Blended Fertilisers as Draw Solutions for Fertiliser Drawn Forward Osmosis Desalination

Sherub Phuntsho[a], Ho Kyong Shon[a*], Tahir Majeed[a], Ibrahim El Saliby[a], Saravanamuthu Vigneswaran[a], Jaya Kandasamy[a], Seungkwan Hong[b], Sangyoup Lee[b]

[a]School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Post Box 129, Broadway, NSW 2007, Australia.

[b]School of Civil, Environmental & Architectural Engineering, Korea University, 1, 5-ka, Anam-Dong, Sungbuk-Gu, Seoul 136-713, Republic of Korea

* Corresponding author: Email: Hokyong.Shon-1@uts.edu.au

ABSTRACT

In fertiliser drawn forward osmosis (FDFO) desalination, the final nutrient concentrations (Nitrogen, Phosphorus, Potassium or NPK) in the product water is essential for direct fertigation and avoid over fertilisation. Our study with 11 selected fertilisers indicate that, blending of two or more single fertilisers as draw solution (DS) can achieve significantly lower nutrient concentration in the FDFO product water rather than using single fertiliser alone. For example, blending KCl and $NH_4H_2PO_4$ as DS can result in 0.61/1.35/1.70 g/L of N/P/K, which is comparatively lower than using individually as DS. The nutrient composition and concentration in the final FDFO product water can also be adjusted by selecting low nutrient fertilisers containing complementary nutrients and in different ratios to produce prescription mixtures. However, blending fertilisers generally resulted in slightly reduced bulk osmotic pressure and water flux in comparison to the sum of the osmotic pressures and water fluxes of the two individual DS as used alone. The performance ratio or PR (ratio of actual water flux to theoretical water flux) of blended fertiliser DS was observed to be between the PR of the two fertiliser solutions tested individually. In some cases such as urea, blending also resulted in significant reduction in N nutrient loss by reverse diffusion in presence of other fertiliser species.

Keywords: Forward osmosis, low energy desalination, fertiliser draw solution, fertiliser blending, fertigation, irrigation.

INTRODUCTION

Membrane technology could play a vital role in meeting the world's water demands through alternative sources such as oceans and seas. Although reverse osmosis (RO) desalination is currently the most efficient desalination technology, it is still considered a high energy demanding process [1]. Besides, membrane fouling poses a major challenge to the efficiency of the pressure-based membrane processes [2-4]. Efforts invested to mitigate membrane fouling often result in increased overall process operation costs [5]. Although irrigation accounts for 72% of the total global water consumption of fresh water [6], prevailing desalination technologies remain uneconomical for such large-scale applications mainly due to energy issues. Since energy and climate change issues are strongly interrelated [5, 7], more energy efficient desalination technologies are required so that the scope of desalination can be extended to large-scale water applications such as irrigation.

Based on the pioneering works of Sydney Loeb and his groups [8-11] and by others [12-14] in the 1970s on pressure retarded osmosis and forward osmosis (FO), the FO process has recently gained renewed interest and is now acknowledged as a novel and emerging low energy desalination technology. The transport of water through the membrane in the FO process is achieved due to concentration or osmotic gradient, without requiring hydraulic pressure like in the RO process. Besides low energy, the other attractive feature of the FO process is its lower membrane fouling propensity during the membrane process [2, 15-17]. However, application of FO desalination for potable water still remains challenging [18] because the separation and recovery of draw solute from FO product water is not easy and still requires energy. Although few promising draw solutes such as NH_3-CO_2 mixture [1, 19] and super magnetic nanoparticles [20] have been suggested for application in drinking water, they are yet to be tested commercially.

However, FO desalination has a significant scope for other non-potable applications such as irrigation and energy drink [21]. Recently, Phuntsho et al. [18, 22] reported on fertiliser drawn forward osmosis (FDFO) desalination, in which fertilisers are used as draw solutions (DS). The novelty of this particular FO process is that the diluted DS after desalination can be directly used for fertigation as it contains essential plant nutrients. Such a process eliminates the need for separation and recovery of draw solutes as required in the case of producing drinking water. Fertilisers are extensively used in agricultural production making them an ideal choice as DS. Besides, fertigation has other advantages such as improvement in the efficiency of fertiliser use, minimising fertiliser loss due to leaching, control of nutrient concentration in soil, control of nutrient form and ratio, and flexibility in the timing of application [23].

Although, Phuntsho et al. [18] observed that most of the soluble fertilisers can be used as DS for FO desalination, one of the limitations identified was the final fertiliser nutrient concentration in the final FDFO product water, which may exceed the required nutrient limit for direct fertigation. The minimum final nutrient concentration is because of the limitation based on the osmotic equilibrium between the feed solution (FS) and DS in the FO process [22]. Even though the minimum concentration of nutrient required for fertigation of crops could vary considerably depending on many factors, such as type of crops, type of nutrients, , soil conditions and composition, cropping season, plant growth stage, etc. [24-27], high fertiliser concentration would increase soil salinity and cause plant toxicity. If the final fertiliser nutrient concentration is higher than required, the final DS must be further diluted using additional fresh water to make the FDFO product water suitable for fertigation, but such situations are not desirable especially when other fresh water sources are unavailable. The dilution required would also be several factors high especially when feed water with high

salinity is used. Other possible alternative include NF as either pre-treatment to reduce the feed TDS or as post-treatment to recover DS in the process reducing the final nutrient concentrations although this may require additional energy [22].

The objective of this study is to investigate the suitability of blending two or more single fertilisers as DS for FDFO desalination, with the objective of achieving lower final nutrient concentrations in the final FDFO product water that could meet the water quality requirement for direct fertigation. The hypothesis is that, if the DS is composed of multiple nutrients, the final concentration of each nutrient could be much lower than using a single fertiliser. It is shown in this study that, nutrients in the final FDFO product water can be significantly lowered by using blended fertilisers as DS rather than using single fertiliser as DS. Bulk blending of fertilisers is very popular in the agriculture industry because it allows prescription mixtures based on specific soil and crop requirements and reduces the transportation costs for farmers [28]. The paper also compares the performances of the single fertiliser and the blended fertilisers in terms of water flux and reverse solute flux during FO process.

THEORETICAL BACKGROUND

In general, water flux (J_w) in FO process can be given by the following equation.

$$J_w = A \Delta \pi = A \left[\pi_{D,b} - \pi_{F,b} \right] \tag{1}$$

Where A is the pure water permeability coefficient of the membrane, $\pi_{D,b}$ and $\pi_{F,b}$ are the bulk osmotic pressures of the DS and FS respectively. However, two types of CP effects uniquely govern the water flux in FO process: concentrative external CP (ECP) on the membrane active layer facing the FS and dilutive internal CP (ICP) inside the membrane support layer facing the DS. Taking ICP and ECP into account, equation 1 can be modified as shown below under FO mode [29]:

$$J_w = A \Delta \pi_m = A \left[\pi_{D,m} - \pi_{F,m} \right] \tag{2}$$

$$J_w = A \Delta \pi_m = A \left[\pi_{D,b} \, e^{(-J_w K)} - \pi_{F,b} e^{(J_w / k_F)} \right] \tag{3}$$

Where $\pi_{D,m}$ and $\pi_{F,m}$ are the osmotic pressures of the DS and FS at the membrane surfaces respectively, k_F is the mass transfer coefficient of the feed and K the solute resistance to diffusion within the membrane support layer defined by:

$$K = \frac{t\tau}{D\varepsilon} \tag{4}$$

Where D is the diffusion coefficient of the draw solute, t, τ and ε are the thickness, tortuosity and porosity of the support layer respectively. One important observation from equation (3) is that:

As $J_w \rightarrow 0$,

$$\pi_{D,m} \quad \text{or} \quad \pi_{D,b} \, e^{(-J_w K)} \quad \rightarrow \quad \pi_{D,b} \quad \text{and} \quad \pi_{F,m} \quad \text{or} \quad \pi_{F,b} e^{(J_w / k_F)} \quad \rightarrow \quad \pi_{F,b}$$

Hence, $\left[\pi_{D,b}\, e^{(-J_w K)} - \pi_{F,b}\, e^{(J_w / k_F)}\right] \rightarrow \left[\pi_{D,b} - \pi_{F,b}\right]$

The significance of this is that, as the water flux decreases due to continuous dilution of the DS, the degree of ICP and ECP effects in FO process also becomes negligible. This indicates that, at lower DS concentrations or lower net osmotic pressure, the water flux in FO process given in equation (2) or (3) can be represented by equation (1). In other words, the net movement of water from DS to the FS will occur until the bulk osmotic pressures of the DS reaches osmotic equilibrium with the bulk osmotic pressure of the FS as verified experimentally in this study.

EXPERIMENTAL

Chemical fertilisers and draw solution preparation. All chemical fertilisers used were reagent grade (Sigma Aldrich, Australia). The DS consisting of one or more single fertilisers were prepared by dissolving fertilisers in deionised (DI) water.

The essential properties of the fertiliser solutions such as the pH, the number and type of species formed, and the osmotic pressures of the fertiliser solutions were determined using OLI Stream Analyser 3.1 software (OLI Systems Inc., Morris Plains, NJ, US). This software uses thermodynamic modelling based on published experimental data to predict properties of solutions over a wide range of concentrations and temperatures [18, 30].

Forward osmosis performance experiments. The performance of the FO process was conducted using a lab scale FO unit with an effective membrane area of 2.002×10^{-3} m^2. The commercial cellulose triacetate (CTA) FO membrane was used (Hydration Technologies Inc., USA) and its characteristics are widely reported [17, 19, 31]. The performance of each fertiliser as DS for FO process was assessed using DI water and model brackish water or BW (5,000 mg/L NaCl) as feed. Detail experimental procedures, are described in Section S1 of supporting information (SI).

RESULTS AND DISCUSSION

FDFO desalination using single fertilisers as draw solutions. Table 1 shows the osmotic pressure and their performances as DS in FO process. The final concentration of the fertiliser (NPK or Nitrogen Phosphorous Potassium) DS after FDFO desalination is compared for seawater and BW feed in Figure 1.

      Properties of single fertiliser solutions. Although urea is highly soluble in water, it is considered a weak electrolyte and therefore does not dissociate to form any charged species in water [32]. As such, the osmotic pressure (23.7 atm) is significantly lower than other soluble fertiliser solutions. Di-ammonium phosphate (DAP) or $(NH_4)_2HPO_4$ and Calcium nitrate or $Ca(NO_3)_2$ showed the highest osmotic pressures amongst the fertilisers, with 50.6 and 48.8 atm respectively at 1 M concentration. Figure S2 in SI shows the variation of osmotic pressures with molar concentration for the selected fertilisers.

