Enhancing Wastewater Reuse by Forward Osmosis with Self-Diluted Commercial Fertilizers as Draw Solutes

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Abstract

Using fertilizers as draw solutes in forward osmosis (FO) can accomplish wastewater reuse with elimination of recycling draw solute. In this study, three commercial fast-release all-purpose solid fertilizers (F1, F2 and F3) were examined as draw solutes in a submerged FO system for water extraction from either deionized (DI) water or the treated wastewater. Systematic optimizations were conducted to enhance water extraction performance, including operation modes, initial draw concentrations and *in-situ* chemical fouling control. Under the active layer facing the feed (AL-F or FO) mode, a maximum of 324 mL water was harvested using 1-M F1, which provided 41% of the water need for fertilizer dilution for irrigation. Among the three fertilizers, F1 containing less urea content was the most favored because of a higher water extraction and a lower reverse solute flux (RSF) of major nutrients. Using the treated wastewater as a feed solution resulted in a comparable water extraction performance (317 mL) to that of DI water in 72 h and a maximum water flux of 4.2 LMH. Phosphorus accumulation on the feed side was mainly due to the FO membrane solute rejection while total nitrogen and potassium accumulation was mainly due to RSF from the draw solute. Reducing recirculation intensity from 100 to 10 mL min⁻¹ did not obviously decrease water flux but significantly reduced the energy consumption from 1.86 to 0.02 kWh m⁻³. These results have demonstrated the feasibility of using commercial solid fertilizers as draw solutes for extracting reusable water from wastewater, and challenges such as reverse solute flux will need to be further addressed.

Keywords: Forward osmosis; Commercial fertilizers; Reverse solute flux; Wastewater reuse; Energy.

1. Introduction

Agricultural irrigation is considered as a water intensive process and consumes 72% of global fresh water withdrawal (Cai and Rosegrant 2003). Exploring alternative water supply for irrigation, for instance via reusing wastewater, will be of great importance (Xie et al. 2015). Current treatment of wastewater can effectively remove the contaminants; however, the effluent is still not widely used for irrigation because of some undesired substances like pathogens (e.g., *Legionella* and *E. coli*) (EPA 2012) and trace organic chemicals (e.g., endocrine-disrupting chemicals) (Wang et al. 2016). Thus, further treatment will be necessary, and to achieve this, membrane technologies can be applied (Achilli et al. 2009). Among the newly developed membrane technologies, forward osmosis (FO) is of strong interest. FO is a membrane separation process known for efficient water recovery by utilizing osmotic pressure gap between a draw solution and a feed solution. It has great merits of high contaminant rejection rate and lower fouling propensity when compared to pressure-driven processes such as reverse osmosis (RO) (Holloway et al. 2007). Because of low or no hydraulic pressure, FO could have potential advantages in low energy consumption, if regeneration of draw solutes can be accomplished without using energy-intensive processes like RO.

One of the key challenges to accomplish sustainable water recovery in FO is the separation and recovery of draw solutes, which accounts for most of the energy consumption (Achilli et al. 2010, McGinnis and Elimelech 2007). Novel draw solutes including the self-separated ionic solution (Bowden et al. 2012, Cai et al. 2015) and thermolytic ammonium bicarbonate ($\text{NH}_3\text{-CO}_2$) (McCutcheon et al. 2005) were proposed for easy regeneration while maintaining high osmotic pressure and desirable water flux. However, regeneration of those draw solutes still bear

problems. For example, recovery of $\text{NH}_3\text{-CO}_2$ requires relatively high decomposition temperature (at least 60 °C), leading to additional energy input, and the thermal-responsive ionic solution may result in potential environmental concerns and health risks due to leakage of ionic solutes.

Fertilizers were proposed and investigated as draw solutes to eliminate the need of regeneration (Table S1, supplementary material). The self-diluted fertilizers can be directly used for agricultural irrigation, providing an alternative to bypass the energy-intensive draw solute recovery process (Hoover et al. 2011). Phuntsho *et al.* proposed nine inorganic chemicals as hypothetical fertilizers and evaluated their osmotic dilution performance in a cross-flow FO system by using DI water as feed (Phuntsho et al. 2011). Subsequent laboratory studies verified the feasibility of continuous water recovery from synthetic brackish groundwater and seawater (Lotfi et al. 2015, Majeed et al. 2015, Phuntsho et al. 2012a, Phuntsho et al. 2012b, Phuntsho et al. 2013, Phuntsho et al. 2014, Sahebi et al. 2015). A pilot-scale fertilizer drawn forward osmosis and nanofiltration (FDFO-NF) was recently established and had been successfully operated for six months (Phuntsho et al. 2016). Although the prior studies have investigated both single chemical reagent such as NH_4NO_3 and KCl , and blended draw solutes containing defined chemicals, commercial all-purpose fertilizers with a full-spectrum supplement of nutrients that are designed for practical applications have not been well examined in FO. A recent study demonstrated the osmotic dilution of the commercial all-purpose liquid fertilizers (Xie et al. 2015); however, liquid fertilizers are less favored than solid fertilizers because of the problems associated with storage and transportation. Therefore, there is a need to study water recovery by using commercially available solid fertilizers.

