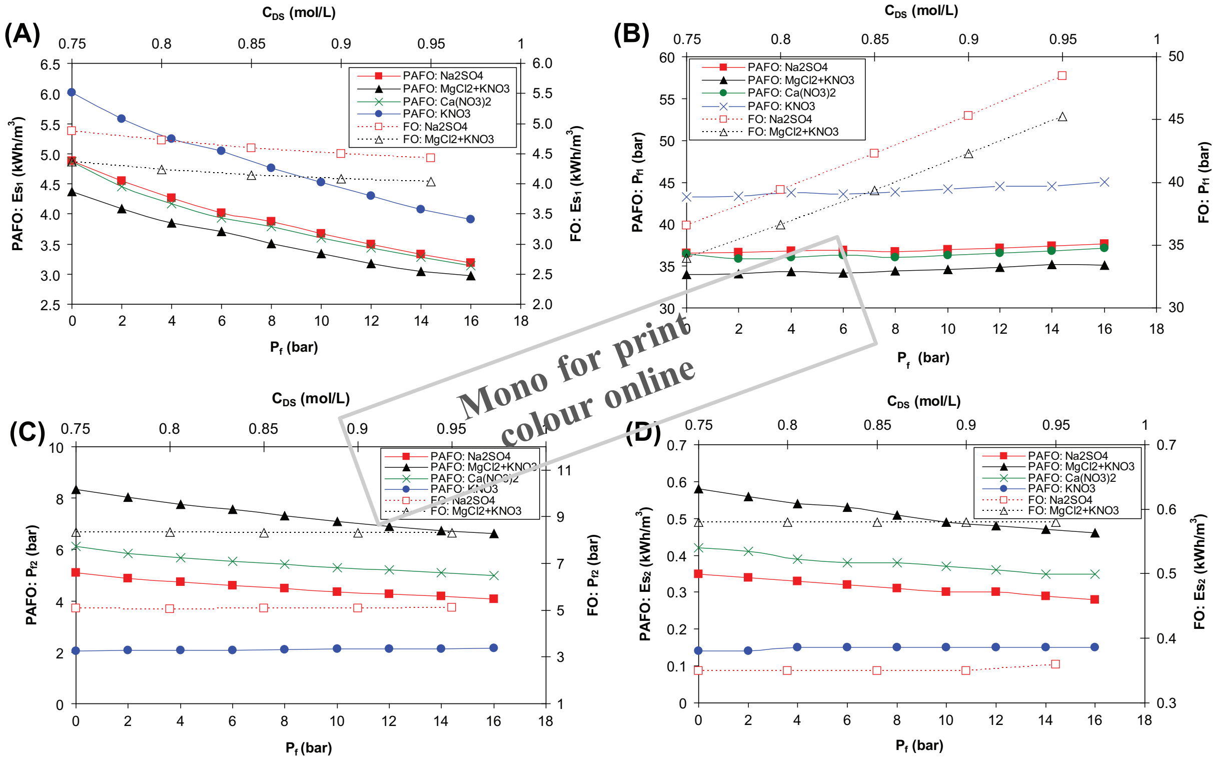

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Fig. 6. Performance of the regeneration system of the PAFO and FO processes (A) specific power consumption in stage one, (B) specific power consumption in stage two, (C) feed pressure in stage one, and (D) feed pressure in stage two,

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respectively. NF membrane rejection rate to $MgCl_2$, the primary draw solution, was more than 90% but to $KNO_3$ was in the range 20–67% (depending on the concentration in solution) [37,38]. In the second stage, BWRO membrane with 90% rejection rate to $MgCl_2$ and $KNO_3$ was used to adjust the concentration of permeate TDS to a desirable level [39]. NF rejection rate to $Na_2SO_4$ was about 96%, hence it was used in stage one and two of the regeneration process of $Na_2SO_4$ [40]. $Ca(NO_3)_2$ rejection rate by NF membrane was about 60%, hence BWRO membranes were used in stage one and two of the regeneration process [38]. Finally, the $KNO_3$ rejection rate by NF membrane was moderately low [37,39], therefore RO and BWRO membranes were used in stage one and two, respectively, of the regeneration process.

