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Blended Fertilizers as Draw Solutions for Fertilizer-Drawn Forward Osmosis Desalination

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Ⓢ *Supporting Information*
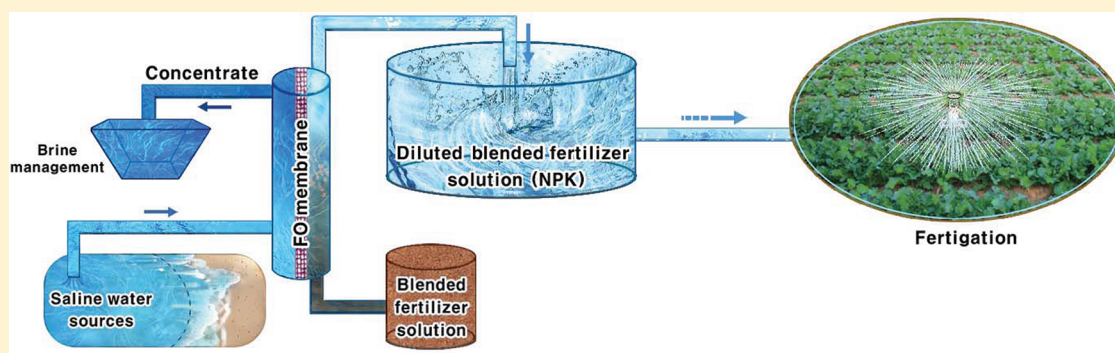
ABSTRACT: In fertilizer-drawn forward osmosis (FDFO) desalination, the final nutrient concentration (nitrogen, phosphorus, potassium (NPK)) in the product water is essential for direct fertigation and to avoid over fertilization. Our study with 11 selected fertilizers indicate that blending of two or more single fertilizers as draw solution (DS) can achieve significantly lower nutrient concentration in the FDFO product water rather than using single fertilizer 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 them individually as DS. The nutrient composition and concentration in the final FDFO product water can also be adjusted by selecting low nutrient fertilizers containing complementary nutrients and in different ratios to produce prescription mixtures. However, blending fertilizers 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 DSs as used alone. The performance ratio or PR (ratio of actual water flux to theoretical water flux) of blended fertilizer DS was observed to be between the PR of the two fertilizer 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 fertilizer species.

■ 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. Because 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 as 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 a 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 nonpotable applications such as irrigation and energy drink.[21] Recently, Phuntsho et al.[18,22] reported on fertilizer-drawn forward osmosis (FDFO) desalination, in which fertilizers 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. Fertilizers 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 fertilizer use, minimizing fertilizer 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 soluble fertilizers can be used as DS for FO desalination, one of the limitations identified was the fertilizer 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 posed by 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 fertilizer concentration would increase soil salinity and cause plant toxicity. If the final fertilizer 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 feedwater with high salinity is used. Other possible alternatives include NF as either pretreatment 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 fertilizers 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 when using a single fertilizer. It is shown in this study that nutrients in the final FDFO product water can be significantly lowered by using blended fertilizers as DS rather than using single fertilizer as DS. Bulk blending of fertilizers 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 fertilizer and the blended fertilizers 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:

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

where A is the pure water permeability coefficient of the membrane, and $\pi_{D,b}$ 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, eq 1 can be modified as shown below under FO mode:[29]

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

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

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 is 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 eq 3 is that

As $J_w \to 0$

$\pi_{D,m}$ or $\pi_{D,b}e^{(-J_wK)} \to \pi_{D,b}$

and $\pi_{F,m}$ or $\pi_{F,b}e^{(J_w/k_F)} \to \pi_{F,b}$

Hence,

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

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 eq 2 or 3 can be represented by eq 1. In other words, the net movement of water from DS to the FS will occur until the bulk osmotic pressure of the DS reaches osmotic equilibrium with the bulk osmotic pressure of the FS as verified experimentally in this study.

EXPERIMENTAL SECTION

Chemical Fertilizers and Draw Solution Preparation. All chemical fertilizers used were reagent grade (Sigma Aldrich, Australia). The DS consisting of one or more single fertilizers was prepared by dissolving fertilizers in deionized (DI) water.