In this study, three commercial fast-release and all-purpose solid fertilizers were examined as draw solutes in a submerged FO system for water extraction from either DI water or the treated wastewater. The submerged FO configuration was employed because it has less energy consumption, rendering a small footprint, more operation flexibility, and easily scalable features (van Haandel and van der Lubbe 2012), compared to cross-flow FO systems. Water flux and recovery as a percentage of required water for fertilizer dilution were evaluated with different fertilizers or concentrations. The detailed nutrient distribution (N/P/K) in both draw and feed as well as nutrient loss were investigated. Operation modes and energy consumption of the FO system were investigated and analyzed.

2. Materials and methods

2.1 Characteristics of fertilizers and preparation of draw solution

The commercial all-purpose solid fertilizers were obtained from retailers with detailed information in Table S2. All three fertilizers (noted as “F1”, “F2”, and “F3”) are widely used on farms and gardens for high yields. Due to the complexity of fertilizer composition, the fertilizer concentration was quantified by total nitrogen concentration, which was calculated based on the information from the manufacturer. For example, 1 M fertilizer in this study means its theoretical total nitrogen concentration is 1 mol L⁻¹. To prepare draw solutions, fertilizer was first dissolved in 100 mL DI water with pH adjustment (0.2 mol L⁻¹ NaOH) to around 7.0 and then centrifuged at 5000 rpm for 10 min to remove undissolved particles/precipitants. Of this 100-mL solution, 10 mL was used to analyze the nutrient concentrations and 85 mL was applied as the draw solution.

The remaining solids were preserved in fridge and could be added to final diluted fertilizers to avoid possible loss of trace elements (not studied here).

2.2 Setup and operation of a submerged FO system

The flat-plate FO cell contained two pieces of cellulose triacetate (CTA) membranes with a total surface area (S) of 0.0025 m² (Hydration Technologies Inc., Albany, OR, USA) and being installed on both sides of the FO cell, creating a middle chamber of 13 mL for draw solution. The CTA membrane had a guaranteed pH tolerance of 2-12 suggested by its manufacturer (Alsvik and Hägg 2013). Plastic mesh was applied outside the FO membranes to prevent potential swelling. The FO cell was submerged in the feed solution in a 1-L plastic beaker (Fig. S1), and the feed solution was either DI water or the treated wastewater (Peppers Ferry Wastewater Treatment Plant, Radford, VA, USA). The feed solution was supplemented periodically to maintain a constant liquid volume of 500 mL. The characteristics of the treated wastewater are shown in Table S3. The FO system was operated under a batch mode with different fertilizers and/or various initial concentrations. For each batch test, 85 mL fertilizer solution was recirculated in the middle chamber of the FO cell at 100 mL min⁻¹ (6.7 cm s⁻¹) unless stated elsewhere. Water samples were taken every 24 h for water quality analysis. The whole experiment was operated in a temperature-controlled lab (20 ± 2 °C) with a centralized air conditioning system.

2.3 Experimental procedure

A series of system optimization experiments (Table S4) were performed with DI water as the feed, including operation mode (i.e. membrane orientation), fouling control, reverse solute flux

(RSF), fertilizer (draw) concentration. The active layer of the CTA membrane faced either draw (AL-D, PRO mode) or feed (AL-F, FO mode) to examine the effect of different operating modes using 1-M F1 as the draw. The F1 concentration was varied at 1M, 2M, and 3M for studying water extraction and dilution rate. Comparison of three fertilizers (F 1-3) was conducted by operating the FO system with each fertilizer at a concentration of 1 M and under the FO mode. The optimized operation conditions (above-mentioned) were applied for examining water recovery from the treated wastewater by using the treated wastewater as the feed and 1-M F1 as the draw. Different recirculation rates, i.e. 10 mL min⁻¹, 50 mL min⁻¹ and 100 mL min⁻¹, were successively investigated towards minimized energy consumption by the FO system. A batch test was terminated if the specific water flux (J_{sp}) at the last hour of each 24-hour cycle was less than 1.0 LMH, according to a previous study (Qin and He 2014).