The performance of the membrane regeneration system was evaluated in terms of energy consumption and irrigation water quality. Fig. 6(A) presents the specific power consumption, $Es_1$ (kWh/m$^3$), in the first stage of the regeneration system. Specific power consumption of the PAFO process decreased with increasing feed pressure although there was a slight increase in the feed pressure of the first membrane regeneration process, $P_{f1}$ (bar), (Fig. 6(B)). To a lesser extent, $Es_1$ of the FO process decreased with increasing concentration of the draw solution despite the higher $P_{f1}$ required in the first stage of the membrane regeneration process (Fig. 6(A) and (B)). As shown in Fig. 6(A), $Es_1$ for PAFO decreased from 4.37 to 2.97 kWh/m$^3$ when the feed pressure increased from 0 to 16 bar; whereas $Es_1$ of the FO stage decreased from 4.88 to

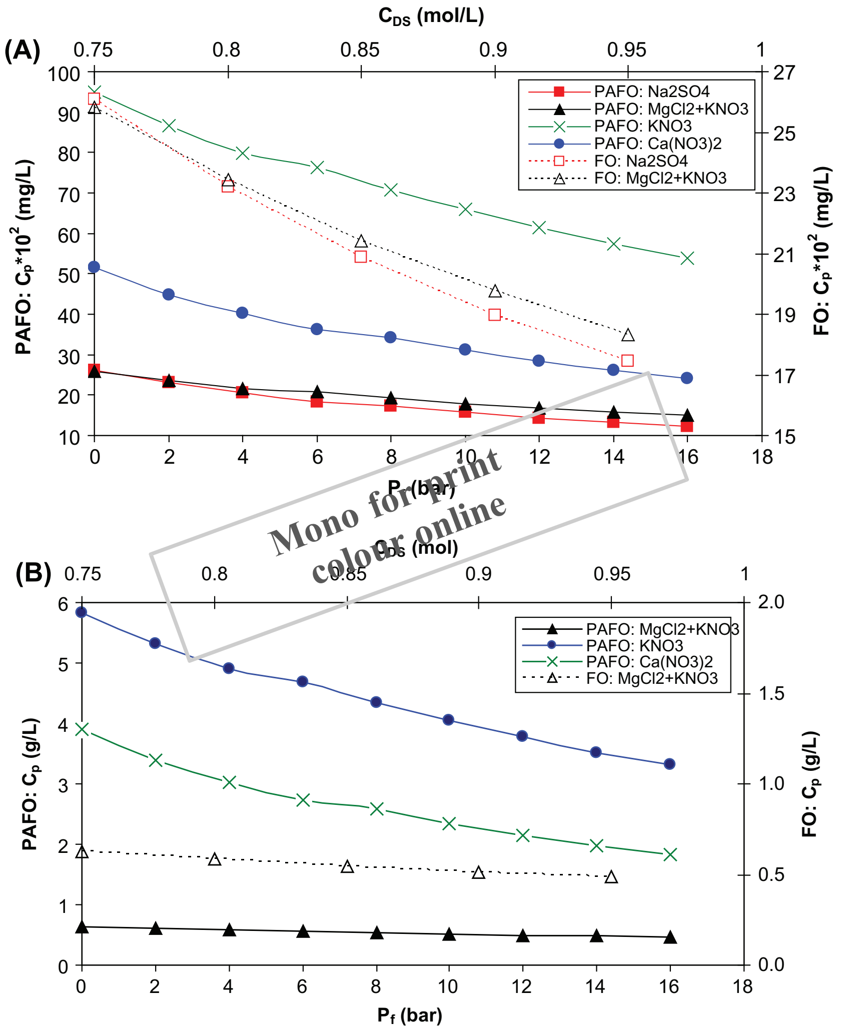

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Fig. 7. Irrigation water quality (A) permeate water TDS and (B) NO$_3$ concentration.