The essential properties of the fertilizer solutions such as the pH, the number and type of species formed, and the osmotic pressures of the fertilizer solutions were determined using OLI Stream Analyzer 3.1 software (OLI Systems Inc., Morris Plains, NJ, USA). This software uses thermodynamic modeling based

Table 1. Performances of Single Fertilizers as DS in the FO Process Using DI Water and BW as Feed[a]

draw solution (1 M)	$\Delta\pi$@1 M (atm)	DI as feedwater			loss of nutrient by reverse diffusion (g L^{-1})			BW as feedwater		
		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%

[a]J_{wt}: theoretical water flux calculated using eq 1; J_w: 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 (5000 mg/L NaCl) taken is 3.9 atm. RSF data is obtained from the DI water as feed.
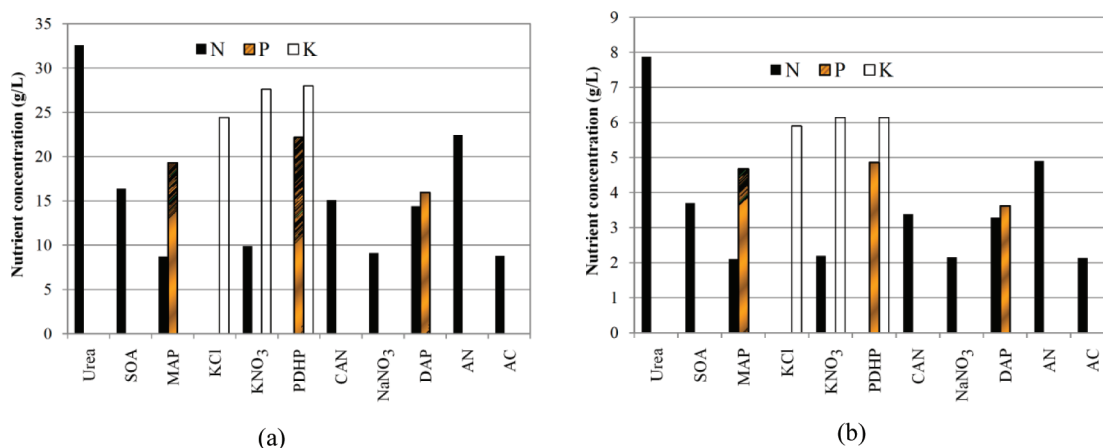

Figure 1. Expected final NPK nutrient concentrations of fertilizer solution after FO desalination or in the final FDFO product water using (a) seawater as feedwater (35 000 mg/L NaCl at 28 atm), and (b) brackish water as feedwater (5000 mg/L NaCl at 3.9 atm).

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 fertilizer as DS for FO process was assessed using DI water and model brackish water or BW (5000 mg/L NaCl) as feed. Detailed experimental procedures are described in Section S1 of Supporting Information (SI).

RESULTS AND DISCUSSION

FDFO Desalination Using Single Fertilizers As Draw Solutions. Table 1 shows the osmotic pressure and their performances as DS in FO process. The final concentration of the fertilizer (NPK or nitrogen−phosphorus−potassium) DS after FDFO desalination is compared for seawater and BW feed in Figure 1.

Properties of Single Fertilizer 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 that of other soluble fertilizer solutions. Diammonium phosphate (DAP) or (NH$_4$)$_2$HPO$_4$ and calcium nitrate or Ca(NO$_3$)$_2$ showed the highest osmotic pressures among the fertilizers, 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 fertilizers.

Pure Water Flux of Single Fertilizer As Draw Solution. The performance test was carried out using DI water and BW as feedwater under similar operating conditions and at 1 M fertilizer DS concentration and the results are presented in Table 1. Consistent with our earlier studies,[18] among the 11 selected fertilizers, KCl showed the highest water flux both with DI water feed (2.57 μm/s) and BW feed (2.31 μm/s). NH$_4$Cl 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 that of any other fertilizer 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$_4$NO$_3$ 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 fertilizers 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 Fertilizers. 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 phosphorus (P) can cause eutrophication and algal blooms in the receiving water.[36,37] Therefore, it is important that the DSs 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 fertilization, the amount of essential nutrients present in the fertilizer is more important than the other nonessential 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 fertilizer 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] fertilizers 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.

Final Nutrient Concentration in the FDFO Product Water Using Single Fertilizers as Draw Solute. At low DS concentrations, eq 1 is valid, indicating that DS can extract water until the bulk osmotic pressures of the DS and feedwater become equal. To verify this, experiments were carried out at different DS concentrations (but at low concentrations) using KCl and $Ca(NO_3)_2 \cdot 4H_2O$ as DS separately with BW as FS (more explanation can be found under Section S2 of SI). The results in Figure S3 of SI show 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, and 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 fertilizers using SW and BW are presented in Figure 1. It is clear from the figure that the nutrient concentration in the final FDFO product water depends on the feedwater salinity and the types of fertilizer 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 1a), 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 1b 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 mol/m^3 or 62 mg/L of P can be toxic to some plants.[46] Therefore, the results in Figure 1b 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 freshwater, it could be a significant impediment where freshwater 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.