The fouling of the FO membrane was studied with or without *in situ* fouling control under an FO mode. The pristine membrane was operated under the FO mode for water extraction (first test), and without any chemical cleaning, it was directly applied in the second test for determination of fouling situation; *in situ* chemical cleaning was then performed prior to the third test to investigate the fouling control performance. Due to the complex characteristics of fertilizer solution, fouling should be expected on the porous supportive layer (draw chamber), including the irreversible clogging by sparingly dissolved FePO₄, Cu₃(PO₄)₂ and Zn₃(PO₄)₂. Effective removal of resistant foulants could be achieved by three-stage chemical washing at the end of each batch test: acid (HCl, pH=3), base (NaOH, pH=11), and oxidant (NaClO, 10% v/v), and each stage lasted for 30 min, followed by 30 min rinse with DI water. The chemical cleaning was applied only to the draw side, where severe fouling was expected. Although using wastewater as

a draw could cause fouling on the feed side of the FO membrane, the treated wastewater contained very low concentrations of organic and inorganic contaminants and the resulted fouling could be removed by backwash and/or flushing. All the cleaning solutions were reused over the 4-month operation, thereby lowering the related cost and limiting their environmental effects under proper control.

2.4 Measurement and analysis

The concentrations of ammonium ($\text{NH}_4^+\text{-N}$), nitrite ($\text{NO}_2^-\text{-N}$), nitrate ($\text{NO}_3^-\text{-N}$), total nitrogen (TN), and total phosphorus were determined by using a spectrophotometer according to the manufacturer instruction (DR 890, HACH Company, USA). The concentration of potassium (K^+) was quantified by ion chromatography (Dionex LC20 ion chromatograph, Sunnyvale, USA) together with an ED40 electrochemical detector. Conductivity was measured with a benchtop conductivity meter with temperature sensor (Mettler-Toledo, Columbus, OH, USA). Water flux of the FO system was determined by the change of weight recorded on an electronic balance (Scort Pro, Ohaus, Columbia, MD, USA) according to the previous studies (Lu and He 2015, Yuan et al. 2016). Because urea (CH_4ON_2) is the dominant organic component in all fertilizers, the concentration of urea-nitrogen (Urea-N) is indirectly estimated by TOC (TOC-Vcsn, Shimadzu, Japan) and calculated with the following equation:

$$C_{\text{Urea-N}} = \frac{C_{\text{org.C}}}{12} \times 2 \quad (\text{Eq. 1})$$

where the unit of $C_{\text{org.C}}$ and $C_{\text{Urea-N}}$ is mg L^{-1} and mmol L^{-1} , respectively.

In the FO process, water extraction is mainly driven by the difference of osmotic pressure between the draw solution and the feed solution. Hence, the theoretical water flux (J_w , L m⁻² h⁻¹, LMH) is described by Eq. 2.

$$J_w = A(\pi_D - \pi_F) \quad (\text{Eq. 2})$$

where A (L m⁻² h⁻¹ bar⁻¹) is the pure water permeability coefficient of a specific membrane; π_D and π_F are osmotic pressure at the draw side and the feed side, respectively. The water permeability coefficient (A), ranging from 0.6-1.0 L m⁻² h⁻¹ bar⁻¹, has been extensively studied for CTA membrane (Cath et al. 2013, Phuntsho et al. 2012b, Xie et al. 2015). The osmotic pressure (π , bar) of a solution is determined by the solute concentration (Eq. 3).

$$\pi = \frac{nRT}{V} \quad (\text{Eq. 3})$$

where n (mol) is the mole of the solute, R is the ideal gas constant (0.083 L bar K⁻¹mol⁻¹), T (K) is absolute temperature, and V (L) is solution volume. DI water has zero osmotic pressure.

The average water flux (J_a) and specific water flux (J_{sp}) are calculated by Eq. 4 and 5, respectively. J_a is defined as the unit permeate water volume (at the draw side) over a certain period of time to demonstrate total tendency, while J_{sp} is defined as the unit permeate water volume in one specific hour to track down subtle performance changes. $m_{t,D}$ and $m_{t-1,D}$ represent the mass of draw solution at a specific time t and t-1 (h), respectively. It is assumed that the mass change of draw solution is mainly attributed to permeate water, and hence water density (ρ) is chosen for volume conversion.