4.43 kWh/m$^3$ when the concentration of the draw solution increased from 0.75 to 0.95 mol/L. This behavior corresponded to 35 and 9% decrease in the $Es_1$ of the PAFO and FO process, respectively. The reason for the decreasing $Es_1$ in the PAFO and FO process with increasing $P_{f1}$ and draw solution concentration, respectively, was attributed to higher recovery rates of the NF/RO regeneration system (Fig. 6(C)).

*Es*, in general, decreased with increasing recovery rate of the NF/RO system since it was inversely related to *Re*, (Eq. (8)). The recovery rate of $MgCl_2 + KNO_3$ in the PAFO process, for example, increased from 27 to 41% as the feed pressure increased from 0 to 16 bar (Fig. 6(C)). Similarly, the recovery rate of $MgCl_2 + KNO_3$ in the FO process increased from 26 to 38% when the concentration increased from 0.75 to 0.95 mol/L. However, it should be noted that there was an optimum *Re* ratio for the membrane beyond which the power consumption of the system increased again with increasing *Re* ratio due to the increase of osmotic pressure of the feed solution [41]. RO membrane fouling was considered insignificant in stage one and two because of the FO pre-treatment of the feedwater. Membrane fouling, in general, reduces membrane flux and increases power consumption. On the other hand, specific power consumption of the second stage, $Es_2$ (kWh/m$^3$), slightly decreased with increasing feed pressure of the PAFO process; whereas $Es_2$ was almost constant in the FO process (Fig. 6(D)). The $Es_2$ of the PAFO process using $MgCl_2 + KNO_3$ draw solution decreased from 0.58 to 0.46 kWh/m$^3$ when the feed pressure increased from 0 to 16 bar; whereas it remained about 0.58 kWh/m$^3$ in the FO process. The decrease of $Es_2$ in the PAFO process was attributed to the slight reduction of the $P_{f2}$ required for the filtration process (Fig. 6(C)).

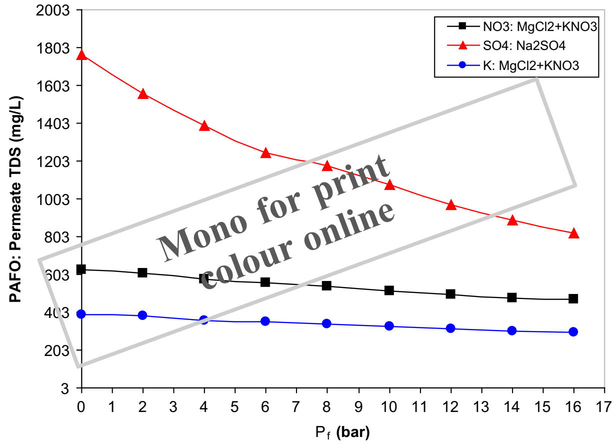

Fig. 8. Concentration of K, $NO_3$, and $SO_4$ in permeate water after PAFO process; dual stage NF90-400-BW30LE440 process was applied for $NO_3$ and K and NF90-400–NF90-400 for $SO_4$.