      Pure water flux of single fertiliser as draw solution. The performance test was carried out using DI water and BW as feed water under similar operating conditions and at 1 M fertiliser DS concentration and the results are presented in Table 1. Consistent with our earlier studies [18], amongst the 11 selected fertilisers, KCl showed the highest water flux

both with DI water feed (2.57 μm/s) and BW feed (2.31 μm/s). NH_4Cl had the next highest water flux at 2.48 μm/s with DI water feed and 2.27 μm/s with BW feed. Urea showed the lowest water flux of only 0.57 μm/s with DI water feed and 0.25 μm/s with BW feed, which is significantly lower than any other fertiliser examined in this study.

Table 1 also presents the performance ratio (PR), calculated as a percentage ratio of actual water flux J_w, to theoretical water flux J_{wt}. PR indicates the bulk osmotic pressure available for effective generation of water flux across the membrane [18, 30]. NH_4NO_3 showed the highest PR of more than 22% both with DI water and BW as feed. NH_4NO_3 is followed by KCl and NH_4Cl with more than 20% with both DI water and BW feed. Urea had the lowest PR of only about 8.5% with DI water and even lower (4.5%) with BW feed. The poor performance of urea in terms of water flux is probably attributed to the unique property of urea solution. Urea has a tendency to self-aggregation due to the hydrophobic effect [33, 34], with urea-urea association increasing at higher concentration [35]. All fertilisers showed a PR higher than 10%, except urea. The PR of DI water and BW feed are observed quite similar probably because of the low salt concentration used in the BW feed except for urea and KNO_3 where the PR with BW was slightly lower than the BW feed.

Loss of nutrient by reverse movement of draw solutes using single fertilisers. In FDFO desalination, reverse movement of draw solutes is not only an economic loss, but also the presence of nutrients in the feed concentrate could make the concentrate management more complex as nitrogen (N) and phosphorous (P) can cause eutrophication and algal blooms in the receiving water [36, 37]. Therefore, it is important that the DS with low reverse solute flux are identified and selected for application. Most recent efforts have been to synthesize FO membrane that has high solute rejection and selectivity and, a number of high performing thin film composite FO membranes have been already reported [38-40]. However, FO process can achieve very high recovery rates without additional energy [41] and therefore concentrate could be managed using simple method such as evaporation ponds for salt recovery especially for inland FDFO desalination.

In other studies [18, 42], the assessment of DS performance is usually done in terms of reverse solute flux or specific reverse solute flux (J_s/J_w or draw solute flux/water flux); however, a slightly different approach of assessment is adopted here. For fertilisation, the amount of essential nutrients present in the fertiliser is more important than the other non-essential elements or species present. Therefore, the reverse solute flux in FDFO has been measured in terms of the loss of macronutrients (NPK) per unit volume of water extracted from the feed instead of the whole fertiliser compound.

The results in Table 1 indicate that, urea as a DS results in a very high loss of nutrient (29.2 g/L of N). High reverse solute flux of urea is due to its low molecular size, and also because urea remains neutral or uncharged in water solution. Uncharged species or low molecular weight compounds more readily diffuse through the membrane by diffusion [43]. Besides high loss of nutrient by reverse diffusion, urea also has significantly lower water flux and, therefore, urea alone is not an ideal draw solute for the FDFO desalination process.

Calcium nitrate showed the lowest loss of nutrient by reverse diffusion (0.122 g/L of N). Consistent with other findings [18, 42], fertilisers containing divalent ions such as Ca^{2+}, HPO_4^{3-}, and SO_4^{2-} have significantly lower loss due to less reverse movement of draw solutes attributed to their relatively larger hydrated ions.

Table 1: Performances of single fertilisers as DS in the FO process using DI water and BW as feed. J_{wt}: theoretical water flux calculated using equation (1): experimental water flux; PR: performance ratio (J_w/J_{wt}). A: pure water permeability coefficient of the FO membrane (A = 0.28194 ± 0.008 μm s^{-1}atm^{-1}). Bulk osmotic pressure of the BW feed (5,000 mg/L NaCl) taken is 3.9 atm. RSF data is obtained from the DI water as feed.

Draw Solution (1 M:1 M)	Δπ@1M (atm)	DI as feed water			Loss of nutrient by reverse diffusion (g L^{-1})			BW as feed water		
		J_w (μm s^{-1})	J_{wt} (μm s^{-1})	PR (J_w/J_{wt})	N	P	K	J_w (μm s^{-1})	J_{wt} (μm s^{-1})	PR (J_w/J_{wt})
Urea	23.7	0.57	6.68	8.5%	29.20			0.25	5.58	4.5%
NH$_4$NO$_3$	33.7	2.13	9.50	22.4%	1.28			1.92	8.40	22.9%
(NH$_4$)$_2$SO$_4$	46.1	1.99	13.00	15.3%	0.34			1.71	11.90	14.4%
MAP	43.8	1.47	12.35	11.9%	0.38	1.01		1.32	11.25	11.7%
KCl	44.0	2.57	12.41	20.7%			0.71	2.31	11.31	20.4%
KNO$_3$	37.2	1.87	10.49	17.8%	0.60		1.28	1.17	9.39	12.5%
KH$_2$PO$_4$	36.5	1.73	10.29	16.8%		0.17	0.13	1.61	9.19	17.5%
Ca(NO$_3$)$_2$	48.8	2.15	13.76	15.6%	0.12			2.04	13.65	14.9%
NaNO$_3$	41.5	1.54	11.70	13.1%	0.55			1.25	10.61	11.8%
DAP	50.6	1.79	14.27	12.5%	0.52	0.26		1.48	13.17	11.2%
NH$_4$Cl	43.5	2.48	12.26	20.2%	0.36			2.27	11.16	20.3%

Final nutrient concentration in the FDFO product water using single fertilisers as draw solute. At low DS concentrations, equation (1) is valid indicating that, DS can extract water until the bulk osmotic pressures of the DS and feed water becomes equal. To verify this, experiments were carried out at different DS concentrations (but at low concentrations) using KCl and Ca(NO$_3$)$_2$.4H$_2$O as DS separately with BW as FS (more explanation can be found under Section S2 of SI). The results in Figure S3 of SI shows that, at low DS concentrations, the water flux in FO process becomes zero when the bulk osmotic pressure of the DS reaches 3.9 atm, i.e in osmotic equilibrium with the bulk osmotic pressure of the BW feed (i.e $\pi_{D,b} = \pi_{F,b} = 3.9$ atm). It may be however acknowledged that, operating FDFO process using low initial DS concentration could result in water flux that is not economically viable. Therefore, an optimum initial DS concentration must be determined which may also depend on other factors such as feed salinity, the total membrane area in the single or multiple membrane module arrays in the FDFO system.

Considering the bulk osmotic equilibrium between the DS and FS in the FO process, the expected NPK nutrient concentrations in the final FDFO product water for the 11 selected single fertilisers using SW and BW are presented in Figure 1. It is clear from the figures that the nutrient concentrations in the final FDFO product water depends on the feed water salinity and the types of fertiliser DS. The lower the feed salinity, the lower will be the nutrient concentrations in the final FDFO product water, and proportionately higher with seawater.

For example, when urea or NH_4NO_3 is used as the DS with seawater as the feed (Figure 1(a)), the final FDFO product water would contain 32.6 and 22.5 g/L of N in the final FDFO product water, respectively. The lowest N concentration is observed for MAP and NH_4Cl, with only about 8 g/L with seawater as the feed. The concentration of P also remained high, with 19.3 and 16.0 g/L for MAP and DAP, respectively with seawater feed. The concentration of K is 24 g/L with KCl and about 28 g/L with KH_2PO_4 and KNO_3.

However, the results in Figure 1(b) indicate that the nutrient concentration in the final FDFO product water can be significantly lower when BW is used as the FS instead of seawater. For example, MAP, $NaNO_3$ and NH_4Cl could achieve a final N concentration of only about 2 g/L, while the N concentration for urea DS could reduce to about 8 g/L. Therefore, these results indicate that FDFO desalination is more suitable for BW with low salinity, especially from the point of view of achieving product water that meets the acceptable nutrient concentration for direct fertigation.

Depending on the types of crops and growing seasons, the required nutrient concentration varies from 15 to 200 mg/L of N, 5 to 60 mg/L of P, and 8 to 250 mg/L of K [23, 44]. For example, if the target crop is tomato, the nutritional requirement by fertigation would vary 120-200 mg/L N, 40-50 mg/L P, 180-300 mg/L K, 10-120 mg/L Ca, 40 to 80 mg/L Mg, etc. for a drip irrigation system, depending on the various plant growth stages [45]. Phosphate ($H_2PO_4^-$) concentration above 2 moles/m^3 or 62 mg/L of P can be toxic to some plants [46]. Therefore, the results in Figure 1(b) indicate that the final nutrient concentration of each nutrient using BW as FS is still high for direct fertigation. The final FDFO product water needs to be diluted several times to lower the nutrient concentrations to desired level. Although, further dilution can be achieved by using fresh water, it could be a significant impediment where fresh water for irrigation is unavailable. Options such as nanofiltration can also be suitably used as post-treatment for partial recovery of the nutrients [47, 48] for further recycling and reuse by FDFO process while the permeate containing significantly lower nutrient concentrations can be used for direct fertigation [22]. However, it is essential that FDFO desalination produce product water that either meets irrigation water quality or requires less dilution water.