$$J_a = \frac{m_{t+\Delta t,D} - m_{t,D}}{\rho \cdot S \cdot \Delta t} \quad (\text{Eq. 4})$$

$$J_{sp} = \frac{m_{t,D} - m_{t-1,D}}{\rho \cdot S} \quad (\text{Eq. 5})$$

The solute build-up (SBU) at feed side and nutrient loss rate (NLR) at draw side are quantified by Eq. 6 and Eq. 7, respectively. Both SBU and NLR are presented in $\text{mmol m}^{-2} \text{h}^{-1}$.

$$SBU = \frac{n_{f,F} - n_{i,F}}{S \cdot t} = \frac{V_F \times (C_{f,F} - C_{i,F})}{S \cdot t} \quad (\text{Eq. 6})$$

$$NLR = \frac{n_{i,D} - n_{f,D}}{S \cdot t} = \frac{V_{i,D} \times C_{i,D} - (V_{i,D} + V_{recovered}) \times C_{f,D}}{S \cdot t} \quad (\text{Eq. 7})$$

where $n_{i,F}$ and $n_{f,F}$ are initial and final mole of target solute in the feed, respectively. $C_{i,F}$ and $C_{f,F}$ are initial and final mole concentration in the feed, respectively. V_F is feed volume (500 mL constant). Likewise, $n_{i,D}$ and $n_{f,D}$ are initial and final mole in the draw (fertilizer) solution. $C_{i,D}$ and $C_{f,D}$ are initial and final mole concentration in the draw, respectively. The final volume of draw should be the sum of initial volume ($V_{i,D}$) and recovered water volume ($V_{recovered}$, L). t stands for operating time (h).

For a specific solute, SBU is typically resulted from the concentrating effect in feed (due to membrane rejection of feed solute) and reverse solute flux (RSF) from draw solution. The RSF ($\text{mmol m}^{-2} \text{h}^{-1}$) and concentrating effect ($\text{mmol m}^{-2} \text{h}^{-1}$) are calculated as Eq. 8 and 9.

$$RSF = \frac{V_F \times C_{f,F} - (V_F + V_{recovered}) \times C_{i,F}}{S \cdot t} \quad (\text{Eq. 8})$$

$$Concentrating\ Effect = \frac{V_{recovered} \times C_{i,F}}{S \times t} \quad (\text{Eq. 9})$$

When DI water is used as feed, $C_{i,F}=0$ and hence no concentrating effect is observed. Under such case, $RSF=SBU$.

Dilution rate (DR, %) is calculated as the volumetric ratio between the recovered water ($V_{\text{recovered}}$, L) and the required water (V_{required} , L) for making applicable (diluted) fertilizer according to Eq. 10. Due to possible nutrition loss via reverse salt flux and/or ammonia volatilization (Overrein and Moe 1967), the required water is less than theoretical water volume suggested by the fertilizer manufacturer (Table S2).

$$DR = \frac{V_{\text{recovered}}}{V_{\text{required}}} = \frac{V_{\text{recovered}}}{V_{\text{theoretical}} \times NLR} \times 100\% \quad (\text{Eq. 10})$$

The specific energy consumption (SEC, (Shaffer et al. 2012)) for unit recovered water (E , kWh m^{-3}) is estimated as Eq. 11:

$$E = \frac{P_{\text{system}}}{Q} \approx \frac{P_{\text{pump}}}{Q} = \frac{P_{\text{pump}} \cdot \rho}{m_{t,D} - m_{t-1,D}} \quad (\text{Eq. 11})$$

where P_{system} and P_{pump} (kW) are the energy consumption of the FO system and recirculation pump, and Q ($\text{m}^3 \text{h}^{-1}$) is recovered water flow rate. It is assumed that the power consumption of FO system is mainly attributed to recirculation pump. However, it should be noted that additional energy would be required for centrifuge, chemical cleaning (pumping and chemical production) and mitigation of salinity build-up at the feed side, and this energy is difficult to quantify at this moment.

3. Results and discussion

3.1 Optimization of self-dilution performance

To establish the feasibility of using commercial fertilizer to recover water and identify the optimal operating conditions such as membrane orientation, fouling control, initial draw concentration, a series of experiments were conducted using F1 as the draw solute and DI water as feed.