Table 2. Performance of the Selected Fertilizer Blend as DS in the FO Process Using DI Water and BW as Feed[a]

fertilizer combinations (1M:1M)	π (atm)	DI as feedwater			BW as feedwater		
		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

[a]J_{wt}: theoretical water flux calculated using eq 1, J_w: experimental water flux; PR: performance ratio (J_w/J_{wt}). Pure water permeability coefficient of the FO membrane ($A = 0.28194 \pm 0.008$ μm/s/atm). Bulk osmotic pressure of the BW feed (5000 mg/L NaCl) taken is 3.9 atm. RSF data is obtained from the DI water as feed. MAP: monoammonium phosphate NH$_4$H$_2$PO$_4$, DAP: diammonium phosphate (NH$_4$)$_2$HPO$_4$, SOA: sulphate of ammonia (NH$_4$)$_2$SO$_4$, CAN: Ca(NO$_3$)$_2$·4H$_2$O. RSF: Reverse solute flux. Additional data on blending is shown in Table S1 of SI

One of the important observations noted from the final nutrient concentrations in Table 1 is that those fertilizers 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 fertilizers and their N concentration in the final FDFO product water, which is the main motivation behind using blended fertilizers as DS.

FDFO Desalination Using Fertilizer DS Blended with Two Single Fertilizers. The assessment of blended fertilizers 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 fertilizer blends are summarized in Table 2. More details on the blended matrix can be found in Table S1 of SI.

Properties of the Blended Fertilizer Draw Solutions. Most selected fertilizers can be blended with each other, except calcium-containing fertilizers with sulfate or phosphate fertilizers which form precipitates. The pH of all blended fertilizers in this study was within the range of 4.0−8.0, compatible to CTA FO membrane used. Blending decreases the solubility of some fertilizers, such as (NH$_4$)$_2$SO$_4$ blended with KCl that forms K$_2$SO$_4$ 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 fertilizer used. Speciation analysis (data not included) using the OLI Stream Analyzer indicated that urea was the only fertilizer that did not dissociate to form different species with any of the fertilizers 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 fertilizer solution was generally lower than the arithmetic sum of the osmotic pressures of the two individual fertilizer solutions, except for NH$_4$Cl blended with some fertilizers. For some fertilizer blends, the net osmotic pressure significantly decreased, while in some cases the decrease was minimal. The decreased osmotic pressure might be explained due to complex interactions between the ions and counterions of each blended component that likely results in decreased number of species formed in the DS. More discussion on the blended properties can be referred to in Section S3 of SI.

Water Flux of Blended Fertilizer Draw Solutions. The highest water flux was observed for the NH$_4$NO$_3$ + NH$_4$Cl blend, with 3.94 μm/s using DI water and 3.52 μm/s using BW as feed; while the lowest water flux was observed for urea + MAP blend with just 1.53 and 1.39 μm/s using DI water and BW as feed, respectively. Blends such as NH$_4$NO$_3$ + DAP, NH$_4$SO$_4$ + KNO$_3$, KCl + NH$_4$Cl, and Ca(NO$_3$)$_2$ + NH$_4$Cl all resulted in water fluxes comparatively higher than other blends. However, in almost all cases, the water fluxes of the blended fertilizer DS were slightly lower than the sum of the two water fluxes if the two single fertilizers 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 fertilizer itself as a DS has a very poor water flux in comparison to any other fertilizers. Table S1 of SI provides additional data on the performance of the blended fertilizer DS.

Table 2 also shows the PR of water flux for the blended fertilizers. Depending on the type of blend, the PR ranged 8−19% with DI water and slightly less with BW feed. NH$_4$SO$_4$ + KNO$_3$ and NH$_4$NO$_3$ + NH$_4$Cl 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$_4$SO$_4$ + MAP blends, with only about 8% both using DI water and BW as feed. When the two fertilizers were blended in the solution, their PR was observed to be between the PR of the two fertilizer solutions tested individually. When two

fertilizers with high PRs were blended together, the fertilizer blend generally tended to have a higher PR. Urea had the lowest PR among all the 11 selected fertilizer DS (Table 1); however, when urea was blended with other fertilizers, 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 fertilizers decreases when blended with low performing fertilizers. Therefore, it might be ideal to blend two high performing fertilizers containing different types of nutrients.

The improved water flux for urea + KNO_3 can be explained as follows. From eqs 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. Because 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 fertilizers 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 Analyzer 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 fertilizer nutrients due to reverse movement of only selected blended fertilizer draw solutes is presented in Table 2. These results indicate that the fertilizer 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 fertilizer 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 losses 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 is 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 fertilizers 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 modeling 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 Fertilizers as Draw Solutions. Table 2 also shows the final nutrient concentration in the product water by FDFO desalination using different types of blended fertilizer DS with BW (more data presented in Table S1 of SI). These results indicate that blending of fertilizer in DS generally resulted in a significant reduction in the final nutrient concentration in comparison to using single fertilizers as the DS.