One of the important observations noted from the final nutrient concentrations in Table 1 is that, those fertilisers containing a lower percentage of a particular nutrient element due to the presence of other elements in the compound result in lower final nutrient concentrations. Figure S4 of SI shows a fairly good correlation between the percentage of N in different fertilisers and their N concentration in the final FDFO product water, which is the main motivation behind using blended fertilisers as DS.
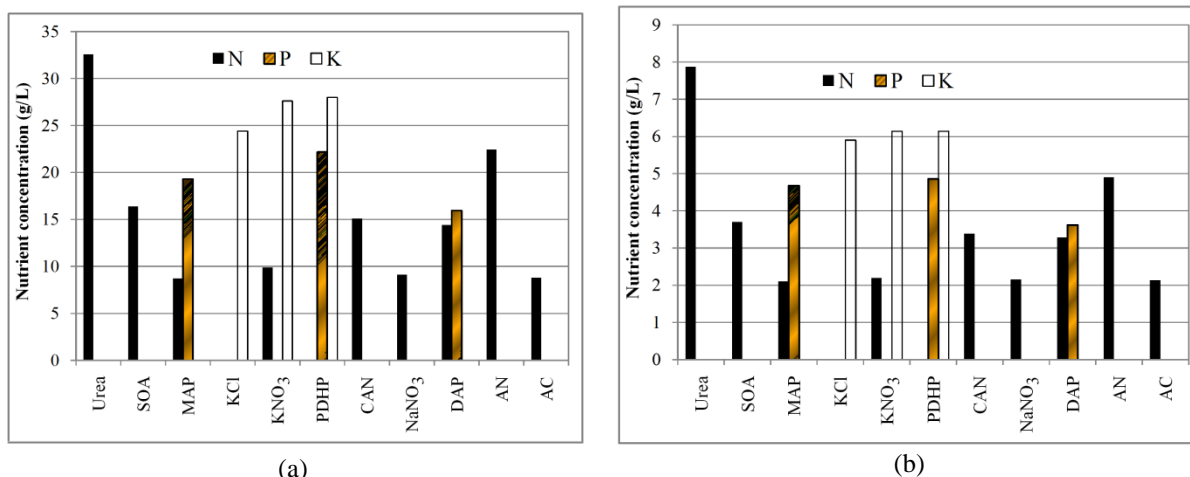
Figure 1: Expected final NPK nutrient concentrations of fertiliser solution after FO desalination or in the final FDFO product water using (a) seawater as feed water (35,000 mg/L NaCl at 28 atm), and (b) brackish water as feed water (5,000 mg/L NaCl at 3.9 atm)

FDFO desalination using fertiliser DS blended with two single fertilisers. The assessment of blended fertilisers was made for BW, since our earlier results indicate that it is more suitable than seawater for FDFO desalination for fertigation. Besides, seawater is likely to have other issues including boron concentration that may exceed and cause plant toxicity and hence require separate studies. The details of the selected fertiliser blends are summarised in Table 2. More details on the blended matrix can be found in Table S1 of SI.

Properties of the blended fertiliser draw solutions. Most selected fertilisers can be blended with each other, except calcium-containing fertilisers with sulphate or phosphate fertilisers which form precipitates. The pH of all blended fertilisers in this study was within the range of pH 4.0 to 8.0, compatible to CTA FO membrane used. Blending decreases the solubility of some fertilisers, such as $(NH_4)_2SO_4$ blended with KCl that forms K_2SO_4 with much lower solubility [45]. When two different compounds were blended in the solution, the number and types of species formed varied depending on the type of fertiliser used. Speciation analysis (data not included) using the OLI Stream Analyser indicated that urea was the only fertiliser that does not dissociate to form different species with any of the fertilisers blended at 25°C. Speciation is important because osmotic pressure is directly related to the number of species formed in the solution.

In most blends, the osmotic pressure of the blended fertiliser solution was generally lower than the arithmetic sum of the osmotic pressures of the two individual fertiliser solutions, except for NH_4Cl blended with some fertilisers. For some fertiliser blends, the net osmotic pressure significantly decreased, while in some cases the decrease was minimal. The decreased osmotic pressure is might be explained due to complex interactions between the ions and counter ions of each blended components that likely results in decreased number of species formed in the DS. More discussion on the blended properties can be referred to section S3 of SI.

Water flux of blended fertiliser draw solutions. The highest water flux was observed for the $NH_4NO_3+NH_4Cl$ blend, with 3.94 μm/s using DI water and 3.52 μm/s using BW as feed; while the lowest pure water flux was observed for urea+MAP blend with just 1.53 μm/s and 1.39 μm/s using DI water and BW as feed, respectively. Blends such as NH_4NO_3+DAP, $NH_4SO_4+KNO_3$, , $KCl+NH_4Cl$ and $Ca(NO_3)_2+NH_4Cl$ all resulted in water

fluxes comparatively higher than other blends. However, in almost all cases, the water fluxes of the blended fertiliser DS were slightly lower than the sum of the two water fluxes if the two single fertilisers were used alone as DS with the exception of urea+KNO_3, urea+$NaNO_3$ and SOA+KO_3 blends (with BW feed). The water flux for urea+KNO_3 blend was 2.83 µm/s, which is 16.2% higher than the sum of the individual fluxes of urea (0.58 µm/s) and KNO_3 (1.86 µm/s) used alone as DS. Likewise, the water flux for the urea+$NaNO_3$ blend was 2.36 µm/s, which is 11.6% higher than the sum of the individual fluxes of urea (0.58 µm/s) and $NaNO_3$ (1.53 µm/s). The increase in water flux with urea blend indicates a promising result since urea fertiliser itself as a DS has a very poor water flux in comparison to any other fertilisers. Table S1 of SI provides additional data on the performance of the blended fertiliser DS.

Table 2 also shows the PR of water flux for the blended fertilisers. Depending on the type of blend, the PR ranged 8-19% with DI water and slightly less with BW feed. NH_4SO_4+KNO_3 and NH_4NO_3+NH_4Cl showed the highest PR of about 19% with DI water feed and about 17% with BW feed. The lowest performance ratio was observed for urea+MAP and NH_4SO_4+MAP blends, with only about 8% both using DI water and BW as feed. When the two fertilisers were blended in the solution, their PR was observed to be between the PR of the two fertiliser solutions tested individually. When two fertilisers with high PRs were blended together, the fertiliser blend generally tended to have a higher PR. Urea had the lowest PR amongst all the 11 selected fertiliser DS (Table 1); however, when urea was blended with other fertilisers, the PR of the DS significantly improved in comparison to using urea alone as the DS. Furthermore, these results also indicate that the PR of high performing fertilisers decreases when blended with low performing fertilisers. Therefore, it might be ideal to blend two high performing fertilisers containing different types of nutrients.

The improved water flux for urea+KNO_3 can be explained as follows. From equations 3 and 4, water flux in the FO process is a function of parameter K, which in turn is a function of diffusion coefficients of the draw solutes. Since all the experiments were performed using the same membrane (same membrane structural parameters), the increase in the performance of the urea+KNO_3 DS could have been influenced by the change in the diffusion coefficient of the draw solute. Blending different fertilisers not only alters the types of species formed in the solution, but the coexistence of the different species could also alter the diffusivity of a particular species. The diffusion coefficient of KNO_3 in the urea+KNO_3 solution was observed to be slightly higher than for KNO_3 alone in water. This increase in the diffusivity of KNO_3 probably helped in lowering the solute resistivity K and, therefore, decreased the ICP effects on the porous side of the membrane, thereby enhancing the water flux. ICP is one of the major factors responsible for limiting the water flux by the FO process [17, 49-52]. For concentrated solutions and solutions containing multiple component species, the diffusion coefficients are difficult to estimate because the solution does not obey the binary form of Fick's Law with the exception of the mixture of weak electrolytes [53]. The diffusion coefficients of each ionic species in the solution were determined by OLI Stream Analyser 3.2, while the average diffusion coefficients of each compound were calculated using equations provided elsewhere [51, 53]. More explanation on this is provided under sections S3 and S4 of SI.

Loss of nutrients by reverse diffusion of draw solutes during FDFO process. The loss of essential fertiliser nutrients due to reverse movement of only selected blended fertiliser draw solutes are also presented in Table 2. These results indicate that the fertiliser

blend containing urea could still result in higher loss of N nutrient by reverse draw solute transfer. However, it is interesting to note that some blends result in either increased or decreased loss of nutrients in comparison to using single fertiliser as DS alone.

For example, when urea is blended with KH_2PO_4, the loss of nutrients measured as N/P/K in g/L is 13.46/0.96/1.01. The loss of urea N in this case is significantly lower than when urea was used as DS alone (29.2 g/L); however, the loss of K and P are higher in urea+KH_2PO_4 blended DS than for KH_2PO_4 alone. In the $(NH_4)_2SO_4$+KH_2PO_4 blend, the loss of all the nutrients are lower than the loss of nutrient that occurs if they are used as DS alone. In contrast, the KH_2PO_4+$NaNO_3$ blend resulted in increased NPK nutrient loss in comparison to their use as individual DS.

The reverse solute flux results for DS blended with two fertilisers indicate that the presence of multiple species (either in ternary system or in quaternary system) in the solution has a bearing on the net diffusion of species across the membrane for each type of species. At this stage, it is not well understood what causes this difference in reverse diffusion of draw solutes in the presence of multiple component species. Further study, including modelling of nutrient loss due to reverse movement of species, would provide an interesting inference on the influence of the multiple species in the draw solution.

Nutrient concentrations in the final FDFO product water using blended fertilisers as draw solutions. Table 2 also shows the final nutrient concentration in the product water by FDFO desalination using different types of blended fertiliser DS with BW (more data presented in Table S1 of SI). These results indicate that, blending of fertiliser in DS generally resulted in a significant reduction in the final nutrient concentration in comparison to using single fertilisers as the DS.

Urea fertiliser has one of the highest nitrogen contents (46.6%); therefore, when urea is used alone as the DS, the final nutrient concentration (measured as N/P/K in g/L) in the product water is 7.87/0/0 with BW feed (Figure 1.b), which is significantly high for direct fertigation. However, when urea is blended with other fertilisers, the final nutrient concentration decreases appreciably. For example, when urea is blended with $(NH_4)_2SO_4$, their final nutrient concentration in the FDFO product water reaches 2.75/0/0, which is a decrease of about 65% from using urea as the DS alone. Likewise, when NH_4NO_3 with the next highest N (35%) fertiliser is blended with KH_2PO_4, the final N concentration is 1.26/1.40/1.76, which has significantly lower N than using NH_4NO_3 alone as DS. Even by blending urea and NH_4NO_3, both containing the highest N, the final N concentration in the FDFO product water decreases considerably.

The decrease of final nutrient concentration in the FDFO product water was more significant when fertilisers containing different major nutrients were blended together. For example, consider the blending of fertilisers containing only N as nutrient such as urea and NH_4NO_3, with others such as KH_2PO_4 that do not contain N. The final nutrient concentrations of all major NPK nutrients for such blends decrease significantly in comparison to using them alone as DS. It is also important to note that it will be easier to achieve significantly reduced nutrient concentration in the final FDFO product water, especially when two fertilisers containing different nutrients at low concentrations are blended together in the solution rather than blending fertilisers containing similar nutrients. For example, when MAP, which contains one of the lowest nutrient percentages (12%N and 27%P), is blended with KCl (containing only K), the final nutrient concentrations achieved in the FDFO product water are

0.61/1.35/1.70, which is one of the lowest in terms of NPK nutrients amongst all the blends studied here. Similar low nutrient concentrations were also achieved with $KH_2PO_4+NH_4Cl$ blends. Although blending two fertilisers containing similar nutrients can also achieve significantly reduced nutrient concentrations in comparison to their parent single fertilisers, the final nutrient concentration for the common nutrient remains comparatively higher than when blending two fertilisers containing different nutrients. Blending to provide all NPK nutrients is even more effective in reducing the final concentration of the nutrients in the FDFO product water. These results confirm that blending two or more standard fertilisers could be useful in preparing a fertiliser DS that can produce FDFO product water of acceptable final nutrient concentration for direct fertigation.