3.1.1 Operation mode

Two operation modes, AL-F (FO mode) and AL-D (PRO mode), were examined in the FO system to maximize water extraction (Fig. 1). The AL-F mode harvested 324 mL of water, 48% more than that of the AL-D mode (219 mL) within 72 h (Fig. 1A). The difference in water extraction should be attributed to internal concentration polarization (ICP) inside the asymmetric FO membrane (McCutcheon and Elimelech 2006). When the porous supportive layer is installed at the feed side (AL-D), the diffused draw solutes (i.e. RSF) will gradually accumulate in the thick support layer, caused by relatively static environment at the supportive layer and a high rejection rate of attached active layer, forming a concentrative ICP and lowering the effective osmotic gap ($\Delta\pi_{\text{eff}}$) (Wang et al. 2016). A dilutive ICP, on the other hand, is normally formed under the AL-F with even lower $\Delta\pi_{\text{eff}}$ and lower theoretical water flux (Cath et al. 2006). However, the observed maximum water flux (Fig. 1B and 1D) for the AL-F (5.8 LMH) outcompeted that of the AL-D (3.6 LMH), which was attributed to the intensified fouling induced by concentrative ICP in porous supportive layer under AL-D, hindering efficient water permeation.

The conductivity profiles of two operation modes were rather similar (Fig. 1C). The slightly lower conductivity of the draw solution in the AL-F mode could be caused by dilution with more permeated water. On the feed side, the higher conductivity in the AL-F mode could be resulted from the enhanced RSF induced by higher water flux. This observation is in agreement with a previous finding that the ratio between water flux and RSF was subjected to Eq. 12 (Phillip et al. 2010) :

$$\frac{Water\ Flux}{RSF} = \frac{A}{B} nRT \quad (Eq. 12)$$

where B is the salt permeability coefficient. Similar to A (Eq. 2), B is recognized as another intrinsic membrane parameter. Hence, for a specific membrane, the fixed ratio renders a positive correlation between water flux and RSF. Because the RSF is comparable between both operation modes, the AL-F mode would be more favored due to improved water extraction (Fig. S2).

3.1.2 Fouling and *in-situ* control

Membrane fouling is a vital issue that should be addressed when utilizing commercial solid fertilizer as draw solutes. Fouling, caused by inorganic scaling/precipitation, organic deposition or attached microorganisms (biofouling), will reduce permeate water flux and aggravate membrane maintenance expenses (Le-Clech et al. 2006, Meng et al. 2009) . To alleviate membrane fouling, physical backwashing as well as chemical cleaning are usually integrated for ideal fouling control (Le-Clech et al. 2005). In the current study, draw solution made from fertilizer can bear moderate fouling propensity, due to some sparingly soluble contents generated from elements such as Cu, Fe, P, and S.

Membrane fouling was evaluated by using 1 M F1 as the draw solution (Fig. 2). Although the AL-D mode exhibited a lower fouling level (Fig. S3), the AL-F mode outcompeted the AL-D mode for water extraction and flux. Thus, the AL-F mode was chosen for this test. In the AL-F mode, the permeate water volume reduced from 152 mL to 129 mL in the 18 h (Fig. 2A), with a decrease in the maximum water flux from 5.8 LMH to 2.8 LMH (Fig. 2B). Due to the submerged configuration and complexity of the foulants (highly resistant), *in-situ* chemical cleaning instead of physical backwashing was employed for fouling control. In the absence of biological

processes, it is assumed that fouling should be mostly attributed to inorganic scaling (potentially irreversible). Successive chemical washing consisting of acid, base, and oxidants was proved to be effective in water flux recovery, followed by sufficient DI rinse to eliminate the dissolved foulants from the FO system. After cleaning, permeated water volume and maximum water flux was 98% and 93% recovered, respectively. Same *in-situ* chemical cleaning was applied for the rest of the study to prolong membrane lifespan. All the chemical solutions were reused to minimize environmental impact.

While aforementioned fouling was effectively controlled with *in-situ* chemical cleaning, using uncentrifuged fertilizer solution may clog the membrane and pose permanent damage to the FO membrane. The measured maximum water flux was 0.95 LMH even after *in-situ* chemical cleaning, representing only 18% of that with the pristine FO membrane (Fig. S4). The water extraction was reduced to 25% of that harvested by pristine FO membrane in 18 h. Therefore, appropriate pretreatment would be required to isolate the undissolved particles (e.g., through filtration) to prevent irreversible fouling of the FO membrane.