Urea fertilizer 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 1b), which is significantly high for direct fertigation. However, when urea is blended with other fertilizers, 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%), fertilizer 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 fertilizers containing different major nutrients were blended together. For example, consider the blending of fertilizers 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 fertilizers containing different nutrients at low concentrations are blended together in the solution rather than blending fertilizers 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 among all the blends studied here. Similar low nutrient concentrations were also achieved with KH_2PO_4 + NH_4Cl blends. Although blending two fertilizers containing similar nutrients can also achieve significantly reduced nutrient concentrations in comparison to their parent single fertilizers, the final nutrient concentration for the common nutrient remains comparatively higher than when blending two fertilizers 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 fertilizers could be useful in preparing a fertilizer DS that can produce FDFO product water of acceptable final nutrient concentration for direct fertigation.

Influence of NPK Blends in Different Ratios Using Two or More Single Fertilizers on the Final Nutrient Concentrations. NPK fertilizer blends can be prepared either using two or more single fertilizers. The earlier data shows
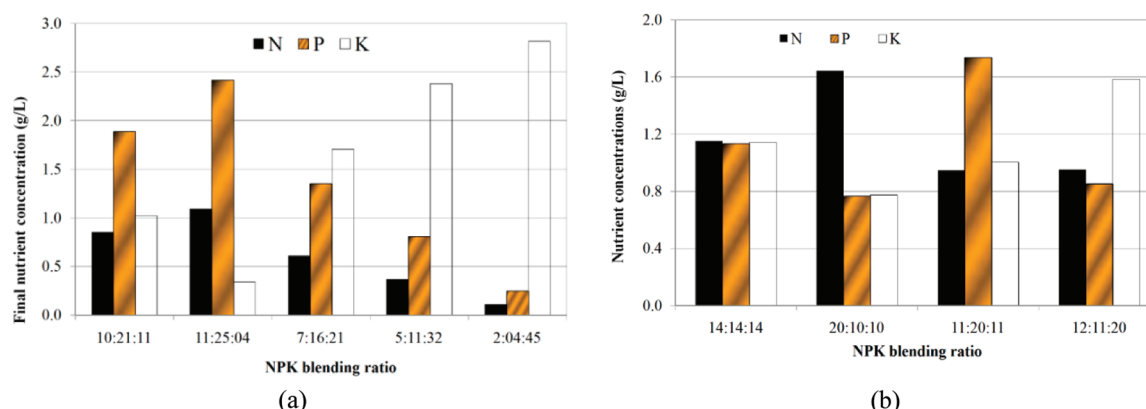
(a) (b)

Figure 2. Final NPK nutrient concentrations of (a) MAP and KCl blended and (b) MAP, KCl, and NH_4NO_3 blended in different ratios.

Table 3. Estimated N/P/K Nutrient Concentrations in the Final FDFO Product Water Using Blended Fertilizer as DS and BW (5000 mg/L NaCl with an Osmotic Pressure of 3.9 atm, Assigned as BW5 in this Table for Clarity) as Feed[a]

plant	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 feedwater 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

[a]DS consisted of blended fertilizer solution prepared in specific N:P:K ratios suitable for three selected plants using four different types of fertilizers [$NaNO_3$, $(NH_4)_2SO_4$, KCl, and KH_2PO_4] that yielded the minimum nutrient concentration in the final product water. BW2, BW3, BW4, and BW5 refer to brackish water feed of TDS 2000, 3000, 4000, and 5000 mg/L of NaCl, respectively.

combinations for only two different fertilizers in equal molar ratio. Here, we show how blending of two or three single fertilizers to prepare different grades of fertilizers 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 fertilizer 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 a 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 fertilizers are used in the blend as shown with MAP + KCl + NH_4NO_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 fertilizers $NaNO_3$, $(NH_4)_2SO_4$, KCl, and KH_2PO_4. Although other fertilizer combinations are also possible, the combination that yielded the lowest nutrient concentration was selected for discussion in Table 3. The data show that it is possible to formulate a specific grade of fertilizer 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 5000 mg/L although it reduces to only about 2 times dilution when feed TDS is 2000 ppm.

It was demonstrated that, by using blended fertilizers as DS instead of single fertilizer, 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 feedwater is used therefore requiring different levels of dilution factor before direct fertigation. Phuntso et al.[22] has suggested nanofiltration as either pretreatment 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 making diluted DS acceptable for direct fertigation.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental procedures and other content as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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