Table 2: Performance of the selected fertiliser blend as DS in the FO process using DI water and BW as feed. J_{wt}: theoretical water flux calculated using equation (1), J_w: experimental water flux; PR: performance ratio (J_w/J_{wt}). Pure water permeability coefficient of the FO membrane (A = 0.28194 ± 0.008 μm/s/atm). Bulk osmotic pressure of the BW feed (5,000 mg/L NaCl) taken is 3.9 atm. RSF data is obtained from the DI water as feed. MAP: monoammonium phosphate - $NH_4H_2PO_4$, DAP: diammonium phosphate $(NH_4)_2HPO_4$, SOA: sulphate of ammonia $(NH_4)_2SO_4$. CAN: $Ca(NO_3)_2.4H_2O$. RSF: Revers solute flux. Additional data on blending is shown in Table S1 of SI

Fertiliser combinations 1M or (1M:1M)	π (atm)	DI as feed water			BW as feed water		
		J_w (μm/s)	PR (%)	N/P/K loss by RSF (g/L)	J_w (μm/s)	PR (%)	Final nutrient N/P/K (g/L)
Urea+SOA	68.6	2.16	11.2	9.41/0/0	2.01	11.0	2.75/0/0
Urea+MAP	66.2	1.53	8.2	10.71/0.26/0	1.39	7.9	2.36/1.74/0
Urea+KNO$_3$	60.0	2.83	16.7	7.93/0/1.40	2.27	14.3	2.38/0/2.21
Urea+KH$_2$PO$_4$	59.2	2.11	12.6	13.46/0.96/1.01	1.73	11.1	1.59/1.76/2.22
Urea+NaNO$_3$	64.4	2.35	12.9	6.78/0/0	2.17	12.71	2.36/0/0
NH$_4$NO$_3$+KH$_2$PO$_4$	78.5	2.81	12.7	1.04/0.01/0.72	2.69	12.8	1.26/1.40/1.76
NH$_4$NO$_3$+DAP	78.5	3.68	16.6	1.98/0.01/0	2.78	13.2	2.27/1.26/0
NH$_4$NO$_3$+NH$_4$Cl	74.8	3.94	18.7	1.55/0/0	3.52	17.6	1.92/0/0
SOA+MAP	89.6	2.09	8.3	0.818/0.624/0	2.05	8.5	1.72/1.27/0
SOA+KNO$_3$	70.2	3.84	19.4	4.40/0/0.77	3.25	17.4	1.55/0/1.44
SOA+KH$_2$PO$_4$	75.1	2.83	13.4	0.03/0.03/0.03	2.56	12.8	1.20/1.33/1.68
MAP+KCl	82.6	3.42	14.7	0.91/0.29/0.75	3.27	14.7	0.61/1.35/1.7
KCl+NH$_4$Cl	88.6	3.71	14.9	0.17/0/0.23	3.43	14.4	0.61/0/1.69
KH$_2$PO$_4$+NH$_4$Cl	82.6	3.18	13.6	0.27/0.01/0.24	3.15	14.2	0.61/1.35/1.70
CAN+NH$_4$Cl	82.0	3.62	15.6	0.74/0/0	3.44	15.6	1.71/0/0

Influence of NPK blends in different ratios using two or more single fertilisers on the final nutrient concentrations. NPK fertiliser blends can be prepared either using two or more single fertilisers. The earlier data shows combinations for only two different fertilisers in equal molar ratio. Here, we show how blending of two or three single fertilisers to prepare different grades of fertilisers can influence the final nutrient concentrations in FDFO product water. Figure 2 shows that, it is possible to prepare DS containing different grades of N:P:K nutrients for particular crop requirement. MAP+KCl, was taken as a sample blend (Figure 2a)

as this blend resulted in one of the lowest final nutrient concentrations (Table 2). It also shows that it is possible to achieve a very low concentration of a particular nutrient by adjusting the blends. For example, a DS with a fertiliser grade of 10:12:11 achieves final nutrient concentrations of 850/1890/1020 mg/L while DS grade of 2:4:45 can achieve about 100/300/2800 mg/L. It shows that, when the concentration of one of the nutrients is adjusted, the concentration of the other nutrients also varies, as their concentrations are dependent. This is not suitable as each nutrient requires different level of dilution to maintain required nutrient concentrations. However, it becomes more convenient to adjust all the nutrient concentrations as desired when more than two different fertilisers are used in the blend as shown with MAP+KCl+NH$_4$NO$_3$ in Figure 2b.

Table 3 shows comparative nutrient concentrations for fertigation of three selected plants (tomato, eggplant and cucumber). The DS was prepared by blending four selected fertilisers NaNO$_3$, (NH$_4$)$_2$SO$_4$, KCl and KH$_2$PO$_4$. While other fertiliser combinations are also possible, the combination that yielded the lowest nutrient concentration was selected for discussion in Table 3. The data shows that it is possible to formulate a specific grade of fertiliser blend suitable for each plant and this is important to avoid variable dilution required when multiple nutrients are present in the FDFO product water. The results in Table 3 indicate that, the nutrient concentrations in the final FDFO product water is still not suitable for direct fertigation and the process will still require dilution before application. For example, for fertigation of tomato, the final FDFO product will require a dilution of 4.8 times with feed TDS of 5,000 mg/L although it reduces to only about 2 times dilution when feed TDS is 2,000 ppm.

(a)   (b)
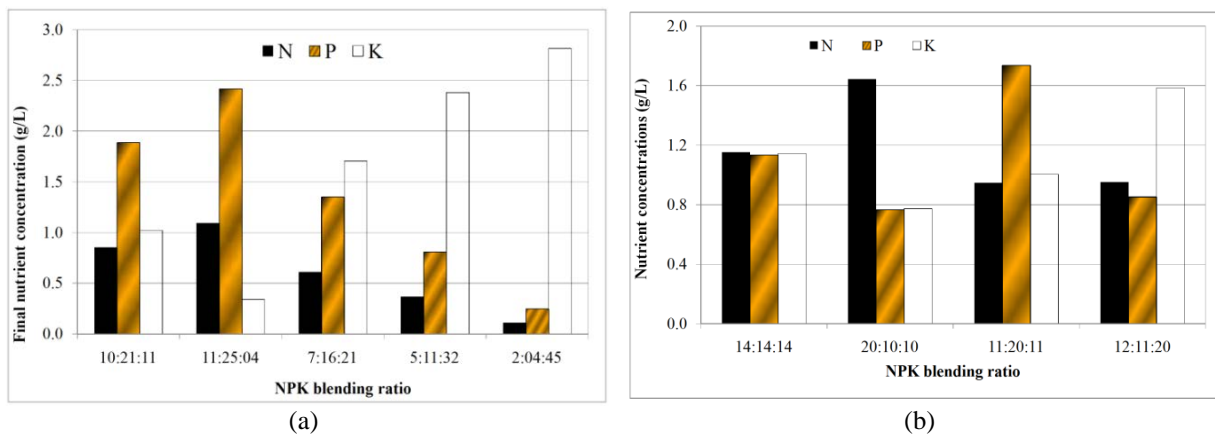
Figure 2: Final NPK nutrient concentrations of: (a) MAP and KCl blended, and (b) MAP, KCl and NH$_4$NO$_3$ blended in different ratios

Table 3: Estimated N/P/K nutrient concentrations in the final FDFO product water using blended fertiliser as DS and BW (5,000 mg/L NaCl with an osmotic pressure of 3.9 atm, assigned as BW5 in this table for clarity) as feed. DS consisted of blended fertiliser solution prepared in specific N:P:K ratios suitable for three selected plants using four different types of fertilisers [NaNO$_3$, (NH$_4$)$_2$SO$_4$, KCl and KH$_2$PO$_4$] that yielded the minimum nutrient concentration in the final product water. BW2, BW3, BW4 and BW5 refer to brackish water feed of TDS 2,000, 3000, 4,000 and 5,000 mg/L of NaCl, respectively.

Plants	Recommended concentration (N/P/K mg/L)	Proposed DS grade N:P:K (%)	Final N/P/K using BW5 feed (mg/L)	Dilution required for different feed water BW2/BW3/BW4/BW5
Tomato	200/50/300 [38]	12:03:19	944/236/1147	1.9/2.8/3.8/4.8
Egg plant	170/60/200 [16]	13:04:15	1067/356/1255	2.5/3.7/5.0/6.3
Cucumber	200/50/200 [16]	14:04:14	1174/300/1168	2.4/3.5/4.7/6.0

It was demonstrated that, by using blended fertilisers as DS instead of single fertiliser, the final nutrient concentration of a particular nutrient could be significantly reduced in FDFO desalination process. However, the study also shows that, because of the limitations offered by the osmotic equilibrium, achieving acceptable nutrient concentrations in the final FDFO product water will still remain a challenge especially when high salinity feed water is used therefore requiring different levels of dilution factor before direct fertigation. Phuntso et al. [22] has suggested nanofiltration as either pre-treatment to reduce TDS or post treatment for partial recovery of draw solutes for further recycling and reuse in the processes reducing the nutrient concentration and make diluted DS acceptable for direct fertigation.

ACKNOWLEDGEMENTS

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Supporting information for

Blended Fertiliser as Draw Solutions for the Fertiliser Drawn Forward Osmosis Desalination

Sherub Phuntsho[a], Ho Kyong Shon[a*], Tahir Majeed[a], Ibrahim El Saliby[a], Saravanamuthu Vigneswaran[a], Jaya Kandasamy[a], Seungkwan Hong[b], Sangyoup Lee[b]

[a]School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Post Box 129, Broadway, NSW 2007, Australia.