3.1.3 Nutrient distribution and loss

The distribution of critical nutrient elements in the fertilizer, i.e. N, P, and K, were examined at the system level (combining that in both the draw and the feed solutions). Fig. 3 shows the concentration and distribution of TN, $\text{NH}_4^+\text{-N}$, and Urea-N with 72-h operation of the FO system. The total amount of TN in the FO system was reduced from 91 to 81 mmol in 72 h (Fig. 3A). Significant RSF occurred within the first 24 h, decreasing the TN in the draw to 44 mmol and increasing its presence in the feed to 47 mmol (Fig. 3 B and C). Given relatively stable TN

amount in the draw but slight decrease in the feed after 24 h, the 11% of the TN loss was possibly related to volatilization of urea on the feed side. Urea is a widely utilized fertilizer, due to its relatively high N content (45%), and in this study, Urea-N made up of more than 85% initial TN in F1. The loss of TN usually goes through urea hydrolysis and ammonia volatilization (Overrein and Moe 1967). Through hydrolysis, Urea-N will be converted to $\text{NH}_4^+\text{-N}$, which is in consistent with the increase of total $\text{NH}_4^+\text{-N}$ in the FO system (Fig. 3A). Since the feed solution had a larger volume and was not completely sealed, the loss of TN from the feed solution could be more intensive than that of draw solution (Fig. 3B). It was observed that 9% of the total loss of potassium (Fig. S5A) and 8% of phosphorus (Fig. S5B) was lost in the FO system, likely related to precipitation and/or salting-out effect on beaker wall induced by long-term operation.

Nutrients will inevitably diffuse to the feed side because of the limitation of the FO membrane (Hancock and Cath 2009). In this study, RSF resulted in about 50% of TN diffusion to the feed side within 24 h (Fig. 3B) with a RSF of $193.95 \text{ mmol m}^{-2} \text{ h}^{-1}$ (Table S5). This RSF rate is consistent with the findings of other studies (Majeed et al. 2015, Phuntsho et al. 2012a, Phuntsho et al. 2012b, Phuntsho et al. 2013). The high mobility of urea across FO membrane can be explained by its small molecular weight and uncharged status in solution, which increases its diffusion tendency (Hancock and Cath 2009). The RSF of $\text{NH}_4^+\text{-N}$ and K were 17.06 and $5.67 \text{ mmol m}^{-2} \text{ h}^{-1}$ (Table S5), respectively. In accordance with the prior studies (Achilli et al. 2010, Phuntsho et al. 2011), multivalent ions with larger hydrated radii (Nightingale Jr 1959), such as P (as in PO_4^{3-}), exhibited the lowest RSF ($0.47 \text{ mmol m}^{-2} \text{ h}^{-1}$) compared to the monovalent ions (Table S5). The loss of the key fertilizer components from the draw side would increase the operational cost and also cause the disposal problems of the feed solution due to accumulation of

those compounds. Although a lower RSF may be achieved through development of advanced membrane materials with higher values of A/B (Tang et al. 2010), complete elimination of RSF is unattainable at the current stage.

3.1.4 Effects of initial fertilizer concentration

Three initial draw concentrations (1M, 2M and 3M) were investigated for water extraction, and as expected, the highest draw concentration of 3 M led to the highest water flux of 12.7 LMH (Fig. 4A). The enhanced osmotic gap (driving force) was formed at a higher draw concentration, resulting in a larger water extraction capability in the FO system (Eq. 2 and 3). According to the water flux baseline of 1 LMH, the operation length varied from 72 h with 1M or 2M to 96 h with 3M. The final amount of TN in the draw exhibited a linear correlation with the initial draw amount (inset, Fig. 4A), and the similar linear tendency was obtained for both K and P ($R^2 > 0.99$, Table S1).

The FO system did not achieve full dilution of the fertilizer to reach its application concentration. For example, 85 mL of the 1-M F1 solution would need 800 mL water (Table S2, nutrient loss rate considered) for its dilution, and the FO recovered 324 mL water (using DI water as a feed); therefore, the FO provided 40.5% of the water need (dilution rate). Although a higher initial draw concentration resulted in more water extraction, the relevant dilution rate actually decreased, because of a higher demand for dilution water. The dilution rate decreased from 40.5 to 23.2 % when the initial draw solution increased from 1 to 3 M (Fig. 4B). Meanwhile, the higher RSF occurred at a higher draw concentration could accelerate solute accumulation on the

feed side. Therefore, a relatively low-concentration fertilizer solution may be more advantageous to achieve diluted fertilizer by the FO system.