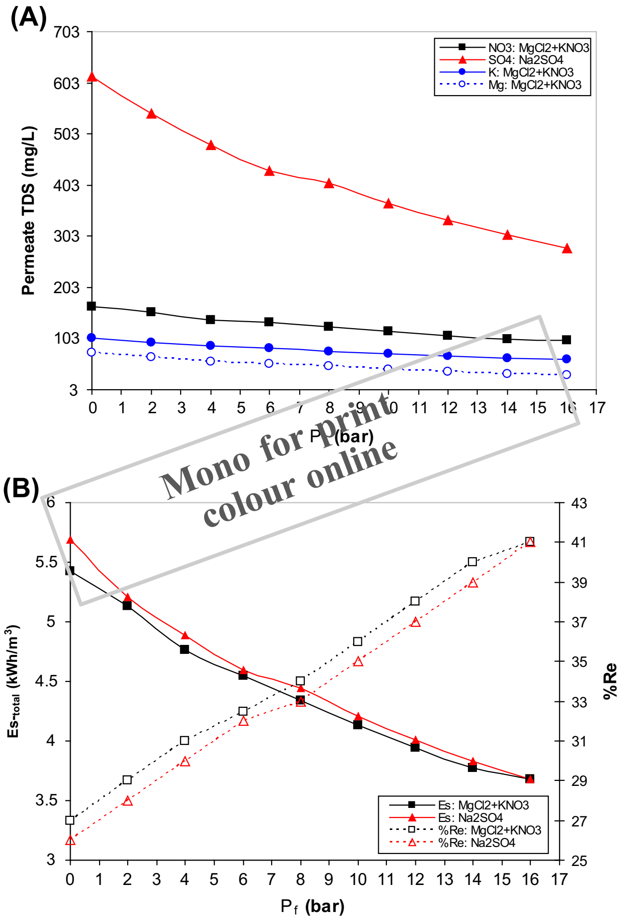

Fig. 9. Performance of PAFO process at different feed pressures (A) product water TDS (B) power consumption and recovery rate; (BW30-4401–BW30LE440 system was used for the regeneration of $MgCl_2 + KNO_3$ BW30-440i–NF90-400 for the regeneration of $Na_2SO_4$).

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Likewise, $P_{f2}$ of the FO process remained almost unchanged, which explained the constant $Es_2$ at different draw solution concentrations. Regardless of the draw solution type, results showed that the total specific power consumption, which was equal to $Es_1 + Es_2$ in the PAFO process, was lower than that in the FO process. The total specific power consumption for regeneration of $MgCl_2 + KNO_3$ draw solution in the PAFO process was 3.43 kWh/m$^3$ at 16 bar feed pressure (Fig. 6(A) and (D)). However, for the FO process, the total specific power consumption for the regeneration of 0.95 mol/L concentration of $MgCl_2 + KNO_3$ draw solution was 4.61 kWh/m$^3$. The data indicated that an increase in the total specific power consumption of the regeneration process in the PAFO process was in the following order; $KNO_3 > Ca(NO_3)_2 > Na_2SO_4 > MgCl_2 + KNO_3$. Furthermore, the results suggested that $MgCl_2 + KNO_3$ was the most cost-effective draw solution for $NO_3$ provision into the irrigation water. This outcome was due to the novel application of $MgCl_2$ and $KNO_3$ as a primary draw solution and a secondary additive for making the FO draw solution. For $SO_4$ supply by $Na_2SO_4$ draw solution, the total specific power consumption was about 3.47 kWh/m$^3$. This latter behavior was attributed to the application of high water permeability NF membranes in stage one and two of the regeneration process of $Na_2SO_4$.

Irrigation water quality from the regeneration process was expected to be suitable for field application with, if required, only minimal treatment or dilution. Fig. 7(A) shows the concentration of the irrigation water after the NF/RO membrane treatment. In the PAFO process, the concentration of the irrigation water, $C_p$, was the lowest for $Na_2SO_4$ then followed by $MgCl_2 + KNO_3$, $Ca(NO_3)_2$ and $KNO_3$, respectively. In the FO process, $C_p$, in general was slightly higher than that in the PAFO process. The lowest $C_p$ for $NO_3$ was $15.16 \times 10^2$ and $18.34 \times 10^2$ mg/L in the PAFO and FO process, respectively, using $MgCl_2 + KNO_3$ draw solution. For $Na_2SO_4$, the lowest $C_p$ was $12.5 \times 10^2$ and $17.45 \times 10^2$ mg/L for PAFO and FO processes, respectively. As such, the PAFO process has an advantage over the FO process when the concentration of $SO_4/NO_3$ in irrigation water should be low enough that no further treatment is required. Furthermore, the total specific power consumption of the PAFO process was lower than that of the FO process (Fig. 6(A) and (D)). In addition, the concentration of $NO_3$ in irrigation water was estimated to evaluate the