[b]School of Civil, Environmental & Architectural Engineering, Korea University, 1, 5-ka, Anam-Dong, Sungbuk-Gu, Seoul 136-713, Republic of Korea

* Corresponding author: Email: Hokyong.Shon-1@uts.edu.au

Total pages: 10 excluding cover page

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SUPPORTING INFORMATION

S1. Forward osmosis experimental procedures

The performance of the FO process was conducted using lab scale FO unit, with similar features described elsewhere (Phuntsho *et al.*, 2011). The commercial FO membrane (Membrane 090128-NW-1, Hydration Technologies Inc., USA) was used which is made from cellulose acetate embedded in a polyester woven mesh and its characteristics are widely reported (McCutcheon *et al.*, 2005; Cath *et al.*, 2006; Tang *et al.*, 2010). The pure water permeability coefficient of the FO membrane was $A = 0.28194 \pm 0.008$ µm s^{-1}atm^{-1}). The coefficient was determined in RO mode at various hydraulic pressures using DI water as feed. The schematic layout of the FO experimental set up is shown in Figure S1.

The DS consisted of either 1.0 M single fertiliser or a blended solution of two or more fertilisers mixed in specific molar proportions. The performances of the DS was comparatively studied using DI water and brackish water or BW (5,000 mg/L) as feed as in other studies (Achilli *et al.*, 2010; Phuntsho *et al.*, 2011). The crossflow was run in a counter-current mode, since the water flux is slightly higher in this conditions (Mi and Elimelech, 2008). Both the feed and DS were supplied at crossflow velocities of 8.5 cm s^{-1}. The temperature of the feed and DS in all cases was maintained at 25 °C. Water flux was measured continuously by connecting DS to a digital mass scale connected to a computer. Each experiment was carried out at least for six hours duration for effective monitoring of the reverse diffusion of draw solutes. When single fertiliser compound was used, reverse solute flux was monitored by recording electrical conductivity (EC) online using a multimeter (CP-500L, ISTEK) with separate probes attached and, connected to a computer for data logging. When blended fertiliser DS was used, reverse solute flux was measured by collecting and analysing the feed water samples at the end of each experiment. Total phosphorous and total nitrogen in the samples were analysed as per APHA 4500 standard while potassium was analysed using ICP-MS (Perkin Elmer Elan DRC-e). Membrane transport parameters such as the pure water permeability coefficient 'A' of FO membrane was evaluated using the methods described elsewhere (Phuntsho *et al.*, 2011).
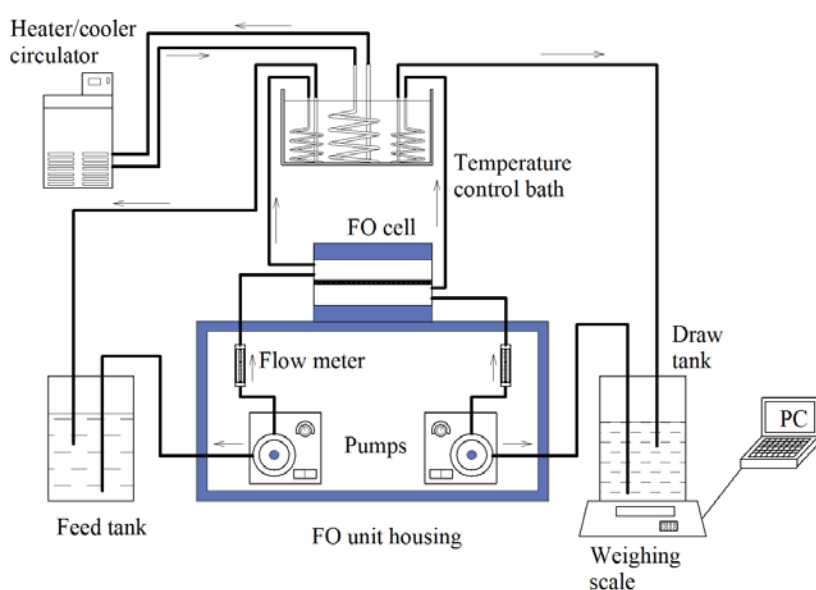

Figure S1: Schematic layout of the lab scale forward osmosis experimental set up
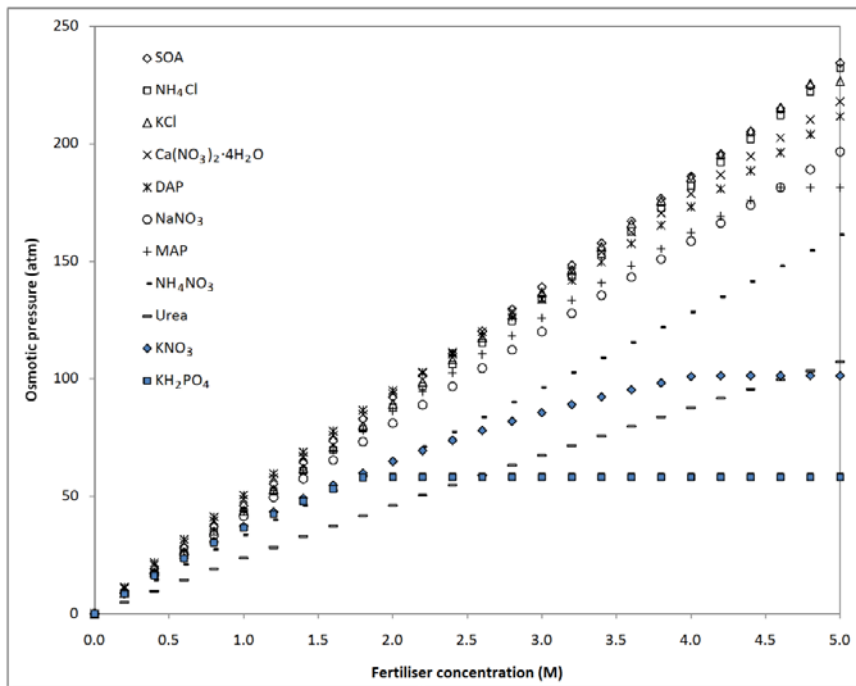
Figure S2. Osmotic pressure of fertiliser DS as a function of molar concentrations. Osmotic pressure was predicted using OLI Stream Analyser 3.1 (OLI Inc, USA) at 25˚C.

S2 Determination of osmotic equilibrium in FO process experimentally

In order to determine the DS concentrations (or the bulk osmotic pressure) at which the water flux reaches zero or near zero, experiments were conducted at different low DS concentrations using BW (5,000 mg/L NaCl) as feed. Two types of DS were selected for the experiments: KCl (containing only monovalent ions) and $Ca(NO_3)_2.4H_2O$ (containing both mono and divalent ions) and the water fluxes are plotted against the bulk osmotic pressure of the DS as shown in Figure S3. From the figure it is clear that, at low DS concentrations, the water flux in FO process becomes zero when the bulk osmotic pressure of the DS reaches osmotic equilibrium with the bulk osmotic pressure of the BW feed (i.e $\pi_{D,b} = \pi_{F,b} = 3.9$ atm) irrespective of types of draw solutes used. This shows that, as the DS becomes more and more diluted due to influx of water from the feed water, the bulk osmotic pressure of the DS decreases thereby reducing the net driving force and ultimately the water flux across the membrane. At low water flux, the CP effects are also comparatively low and if the process is allowed to continue, the osmotic process can continue until the bulk osmotic pressures of the DS and the FS becomes equal (osmotic equilibrium).

However, in reality it may not be economically viable for osmotic process to continue using DS concentration below certain level because the cost of energy for pumping the DS and FS would far outweigh the amount of water it can extract within a specific time. An optimum initial DS concentration could be determined based on the total membrane area in a single membrane module arrays and the feed salinity concentrations.
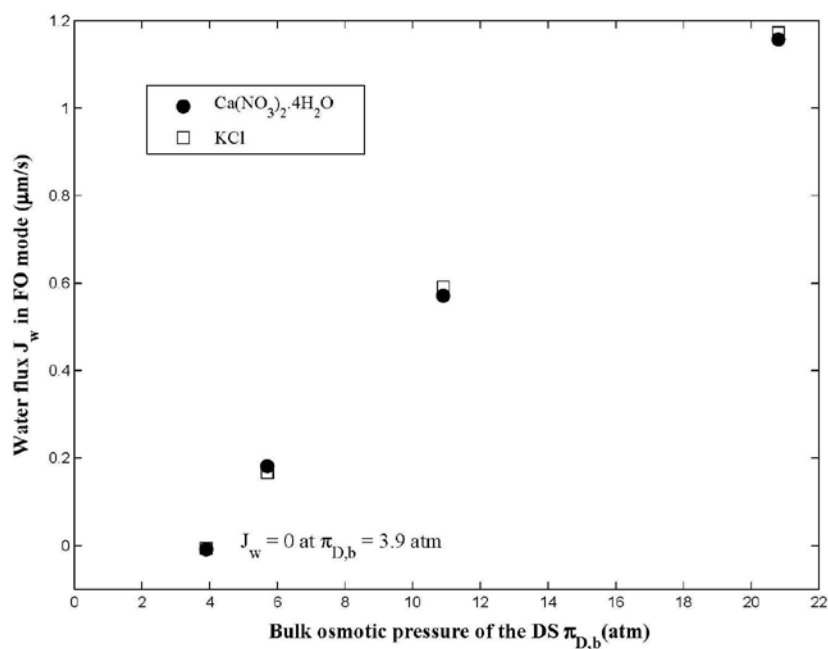
Figure S3. Variation of water flux in FO process at low DS concentrations or bulk osmotic pressure. The water flux at $\pi_{D,b}$=3.9 atm was zero.
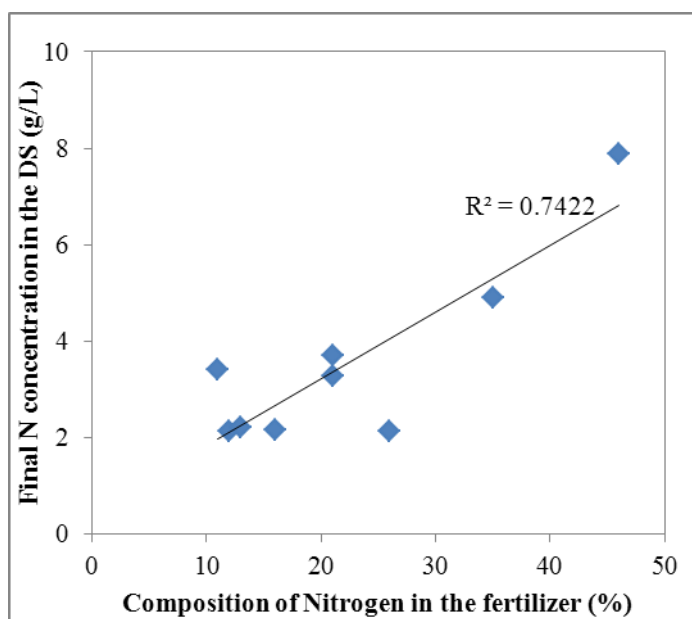
Figure S4: Comparison between % of N composition of N containing fertilisers and the N nutrient concentration in the final DS or desalted water with brackish water as feed water.