3.2 Performance with different fertilizers

Another two commercially available solid fertilizers (F2 and F3) were also examined for water extraction at a 1-M concentration, and the comparison of the three fertilizers is shown in Fig. 5. The ratio of Urea-N in TN was different among these three fertilizers with the following order: $F2 > F1 > F3$. As expected, the maximum water flux was in contrast to Urea-N content: $F3 > F1 > F2$ (Fig. 5A). The F2 had the lowest water flux of 4.32 LMH and its extraction only lasted for 48 h when reaching the specific water flux < 1 LMH, resulting in water extraction of only 177.4 mL. The operating period with the F3 doubled that of the F2 for 96 h, likely benefited from its higher ratio of $\text{NH}_4^+\text{-N}$; the volume of the recovered water tripled to 545.6 mL. However, the F2 achieved a much higher dilution rate of 55.0% than that of the F1 (40.5%) or the F3 (36.5%), because of its lower requirement of the dilution water volume (0.39 L, Table S2). The F3 had the highest required water volume for dilution (1.51 L). Regarding the RSF, the F1 has the lowest value except for Urea-N (Fig. 5B). The comparison suggests that those three commercial solid fertilizers can act as draw solutes with different levels of water extraction, and the fertilizer with a lower urea content could be favored because of higher water extraction and lower RSF. Because the 1-M F1 had low RSF and relatively high water extraction and dilution rate, it was used for examining water recovery from the treated wastewater effluent.

3.3 Water recovery from the treated wastewater

The wastewater effluent was collected from a local municipal wastewater treatment plant and tested with 1-M F1 as the draw. The FO system recovered 317 mL of water within 72 h, which was comparable to that from the DI water (324 mL, Fig. 6A). A notable lag in specific water flux was observed with the treated wastewater at the beginning, resulting in a reduced maximum water flux of 4.20 LMH (Fig. 6B) affected by the higher conductivity (thus lower osmotic gap) of the treated wastewater in the presence of various compounds (Table S3), such as inorganic ions ($\text{NH}_4^+\text{-N}$, K^+ , $\text{PO}_4^{3-}\text{-P}$) and soluble microbial products (SMP). The RSF of the major ions were similar under both operation conditions (DI vs treated effluent, data not shown). The dilution rate with the treated wastewater was 38.2%, slightly lower than that of the DI water. Organic fouling of the FO membrane on the feed side (active layer) due to the wastewater would take a long time to appear, because of extremely low COD and TOC concentration in the treated wastewater (Table S3). Thus, the proposed *in-situ* chemical cleaning at draw side was sufficient for fouling control (wastewater as feed). It is worth noting that the elevated nutrient concentration was detected in the final concentrated feed: the $\text{NH}_4^+\text{-N}$ concentration increased from 2 mg L⁻¹ to 40 mg L⁻¹, K^+ increased from 10.5 mg L⁻¹ to 69.5 mg L⁻¹, while $\text{PO}_4^{3-}\text{-P}$ increased from 2.5 mg L⁻¹ to 5 mg L⁻¹. As Fig. 6C indicates, the solute build-up in the final feed solution was mainly attributed to reverse solute flux (RSF) for $\text{NH}_4^+\text{-N}$ (92%), TN (98%) and K (75%). However, the concentrated P mostly came from treated wastewater by salt rejection of FO membrane (concentrating effect, 81%). The increased nutrient concentrations in the treated wastewater must be addressed, and additional treatment such as nitrogen removal (e.g., anammox) may be needed (Li et al. 2015).

3.4 Energy consumption of the FO system

Although the FO process has been widely studied as an energy efficient process, the performance and data of energy consumption was rarely reported in the literature. In the present FO system, the pump for recirculation of the draw solution was the major energy consumer for water recovery, and its energy consumption was expressed in kWh m⁻³. Three recirculation rates, 10 mL min⁻¹, 50 mL min⁻¹ and 100 mL min⁻¹, were examined. As shown in Fig. 7A, the amount of the recovered water within 24-h operation was similar among the three recirculating conditions with comparable specific water flux. It is expected that increasing recirculation rate can reduce the external concentration polarization (ECP), resulting in a higher and more stable $\Delta\pi_{\text{eff}}$. However, a relatively low water flux generated by the present FO renders a negligible ECP, and hence limited improvement in water recovery capacity was obtained at higher recirculation rates. In addition, the relatively short testing time (24 hours) would not allow the development of cake layer under low recirculation rates, which could cause water flux decrease in long-term operation. The energy consumption profile at different recirculation rates was presented in Fig.7B. The highest recirculation rate of 100 mL min⁻¹ required 1.86 ± 0.47 kWh m⁻³, which was reduced to 0.47 ± 0.13 kWh m⁻³ at 50 mL min⁻¹. Further reduction of the recirculation rate to 10 mL min⁻¹ exhibited the lowest energy consumption of 0.02 ± 0.01 kWh m⁻³, which was about 1.1% and 4.3% of energy consumption with 100 mL min⁻¹ and 50 mL min⁻¹, respectively. The energy consumption of the present FO system (at 10 mL min⁻¹) for water recovery was significantly lower than other water recovery approaches such as reverse osmosis (as low as 2 kWh m⁻³) (Shannon et al. 2008), mechanical vapor compression (down to 20 kWh m⁻³) (Elimelech and Phillip 2011, Thiel et al. 2015), and even self-supplied FO with thermolytic ammonium bicarbonate (0.1 kWh m⁻³) (Qin and He 2014).