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Table 6
Concentration of K, $NO_3$, Mg, and $SO_4$ in permeate water after PAFO process. The concentration of fertilizer water in the PAFO process at different feed pressures and the recommended concentration suggested by Food and Agriculture Organization, United nation [34]. Fertilizer water concentrations are within the recommended levels at hydraulic pressure 12 bar or more

| PAFO | $MgCl_2 + KNO_3$<br>BW30-4401–BW30LE440 | | | $Na_2SO_4$<br>BW30-440i–NF90-400 |
|---|---|---|---|---|
| Feed pressure (bar) | $K^+$ (mg/L) | $NO_3^-$ (mg/L) | $Mg^{2-}$ (mg/L) | $SO_4^{2-}$ (mg/L) |
| 8 | 78 | 125 | 48 | 406 |
| 10 | 73 | 117 | 43 | 367 |
| 12 | 68 | 109 | 38 | 334 |
| 14 | 64 | 102 | 34 | 305 |
| 16 | 62 | 99 | 32 | 280 |
| Recommended Level (mg/L) | 15–250 | 50–200 | 48–65 | ~321 |

efficiency of PAFO and FO processes for irrigation water supply (Fig. 7(B)).

Unfortunately, nitrate ions have relatively low rejection rates by NF and to a lesser extent by RO membranes. In general, the concentration of nitrate in irrigation water decreased with increasing feed pressure or draw solution concentration in the PAFO and FO processes, respectively (Fig. 7(B)). However, the lowest concentration of nitrate in irrigation water was relatively high, 3,300 mg/L, when $KNO_3$ was the draw solution for the PAFO process. The concentration of nitrate in irrigation water was 469 and 485 mg/L in the PAFO and FO processes, respectively, when $MgCl_2 + KNO_3$ was the draw solution. For $Ca(NO_3)_2$, the concentration of nitrate in irrigation water was about 1,822 mg/L (feed pressure 16 bar) which was ca. four times higher than that for $MgCl_2 + KNO_3$ draw solution. These results indicated that $MgCl_2 + KNO_3$ draw solution was a better option for $NO_3$ provision into the irrigation water, especially when it was required in small concentrations.

The results showed that the concentrations of $K^+$, $NO_3^-$, and $SO_4^{2-}$ in the permeate solution were higher than required in irrigation water [33,36]. The concentrations of $K^+$, and $NO_3^-$ at 16 bar feed pressure were 295 and 469 mg/L, respectively. At the same feed pressure, $SO_4^{2-}$ concentration was 821 mg/L (Fig. 8). Depending on the crop type, the required nutrient concentration varied from 50 to 200 mg/L for $NO_3^-$, 15–250 mg/L for $K^+$, and about 321 mg/L for $SO_4^{2-}$. These latter concentrations were lower than what could be achieved by the FO and PAFO aforementioned methods. Therefore, further dilution using a freshwater source was required to reduce the concentration of the permeate product. Notably, freshwater resources are not always available in arid areas and using desalinated water can be an expensive option.

Alternatively, a higher rejection membrane (such as Filmtec BW30-440i) is suggested to replace NF90-400 in the first stage of the regeneration stage. BW30-440i rejection rate to monovalent ions is more than 99.5%. PAFO results show that the concentrations of $K^+$, $NO_3^-$, $Mg^{2-}$, and $SO_4^{2-}$ dropped to a desirable level after the regeneration process (Fig. 9(A)).

The concentrations of $K^+$, $NO_3^-$, $Mg^{2-}$, and $SO_4^{2-}$ at 16 bar feed pressure were 62, 99, 32, and 280 mg/L, respectively. The latter concentrations were within the range recommended for irrigation water (Table 6).