S3. Properties of the blended fertiliser draw solutions

Table S1 shows the pH and the osmotic pressure of the blended fertilisers DS. Most of the selected fertilisers could blend with each other and only few combinations resulted in the formation of precipitates especially when calcium containing fertilisers were blended with sulphate or phosphate fertilisers. For example, $(NH_4)_2SO_4$ and $Ca(NO_3)_2$ blend resulted in the

formation of $CaSO_4$ (gypsum) precipitate while $NH_4H_2PO_4$, $(NH_4)_2HPO_4$ and KH_2PO_4 with $Ca(NO_3)_2$ formed $CaHPO_4$ precipitates. Therefore these combinations are not suitable for fertiliser blending. Blending also decreased solubility of some fertilisers. For example, when $(NH_4)_2SO_4$ was blended with KCl, one of the products formed is K_2SO_4 which has much lower solubility than their original basic fertilisers (Imas, 1999). The decrease in the solubility could reduce the recovery rate at which FDFO desalination can operate because recovery rates depend on the fertiliser solubility. Higher fertiliser solubility leads to higher osmotic pressure for a particular fertiliser draw solution and therefore higher feed recovery rates are possible. The pH of all blended fertilisers in this study was within the range of pH 4.0 to 8.0, indicating that they are compatible with the commercially available cellulose acetate FO membrane.

When two different compounds were blended in the solution, the number and types of species formed varied depending on the type of fertiliser used. Speciation analysis using the OLI Stream Analyser indicated that urea was the only fertiliser that does not dissociate to form different species with any of the fertilisers blended at 25°C. Speciation is important because osmotic pressure is directly related to the number of species formed in the solution. While a number of species are important, the nature of the species is also important since non-charged species tend to diffuse more easily through the membrane.

In most blends, the osmotic pressure of the blended fertiliser solution was generally lower than the arithmetic sum of the osmotic pressures of the two individual fertiliser solutions, except for NH_4Cl blended with some fertilisers. For some fertiliser blends, the net osmotic pressure significantly decreased, while in some cases the decrease was minimal. For example, most fertilisers blended with KNO_3 and DAP resulted in lowering osmotic pressure in some cases by more than 10% with the highest reduction observed for KNO_3 and DAP blend at 22.6%. NH_4NO_3 with KH_2PO_4 and $Ca(NO_3)_2$ and, NH_4Cl with $Ca(NO_3)_2$ also decreased the net osmotic pressure by more than 10%. The reduction in the resultant osmotic pressure of the blended solution may be due to the change in the properties of the blended fertiliser solutions probably due to the formation of more complex species. Table S2 shows the comparative properties of KNO_3 and DAP and their blended solution as a typical example. When KNO_3 and DAP are blended (1 M : 1 M), the total number of species decreased to 4.45 M from 4.98 M for the combined species of the two different solutions and this has direct implications on the osmotic pressure. This blend also formed about 0.5 M of uncharged species (NH_4NO_3) which might played a role in lowering the osmotic pressure.

However, when NH_4Cl is blended with other fertilisers, the blended solution mostly resulted in increased osmotic pressure except when blended with urea, KNO_3 and $Ca(NO_3)_2$. The highest increase in osmotic pressure was observed for $(NH_4)_2SO_4 + NH_4Cl$ with about 10% increase. Urea has low osmotic pressure and therefore not suitable for use alone as DS. But when urea is blended with other fertilisers, there is no appreciable decrease in the net osmotic pressure except with $Ca(NO_3)_2$ and KNO_3. This indicates that urea blended fertilisers can be used as DS for FO desalination and this is significant because, urea is one of the most commonly used N fertilisers in the world.

Table S1: Details of different fertilisers blended as draw solution for FDFO desalination using brackish water feed. MAP: Monoammonium phosphate - $NH_4H_2PO_4$, DAP: Diammonium phosphate $(NH_4)_2HPO_4$, SOA: sulphate of ammonia $(NH_4)_2SO_4$. A: Membrane permeability coefficient of the FO membrane determined in RO mode at different pressure using DI water A = 0.28194±0.008 µm s⁻¹atm⁻¹.

Fertiliser draw solution blends in 1M:1M (DS1+DS2)	Blended DS (pH)	Blended DS π (atm)	Sum of π1+π2 (atm)	M@3.9 atm	N/P/K concentrations in the final FDFO product water using BW as feed (gL⁻¹)			Actual Water Flux Jw (µm s⁻¹)			J_{wt} (µm s⁻¹)	Performance ratio $(J_w/J_{wt}$ %)		
					DS1	DS2	Blended DS	DS1	DS2	Blended DS		DS1	DS2	Blended DS
Urea Blended Draw Solutions														
Urea+NH$_4$NO$_3$	4.96	56.9	57.4	0.059	7.87/0/0	4.90/0/0	3.30/0/0	0.57	2.13	2.43	16.04	8.5	22.9	15.1
Urea+SOA	5.14	68.6	69.8	0.0491	7.87/0/0	3.70/0/0	2.75/0/0	0.57	1.99	2.16	19.34	8.5	14.4	11.2
Urea+MAP	4.2	66.2	67.5	0.0561	7.87/0/0	2.11/4.68/0	2.36/1.74/0	0.57	1.47	1.53	18.66	8.5	11.7	8.2
Urea + KCl	7	66.9	67.7	0.0561	7.87/0/0	0/0/5.9	1.57/0/2.19	0.57	2.57	3.21	18.86	8.5	20.4	17.0
Urea+KNO$_3$	6.98	60	60.9	0.0566	7.87/0/0	2.20/0/6.14	2.38/0/2.21	0.57	1.87	2.83	16.91	8.5	12.5	16.8
Urea+KH$_2$PO$_4$	4.19	59.2	60.2	0.0567	7.87/0/0	0/4.86/6.14	1.59/1.76/2.22	0.57	1.73	2.11	16.69	8.5	17.5	12.6
Urea+Ca(NO$_3$)$_2$	6.8	69.9	72.5	0.0468	7.87/0/0	3.39/0/0	2.62/0/0	0.57	2.15	2.05	19.70	8.5	14.9	10.4
Urea+NaNO$_3$	7	64.4	65.2	0.0563	7.87/0/0	2.16/0/0	2.36/0/0	0.57	1.54	2.35	18.15	8.5	11.8	12.9
Urea+ DAP	7.8	73.2	74.3	0.046	7.87/0/0	3.28/3.62/0	2.58/1.43/0	0.57	1.79	2.03	20.64	8.5	11.2	9.8
Urea+NH$_4$Cl	4.8	66.2	67.2	0.0561	7.87/0/0	2.13/0/0	2.36/0/0	0.57	2.48	2.73	18.66	8.5	20.3	14.6
Ammonium Nitrate Blended Draw Solutions														
NH$_4$NO$_3$+Urea	4.96	56.9	57.4	0.059	7.87/0/0	4.90/0/0	3.30/0/0	2.13	0.57	2.43	16.04	22.9	8.5	15.1
NH$_4$NO$_3$+SOA	5.15	79.6	79.8	0.0363	3.7/0/0	4.90/0/0	2.03/0/0	2.13	1.99	2.96	22.44	22.9	14.4	13.2
NH$_4$NO$_3$+MAP	4.13	74.7	77.5	0.0457	2.11/4.68/0	4.90/0/0	1.92/1.42/0	2.13	1.47	2.86	21.06	22.9	11.7	13.6
NH$_4$NO$_3$+KCl	4.93	76.5	77.7	0.0448	0/0/5.9	4.90/0/0	1.25/0/1.75	2.13	2.57	3.53	21.57	22.9	20.4	16.4
NH$_4$NO$_3$+KNO$_3$	5.06	66.6	70.9	0.0461	2.2/0/6.14	4.90/0/0	1.94/0/1.80	2.13	1.87	3.13	18.77	22.9	12.5	16.7
NH$_4$NO$_3$+KH$_2$PO$_4$	7.74	78.5	70.2	0.045	0/4.86/6.14	4.90/0/0	1.26/1.40/1.76	2.13	1.73	2.81	22.13	22.9	17.5	12.7
NH$_4$NO$_3$+Ca(NO$_3$)$_2$	5.18	75.7	82.5	0.0415	3.39/0/0	4.90/0/0	2.32/0/0	2.13	2.15	3.33	21.34	22.9	14.9	15.6
NH$_4$NO$_3$+NaNO$_3$	5.09	72.4	75.2	0.0459	2.16/0/0	4.90/0/0	1.93/0/0	2.13	1.54	3.16	20.41	22.9	11.8	15.5
NH$_4$NO$_3$+DAP	7.7	78.5	84.3	0.0406	3.28/3.62/0	4.90/0/0	2.27/1.26/0	2.13	1.79	3.68	22.13	22.9	11.2	16.6
NH$_4$NO$_3$+NH$_4$Cl	4.75	74.8	77.2	0.0457	4.9/0/0	2.13/0/0	1.92/0/0	2.13	2.48	3.95	21.09	22.9	20.3	18.7
Ammonium Sulphate Blended Draw Solutions														
SOA+Urea	5.14	68.6	69.8	0.0491	7.87/0/0	3.70/0/0	2.75/0/0	1.99	0.57	2.16	19.34	14.4	8.5	11.2
SOA+NH$_4$NO$_3$	5.15	79.6	79.8	0.0363	3.7/0/0	4.90/0/0	2.03/0/0	1.99	2.13	2.96	22.44	14.4	22.9	13.2
SOA+MAP	4	89.6	89.9	0.041	3.7/0/0	2.11/4.68/0	1.72/1.27/0	1.99	1.47	2.09	25.26	14.4	11.7	8.3
SOA+KCl	5.1	89.6	90.1	0.0353	3.7/0/0	0/0/5.90	0.99/0/1.38	1.99	2.57	3.32	25.26	14.4	20.4	13.2
SOA+KNO$_3$	5.28	70.2	83.3	0.0368	3.7/0/0	2.20/0/6.14	1.55/0/1.44	1.99	1.87	3.84	19.79	14.4	12.5	19.4
SOA+ KH$_2$PO$_4$	4	75.1	82.6	0.043	3.7/0/0	0/4.86/6.14	1.20/1.33/1.68	1.99	1.73	2.83	21.17	14.4	17.5	13.4
SOA+ Ca(NO$_3$)$_2$														
SOA+NaNO$_3$	5.3	83	87.6	0.035	3.7/0/0	2.16/0/0	1.47/0/0	1.99	1.54	3.44	23.40	14.4	11.8	14.7
SOA+DAP	7.6	95	96.7	0.0344	3.7/0/0	3.28/3.62/0	1.93/1.07/0	1.99	1.79	2.53	26.78	14.4	11.2	9.4
SOA+ NH$_4$Cl	5	98.5	89.6	0.0343	3.7/0/0	2.13/0/0	1.44/0/0	1.99	2.48	3.40	27.77	14.4	20.3	12.2
Monoammonium phosphate Blended Draw Solutions														
MAP + Urea	4.2	66.2	67.5	0.0561	7.87/0/0	2.11/4.68/0	2.36/1.74/0	1.47	0.57	1.53	18.66	11.7	8.5	8.2
MAP+NH$_4$NO$_3$	4.13	74.7	77.5	0.0457	2.11/4.68/0	4.90/0/0	1.92/1.42/0	1.47	2.13	2.86	21.06	11.7	22.9	13.6
MAP+SOA	4	89.6	89.9	0.041	3.7/0/0	2.11/4.68/0	1.72/1.27/0	1.47	1.99	2.09	25.26	11.7	14.4	8.3
MAP+KCl	4.1	82.6	87.8	0.0436	2.11/4.68/0	0/0/5.90	0.61/1.35/1.7	1.47	2.57	3.42	23.28	11.7	20.4	14.7
MAP+KNO$_3$	4.12	69.6	81	0.045	2.11/4.68/0	2.20/0/6.14	1.26/1.40/1.76	1.47	1.87	2.79	19.62	11.7	12.5	14.2
MAP+ KH$_2$PO$_4$	4.05	75.5	80.3	0.0438	2.11/4.68/0	0/4.86/6.14	0.61/2.72/1.71	1.47	1.73	2.28	21.29	11.7	17.5	10.7
MAP+ Ca(NO$_3$)$_2$	Precipitation occurs													
MAP+NaNO$_3$	4.07	77.1	85.3	0.0447	2.11/4.68/0	2.16/0/0	1.25/1.39/0	1.47	1.54	3.04	21.73	11.7	11.8	14.0