It should be noted that, in a typical FO system, additional energy will be required for further treatment of concentrated feed solution. Because of reverse salt flux, concentrating effect and high membrane rejection, salinity build-up (or salt accumulation) at the feed side is inevitable and will need to be properly controlled, and a number of methods have been investigated including electrodialysis (ED), integrated biological degradation, filtration (microfiltration for instance) and/or bioelectrochemical systems (BES) with recoverable draw solutes (Lu and He 2015, Luo et al. 2015, Qin and He 2014, Zou et al. 2014). Energy-efficient strategies of salinity mitigation warrant further investigation to proper evaluation of the viability of FO system.

4. Conclusions

The results of this study have demonstrated the feasibility of water recovery using commercial solid fertilizers, though some challenges remain to be addressed including alleviating reverse salt flux, examining its long-term performance and fouling on the feed side of the FO membrane with using treated wastewater as a feed.

- Under the AL-F mode, the recovered water could provide up to 41% of the required water for diluting fertilizer by using 1-M F1, and a higher initial fertilizer concentration (3-M F1) resulted in a lower dilution rate (23.2%) because of its higher demand for dilution water.
- The water extraction capacity of the FO was affected by different fertilizers with a negative correlation to the corresponding urea content. The rate of RSF of the individual components followed the trend: Urea-N > NH₄-N > K > P.
- Solute build-up on the feed side was observed and mainly attributed to the concentrating effect for phosphorous (81%) and RSF for total nitrogen (98%) and potassium (75%).

- Membrane fouling was effectively controlled during the entire experiment with *in-situ* and reusable chemical cleaning, with 98% and 93% of recovery for permeated water volume and maximum water flux, respectively.
- Reducing recirculation intensity from 100 to 10 mL min⁻¹ did not obviously decrease water flux but significantly reduced the energy consumption from 1.86 to 0.02 kWh m⁻³.

Appendix A. Supplementary materials

Supplementary figures and tables related to this article can be found in the supporting materials. The schematic of the submerged FO system and more data of the FO performance and ion distribution are shown in Figures S1-S5. The studies about fertilizer-driven forward osmosis with different feed solutions, characteristics of different commercial fertilizers characteristics of treated wastewater, detailed experiment procedures and reverse solute flux of different fertilizers are shown in Table S1-S5.

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Figure Captions

Figure 1. The performance of the FO system affected by membrane orientations, activated layer facing draw (AL-D, PRO mode) and activated layer facing feed (AL-F, FO mode): (A) accumulated water volume; (B) average water flux, (C) solution conductivity; and (D) specific water flux.

Figure 2. Comparison of (A) accumulated water volume and (B) average water flux with or without *in-situ* chemical cleaning under AL-F mode (FO mode). In the first test, pristine FO membrane was used and, without any chemical cleaning, it was then applied in the second test to determine fouling situation. A third test was performed after the membrane (second test) was *in-situ* chemically cleaned. During each test, 1M F1 and DI water were applied as draw and feed, respectively.

Figure 3. Distribution of nitrogen within 72-h operation under the AL-F (FO mode): the mole profiles of total nitrogen (both urea and ammonia nitrogen) in (A) the whole FO system; (B) the draw solution; and (C) the feed solution.

Figure 4. The performance of the FO system affected by the concentration of the F1: (A) specific water flux and total nitrogen amount; and (B) the collected/required water volume and corresponding dilution rates. The fertilizer concentration is quantified by mole concentration of total nitrogen (1M, 2M and 3M).

Figure 5. The performance of the FO system with three different fertilizers (F1, F2, and F3) at a concentration of 1 M: (A) the accumulated water volume and specific water flux; and (B) reverse solute flux of main nutrient elements.

Figure 6. The FO performance with the treated wastewater using 1-M F1 as a draw solution: (A) recovered water volume; (B) specific water flux; and (C) percentage of solute build-up at feed side. Both A and B provide a direct comparison of FO performance by using either DI water or treated wastewater as feed solution. C represents the solute build-up by applying treated wastewater as feed.

Figure 7. Water recovery (A) and energy consumption (B) of the FO system with three different recirculation rates (100, 50, 10 mL min⁻¹) by using the treated wastewater as feed and 1-M F1 as draw.

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