In effect, the concentrations of $K^+$, $NO_3^-$, and $Mg^{2-}$ were within the recommended level at feed pressures between 8 and 16 bar as shown in Table 6. However, at 12 bar feed pressure the concentration of $SO_4^{2-}$ was about 334 mg/L which was close to the recommended level for irrigation water (321 g/L). Using high rejection rate BW30-440i membrane impacted the power consumption of the regeneration process. Total power consumption ($Es_{total}$) in the high pressure membrane filtration processes; i.e. NF and BWRO processes, was estimated using Eq. (8). $Es_{total}$ of the $MgCl_2 + KNO_3$ and $Na_2SO_4$ systems was 3.68 kWh/m$^3$ at 16 bar feed pressure (Fig. 9(B)); this was about 7 and 6% higher than $Es_{total}$ for $MgCl_2 + KNO_3$ and $Na_2SO_4$ when NF90-400 membrane was used in stage one of the regeneration process. Interestingly, $Es_{total}$ decreased with increasing feed pressure as shown in Fig. 9(B).

This behavior was due to the membrane recovery rate at higher feed pressures. Apparently, *Es* was inversely proportional to the recovery rate as shown in Eq. (8). Therefore, $Es_{total}$ of the regeneration process AQ2 decreased with increasing system recovery rate. It is pointed out that *Es* of RO seawater desalination was about 3 kWh/m$^3$; however, the majority of RO desalination plants operate at *Es* close to 4 kWh/m$^3$ [42,43]. This result indicated that power consumption of the RO system was close to the theoretical *Es* of the PAFO process (Fig. 9(B)).

Finally, results indicated that the PAFO process was more economical than the FO process because of its lower power consumption. PAFO coupled with dual stage membrane treatment for draw solution regeneration and reuse was able to produce fertilizer irrigation water which could be applied directly to a field. Using a high rejection rate BW30-440i membrane enhanced the quality of irrigation water albeit at the expense of a slight increase of *Es*. However, the *Es* of the PAFO process was close to that of an RO desalination process if we take into account the energy required for fertilizing water preparation and dilution in the latter process. It should be noted that the estimated specific power consumption of the RO process is about 3 kWh/m$^3$ for 35 g/L feed salinity and negligible fouling effects [44]; the real power consumption of the RO desalination increases over time due to the membrane fouling. Membrane fouling is avoided or reduced in the FO-RO system due to the high purity of feed solution [43,44]. Furthermore, it was more convenient to deliver fertilizer irrigation water ready to use without an additional treatment. In summary, PAFO systems offer several advantages such as those mentioned here and this method may offer benefits relative to conventional seawater desalination RO processes.

## 4. Conclusions

FO-membrane hybrid system was applied for seawater treatment and irrigation water supply. PAFO and FO processes were applied for seawater treatment and the diluted seawater was further treated by a series of NF/RO membranes for draw solution regeneration and reuse. $KNO_3$, $Na_2SO_4$, $CaNO_3$, and $MgCl_2 + KNO_3$ draw solutions were used in the FO process. The results showed that PAFO was more economical than FO process in terms of chemicals use. Power consumption for draw solution regeneration and irrigation water supply was lower in the PAFO than in the FO process. The TDS of irrigation water varied from 1,200 to 5,000 mg/L which can be applied after minimum treatment. Irrigation water quality was further improved and was within the recommended level of fertilizer irrigation waters when a dual stage BWRO membrane system were applied in the regeneration unit. The results also showed that $MgCl_2 + KNO_3$ draw solution provided lower TDS irrigation water than $KNO_3$ and $Ca(NO_3)_2$ draw solutions.

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## Appendix A

The concentrations of nutrients in irrigation water are shown in Table A1.

Table A1
Recommended nutrient concentrations in fertilizer containing irrigation water for different types of crops

| Type of crop | N (mg/L) | K (mg/L) |
|---|---|---|
| Citrus | 50 | 15 |
| Bananas | 50 | 40 |
| Tomatoes | 180 | 250 |
| Cucumbers | 200 | 200 |
| Bell peppers | 170 | 200 |
| Cabbages | 100 | 200 |
| Onion | 100 | 150 |
| Squashes | 200 | 200 |
| Potatoes | 150 | 180 |
| Groundnuts | 120 | 200 |
| Watermelons | 150 | 150 |

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