MAP+DAP	6	83.5	94.4	0.0391	2.11/4.68/0	3.28/3.62/0	1.64/2.42/0	1.47	1.79	2.21	23.54	11.7	11.2	9.4
MAP+ NH₄Cl	4.04	88.5	87.3	0.0433	2.11/4.68/0	2.13/0/0	1.21/1.34/0	1.47	2.48	3.21	24.95	11.7	20.3	12.8
Potassium Chloride Blended Draw Solutions														
KCl+Urea	7	66.9	67.7	0.0561	7.87/0/0	0/0/5.9	1.57/0/2.19	2.57	0.57	3.21	18.86	20.4	8.5	17.0
KCl+NH₄NO₃	4.93	76.5	77.7	0.0448	0/0/5.9	4.90/0/0	1.25/0/1.75	2.57	2.13	3.53	21.57	20.4	22.9	16.4
KCl+SOA	5.1	89.6	90.1	0.0353	3.7/0/0	0/0/5.90	0.99/0/1.38	2.57	1.99	3.32	25.26	20.4	14.4	13.2
KCl+MAP	4.1	82.6	87.8	0.0436	2.11/4.68/0	0/0/5.90	0.61/1.35/1.7	2.57	1.47	3.42	23.28	20.4	11.7	14.7
KCl+KNO3	6.95	77.1	81.2	0.0437	0/0/5.9	2.2/0/6.14	0.61/1.35/3.42	2.57	1.87	2.53	21.73	20.4	12.5	11.6
KCl+ KH₂PO₄	4.07	76.1	80.5	0.0438	0/0/5.9	0/4.86/6.14	0/1.36/3.43	2.57	1.73	3.34	21.45	20.4	17.5	15.6
KCl+ Ca(NO₃)₂	6.76	95.6	92.8	0.0326	0/0/5.9	3.39/0/0	0.91/0/1.27	2.57	2.15	3.08	26.95	20.4	14.9	11.4
KCl+NaNO₃	6.97	83.7	85.5	0.0435	0/0/5.9	2.16/0/0	0.61/0/1.70	2.57	1.54	3.16	23.60	20.4	11.8	13.4
KCl+DAP	7.8	79.7	94.6	0.039	0/0/5.9	3.28/3.62/0	1.09/1.21/1.52	2.57	1.79	3.34	22.47	20.4	11.2	14.9
KCl+ NH₄Cl	4.8	88.6	87.5	0.0433	0/0/5.9	2.13/0/0	0.61/0/1.69	2.57	2.48	3.71	24.98	20.4	20.3	14.9
Potassium Nitrate Blended Draw Solutions														
KNO₃+Urea	6.98	60	60.9	0.0566	7.87/0/0	2.20/0/6.14	2.38/0/2.21	1.87	0.57	2.83	16.91	12.5	8.5	16.8
KNO₃+NH₄NO₃	5.06	66.6	70.9	0.0461	2.2/0/6.14	4.90/0/0	1.94/0/1.80	1.87	2.13	3.13	18.77	12.5	22.9	16.7
KNO₃+SOA	5.28	70.2	83.3	0.0368	3.7/0/0	2.20/0/6.14	1.55/0/1.44	1.87	1.99	3.84	19.79	12.5	14.4	19.4
KNO₃+MAP	4.12	69.6	81	0.045	2.11/4.68/0	2.20/0/6.14	1.26/1.40/1.76	1.87	1.47	2.79	19.62	12.5	11.7	14.2
KNO₃+KCl	6.95	77.1	81.2	0.0437	0/0/5.9	2.2/0/6.14	0.61/1.35/3.42	1.87	2.57	2.53	21.73	12.5	20.4	11.6
KNO₃+ KH₂PO₄	4.1	63.9	73.7	0.0442	2.2/0/6.14	0/4.86/6.14	0.62/1.37/3.46	1.87	1.73	3.13	18.01	12.5	17.5	17.4
KNO₃+ Ca(NO₃)₂	6.8	86	86	0.0329	2.2/0/6.14	3.39/0/0	1.38/0/1.29	1.87	2.15	3.23	24.24	12.5	14.9	13.3
KNO₃+NaNO₃	6.97	73	78.7	0.0439	2.2/0/6.14	2.16/0/0	1.23/0/1.72	1.87	1.54	2.61	20.58	12.5	11.8	12.7
KNO₃+DAP	7.89	68	87.8	0.0404	2.2/0/6.14	3.28/3.62/0	1.70/1.25/1.58	1.87	1.79	3.41	19.17	12.5	11.2	17.8
KNO₃+NH4Cl	4.93	76.5	80.7	0.0448	2.2/0/6.14	2.13/0/0	1.25/0/1.75	1.87	2.48	3.39	21.57	12.5	20.3	15.7
Potassium Dihydrogen Phosphate Blended Draw Solutions														
KH₂PO₄+Urea	4.19	59.2	60.2	0.0567	7.87/0/0	0/4.86/6.14	1.59/1.76/2.22	1.73	0.57	2.11	16.69	17.5	8.5	12.6
KH₂PO₄+NH₄NO₃	7.74	78.5	70.2	0.045	0/4.86/6.14	4.90/0/0	1.26/1.40/1.76	1.73	2.13	2.81	22.13	17.5	22.9	12.7
KH₂PO₄+SOA	4	75.1	82.6	0.043	3.7/0/0	0/4.86/6.14	1.20/1.33/1.68	1.73	1.99	2.83	21.17	17.5	14.4	13.4
KH₂PO₄+MAP	4.05	75.5	80.3	0.0438	2.11/4.68/0	0/4.86/6.14	0.61/2.72/1.71	1.73	1.47	2.28	21.29	17.5	11.7	10.7
KH₂PO₄+KCl	4.07	76.1	80.5	0.0438	0/0/5.9	0/4.86/6.14	0/1.36/3.43	1.73	2.57	3.34	21.45	17.5	20.4	15.6
KH₂PO₄+KNO₃	4.1	63.9	73.7	0.0442	2.2/0/6.14	0/4.86/6.14	0.62/1.37/3.46	1.73	1.87	3.13	18.01	17.5	12.5	17.4
KH₂PO₄+ Ca(NO₃)₂														
KH₂PO₄+NaNO₃	4.05	73.2	78	0.0439	0/4.86/6.14	2.16/0/0	0.61/1.36/1.72	1.73	1.54	1.52	20.64	17.5	11.8	7.4
KH₂PO₄+DAP	6.14	74.7	87.1	0.0393	0/4.86/6.14	3.28/3.62/0	1.10/2.44/1.54	1.73	1.79	2.45	21.06	17.5	11.2	11.6
KH₂PO₄+ NH₄Cl	4.06	82.6	80	0.0436	0/4.86/6.14	2.13/0/0	0.61/1.35/1.70	1.73	2.48	3.18	23.28	17.5	20.3	13.6
Calcium Nitrate Blended Draw Solutions														
Ca(NO₃)₂+Urea	6.8	69.9	72.5	0.0468	7.87/0/0	3.39/0/0	2.62/0/0	2.15	0.57	2.05	19.70	14.9	8.5	10.4
Ca(NO₃)₂+NH₄NO₃	5.18	75.7	82.5	0.0415	3.39/0/0	4.90/0/0	2.32/0/0	2.15	2.13	3.33	21.34	14.9	22.9	15.6
Ca(NO₃)₂+SOA						Precipitation occurs								
Ca(NO₃)₂+MAP						Precipitation occurs								
Ca(NO₃)₂+KCl	6.76	95.6	92.8	0.0326	0/0/5.9	3.39/0/0	0.91/0/1.27	2.15	2.57	3.08	26.95	14.9	20.4	11.4
Ca(NO₃)₂+KNO₃	6.8	86	86	0.0329	2.2/0/6.14	3.39/0/0	1.38/0/1.29	2.15	1.87	3.23	24.24	14.9	12.5	13.3
Ca(NO₃)₂+KH₂PO₄						Precipitation occurs								
Ca(NO₃)₂ + NaNO₃	6.81	96.8	90.3	0.0326	3.39/0/0	2.16/0/0	1.37/0/0	2.15	1.54	2.89	27.29	14.9	11.8	10.6
Ca(NO₃)₂ + DAP						Precipitation occurs								
Ca(NO₃)₂ +NH4Cl	5.07	82	92.3	0.0407	3.39/0/0	2.13/0/0	1.71/0/0	2.15	2.48	3.62	23.12	14.9	20.3	15.6
Sodium Nitrate Blended Draw Solutions														
NaNO₃+Urea	7	64.4	65.2	0.0563	7.87/0/0	2.16/0/0	2.36/0/0	1.54	0.57	2.35	18.15	11.8	8.5	12.9
NaNO₃+NH₄NO₃	5.09	72.4	75.2	0.0459	2.16/0/0	4.90/0/0	1.93/0/0	1.54	2.13	3.16	20.41	11.8	22.9	15.5
NaNO₃+SOA	5.3	83	87.6	0.035	3.7/0/0	2.16/0/0	1.47/0/0	1.54	1.99	3.44	23.40	11.8	14.4	14.7

NaNO₃+MAP	4.07	77.1	85.3	0.0447	2.11/4.68/0	2.16/0/0	1.25/1.39/0	1.54	1.47	3.04	21.73	11.8	11.7	14.0
NaNO₃+KCl	6.97	83.7	85.5	0.0435	0/0/5.9	2.16/0/0	0.61/0/1.70	1.54	2.57	3.16	23.60	11.8	20.4	13.4
NaNO₃+KNO₃	6.97	73	78.7	0.0439	2.2/0/6.14	2.16/0/0	1.23/0/1.72	1.54	1.87	2.61	20.58	11.8	12.5	12.7
NaNO₃+KH₂PO₄	4.05	73.2	78	0.0439	0/4.86/6.14	2.16/0/0	0.61/1.36/1.72	1.54	1.73	1.52	20.64	11.8	17.5	7.4
NaNO₃+Ca(NO₃)₂	6.81	96.8	90.3	0.0326	3.39/0/0	2.16/0/0	1.37/0/0	1.54	2.15	2.89	27.29	11.8	14.9	10.6
NaNO₃+DAP	7.84	50.7	92.1	0.0403	2.16/0/0	3.28/3.62/0	1.69/1.25/0	1.54	1.79	2.26*	14.29	11.8	11.2	15.8
NaNO₃+ NH₄Cl	4.95	81.5	85	0.0446	2.16/0/0	2.13/0/0	1.25/0/0	1.54	2.48	3.38	22.97	11.8	20.3	14.7
Diammonium Phosphate Blended Draw Solutions														
DAP+Urea	7.8	73.2	74.3	0.046	7.87/0/0	3.28/3.62/0	2.58/1.43/0	1.79	0.57	2.03	20.64	11.2	8.5	9.8
DAP+NH₄NO₃	7.7	78.5	84.3	0.0406	3.28/3.62/0	4.90/0/0	2.27/1.26/0	1.79	2.13	3.68	22.13	11.2	22.9	16.6
DAP+SOA	7.6	95	96.7	0.0344	3.7/0/0	3.28/3.62/0	1.93/1.07/0	1.79	1.99	2.53	26.78	11.2	14.4	9.4
DAP+MAP	6	83.5	94.4	0.0391	2.11/4.68/0	3.28/3.62/0	1.64/2.42/0	1.79	1.47	2.21	23.54	11.2	11.7	9.4
DAP+KCl	7.8	79.7	94.6	0.039	0/0/5.9	3.28/3.62/0	1.09/1.21/1.52	1.79	2.57	3.34	22.47	11.2	20.4	14.9
DAP+KNO₃	7.89	68	87.8	0.0404	2.2/0/6.14	3.28/3.62/0	1.70/1.25/1.58	1.79	1.87	3.41	19.17	11.2	12.5	17.8
DAP+KH₂PO₄	6.14	74.7	87.1	0.0393	0/4.86/6.14	3.28/3.62/0	1.10/2.44/1.54	1.79	1.73	2.45	21.06	11.2	17.5	11.6
DAP+Ca(NO₃)₂						Precipitation occurs								
DAP+NaNO₃	7.84	50.7	92.1	0.0403	2.16/0/0	3.28/3.62/0	1.69/1.25/0	1.79	1.54	2.26*	14.29	11.2	11.8	15.8
DAP+ NH₄Cl	7.67	89.4	94.1	0.0389	3.28/3.62/0	2.13/0/0	1.63/1.21/0	1.79	2.48	3.16	25.20	11.2	20.3	12.5
Ammonium Nitrate Blended Draw Solutions														
NH₄Cl +Urea	4.8	66.2	67.2	0.0561	7.87/0/0	2.13/0/0	2.36/0/0	2.48	0.57	2.73	18.66	20.3	8.5	14.6
NH₄Cl +NH₄NO₃	4.75	74.8	77.2	0.0457	4.9/0/0	2.13/0/0	1.92/0/0	2.48	2.13	3.95	21.09	20.3	22.9	18.7
NH₄Cl +SOA	5	98.5	89.6	0.0343	3.7/0/0	2.13/0/0	1.44/0/0	2.48	1.99	3.40	27.77	20.3	14.4	12.2
NH₄Cl +MAP	4.04	88.5	87.3	0.0433	2.11/4.68/0	2.13/0/0	1.21/1.34/0	2.48	1.47	3.21	24.95	20.3	11.7	12.8
NH₄Cl +KCl	4.8	88.6	87.5	0.0433	0/0/5.9	2.13/0/0	0.61/0/1.69	2.48	2.57	3.71	24.98	20.3	20.4	14.9
NH₄Cl +KNO₃	4.93	76.5	80.7	0.0448	2.2/0/6.14	2.13/0/0	1.25/0/1.75	2.48	1.87	3.39	21.57	20.3	12.5	15.7
NH₄Cl +KH₂PO₄	4.06	82.6	80	0.0436	0/4.86/6.14	2.13/0/0	0.61/1.35/1.70	2.48	1.73	3.18	23.28	20.3	17.5	13.6
NH₄Cl +Ca(NO₃)₂	5.07	82	92.3	0.0407	3.39/0/0	2.13/0/0	1.71/0/0	2.48	2.15	3.62	23.12	20.3	14.9	15.6
NH₄Cl +NaNO₃	4.95	81.5	85	0.0446	2.16/0/0	2.13/0/0	1.25/0/0	2.48	1.54	3.38	22.97	20.3	11.8	14.7
NH₄Cl +DAP	7.67	89.4	94.1	0.0389	3.28/3.62/0	2.13/0/0	1.63/1.21/0	2.48	1.79	3.16	25.20	20.3	11.2	12.5

*experiment conducted at DS concentration of (0.625 M : 0.625 M) since at 1 M:1 M, the blend was not easily soluble.

Table S2: Comparative properties of KNO₃, DAP and KNO₃+DAP fertiliser solutions

Properties	KNO$_3$	(NH$_4$)$_2$HPO$_4$	Blended (1 M :1 M)
pH	6.970	7.780	7.890
Osmotic pressure (atm)	37.190	50.560	68.030
Ionic strength (mol/mol)	0.017	0.051	0.058
EC (mS/cm)	89.729	137.073	140.397
K$^+$ (mol)	1.000		1.000
NO$_3^-$ (mol)	1.000		0.506
NH$_3$ aqueous (mol)	0.026		
NH$_4^+$ (mol)		1.974	1.483
P$_2$O$_7^{4-}$ (mol)		0.011	
HPO$_4^{3-}$ (mol)		0.947	0.965
H$_2$PO$_4^-$ (mol)		0.021	
NH$_4$NO$_3$ (aqueous) (mol)			0.494
Total charged species (mol)	2.000	2.952	3.950
Total uncharged species (mol)	0.026	NIL	0.494
Total species (mol)	2.026	2.952	4.448

S4. Explanations on the performance of certain blended fertiliser draw solutions

The decrease or increase in water flux for the blended fertilisers is explained below. Using DI water as feed water (bulk osmotic pressure of the feed is zero), the actual or experimental water flux J_w in FO mode is given by the following equation (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007), which takes into account the influence of internal concentration polarisation (ICP) on the DS side facing the porous support layer of the membrane.

$$J_w = A\sigma\left[\pi_d \exp(-J_w K)\right] \tag{S1}$$

Where A is the pure water permeability coefficient, π_d is the bulk osmotic pressure of the DS, σ the reflection coefficient (considered σ =1 in this case) and K the solute resistance to diffusion within the membrane support layer. K is in fact a measure of how easily a draw solute can diffuse into or out of the membrane support layer and thus measures the severity of ICP (McCutcheon and Elimelech, 2006; McCutcheon and Elimelech, 2007). K is given by the following equation:

$$K = \frac{t\tau}{D\varepsilon} \tag{S2}$$

Where t, τ and ε are all related to the structural properties of the membrane such as thickness, tortuosity and porosity of the membrane support layer and, D the diffusion coefficient of the draw solutes. Since all the experiments were performed using the same membrane, the performance of each DS is a function of K which in turn is a function of diffusion coefficient of the draw solutes from equation (1) and (2). Therefore, blending different fertilisers would not only alter the types of species formed in the solution but the coexistence of different species could also alter the diffusivity of a particular species.

Blended fertiliser solutions have multiple component species in comparison to basic fertiliser solutions. For concentrated solutions and solutions containing multiple component species,

the diffusion coefficients are difficult to estimate because the solution does not obey the binary form of Fick's law however one of the exceptions is the mixture of weak electrolytes (Cussler, 2007). Urea being a weak electrolyte in this study, has been chosen as a typical example to explain the variations of flux and reverse diffusion of draw solutes in the blended draw solution.

For example, the average diffusion coefficient of KNO_3 in 1 M pure solution is 1.784×10^{-9} m^2/s however, its diffusion coefficient increases to 1.927×10^{-9} m^2/s in the urea+KNO_3 blended solution. The diffusion coefficient of urea did not alter significantly when blended with KNO_3. Similarly, the average diffusion coefficient of $NaNO_3$ also increased from 1.4241×10^{-9} m^2/s to 1.519×10^{-9} m^2/s when blended with urea in the solution. The average diffusion coefficients were calculated using equations provided elsewhere (Cussler, 2007; Tan and Ng, 2008). The diffusion coefficients of each ionic species in the solution were determined by OLI Stream Analyser 3.2. This increase in the draw solute diffusivity helps in lowering the solute resistivity K (equation 2) and therefore decreasing the ICP effects on the porous side of the membrane thereby enhancing the water flux. ICP is one of the major factors responsible for limiting the water flux by FO process (Gray *et al.*, 2006; McCutcheon and Elimelech, 2006; Tan and Ng, 2008; Tang *et al.*, 2010; Wang *et al.*, 2010). Even at the same osmotic pressure, each type of DS has been observed to have different pure water flux indicating that, each type of DS offer different degree of ICP effects in the FO process (Achilli *et al.*, 2010; Phuntsho *et al.*, 2011). The degree of ICP is higher at higher DS concentration and due to reduced diffusivity of the draw solutes at higher concentration (Tan and Ng, 2008).

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