Evaluation of fertilizer-drawn forward osmosis for sustainable agriculture and water reuse in arid regions

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ABSTRACT

The present study focused on the performance of the FDFO process to achieve simultaneous water reuse from wastewater and production of nutrient solution for hydroponic application. Bio-methane potential (BMP) measurements were firstly carried out to determine the effect of osmotic concentration of wastewater achieved in the FDFO process on the anaerobic activity. Results showed that 95% water recovery from the FDFO process is the optimum value for further AnMBR treatment. Nine different fertilizers were then tested based on their FO performance (i.e. water flux, water recovery and reverse salt flux) and final nutrient concentration. From this initial screening, ammonium phosphate monobasic (MAP), ammonium sulfate (SOA) and mono-potassium phosphate were selected for long term experiments to investigate the maximum water recovery achievable. After the experiments, hydraulic membrane cleaning was performed to assess the water flux recovery. SOA showed the highest water recovery rate, up to 76% while KH₂PO₄ showed the highest water flux recovery, up to 75% and finally MAP showed the lowest final nutrient concentration. However, substantial dilution was still necessary to comply with the standards for fertigation even if the recovery rate was increased.

Keywords: Forward osmosis, fertilizer draw solution, hydroponic, nutrient, water reuse.
1 Introduction

Freshwater resources are getting scarcer, particularly in arid, semi-arid and coastal areas, while agricultural sector consumes about 70% of the accessible freshwater with about 15-35% of water being used unsustainably (Assessment, 2005; Clay, 2013). In arid regions, the development of agriculture is not only hindered by the limited freshwater resources but also by the scarcity of fertile lands. Hydroponics is a subset of hydroculture with several advantages over conventional soil culture. In fact, it is a soilless process using synthetic mineral solution to grow crops (Jensen, 1997). As such, it eliminates the problems associated with soil culture; i.e. poor soil culture, poor drainage, soil pollution and soil-borne pathogens. Therefore, hydroponics has been widely used in commercial greenhouse vegetable production around the world. However, hydroponics requires a nutrient solution to fertilize the plants under a controlled environment (e.g., concentration, flow rate, temperature). As a result, this process also consumes a large amount of fresh water to prepare the fertilizer solution. This water-food nexus is becoming a critical issue in most arid regions and therefore, sustainable solutions to assure water and food security must be explored.

Recently, increased consideration has been given to the concept of fertilizer drawn forward osmosis (FDFO) process. In fact, the novelty of the concept relies on the low-energy osmotic dilution of the fertilizer draw solution (DS) which can then be applied directly for irrigation since it contains the essential nutrients required for plant growth. Although early studies on FDFO (Phuntsho, Shon et al., 2011; Phuntsho, Shon et al., 2012a) demonstrated that most fertilizers can be suitable DS, the limit posed by the osmotic equilibrium between the feed and the draw solutions will dictate the final nutrient concentration, which, in most cases, was found to exceed the standards for irrigation. This means that the final DS still requires additional dilution which is not acceptable, especially in the context of freshwater scarcity.

To circumvent this issue, nanofiltration (NF) was proposed as pre or post-treatment for FDFO with the aim of reducing the nutrient concentration in the final product water (Phuntsho, Hong et al., 2013). Results from this study showed that the product water was suitable for direct application when NF was used as post-treatment and when brackish water with low TDS (i.e. < 4000 mg/L) was employed as feed solution (FS). However, the use of an additional process will increase the energy consumption of the system and thus the final cost of produced water especially because NF is a pressure-driven membrane process. Recently,
pressure-assisted forward osmosis (PAFO) was tested as an alternative solution to eliminate
the need for NF post-treatment (Sahebi, Phuntsho et al., 2015). The PAFO process used an
additional hydraulic driving force to simultaneously enhance the water flux and dilute the DS
beyond the point of osmotic equilibrium. In this study, it was concluded that the use of PAFO
instead of NF can further dilute the fertilizer DS, thereby producing permeate water that
meets the acceptable nutrient concentrations for direct fertigation.

To date, all FDFO studies have either used brackish water (Phuntsho, Hong et al., 2013;
Phuntsho, Lotfi et al., 2014; Raval and Koradiya, 2016), treated coalmine water with a TDS
of about 2.5 g/L (Phuntsho, Kim et al., 2016) or seawater (Phuntsho, Shon et al., 2011;
Phuntsho, Shon et al., 2012a; Phuntsho, Shon et al., 2012b; Phuntsho, Sahebi et al., 2013) as
the FS. However, the relatively low salinity of most impaired waters makes them potentially
suitable candidate for such dilution (Lew, Hu et al., 2005). Besides, drawing the water from
impaired sources to produce nutrient solution for hydroponic culture seems a very promising
and sustainable approach to solve the freshwater scarcity issue in most arid regions. This
concept can be further extended if the concentrated impaired water from the FDFO process is
sent to an anaerobic membrane bioreactor (AnMBR) for additional treatment and biogas
production to supply energy to the hybrid process.

The main objective of this study is therefore to evaluate the potential of FDFO process for
simultaneous water reuse and sustainable agriculture. The optimum recovery rate for feeding
the AnMBR process will be first determined through bio-methane potential measurements.
Then, bench-scale FO experiments will be carried out to optimize the fertilizer formula and
process configuration in order to simultaneously achieve the optimum recovery rate and
favourable nutrient supply for hydroponics.

2 Materials and Methods

2.1 FO membrane and draw solutions

The FO membrane used in this study was a commercial thin film composite (TFC) polyamide
(PA) FO membrane (Toray Industry Inc.).

All chemical fertilizers used in this study were reagent grade (Sigma Aldrich, Australia).
Draw solutions were prepared by dissolving fertilizer chemicals in deionized (DI) water. Detail information of fertilizer chemicals are provided in Table 1. Osmotic pressure and diffusivity were obtained by OLI Stream Analyzer 3.1 (OLI System Inc., Morris Plains, NJ, USA).

Table 1

2.2 Bio-methane potential experiments

The bio-methane potential (BMP) experiment was carried out using the BMP apparatus described in our previous study (Kim, Chekli et al., 2016) to investigate the effect of water recovery in the FO process on the performance of the post-AnMBR process. The BMP apparatus consisted of 6 fermentation bottles submerged in a water bath connected to a temperature control device to maintain a temperature of 35±1 °C. These bottles were connected to an array of inverted 1,000 mL plastic mass cylinders submerged in the water bath filled with 1 M NaOH solution to collect and measure the biogas. The NaOH solution plays an important role to sequester both CO₂ and H₂S to evaluate only CH₄ production potential. Air volume in each mass cylinder was recorded twice a day. Detailed description of BMP apparatus used in this study is given elsewhere (Nghiem, Nguyen et al., 2014; Ansari, Hai et al., 2015).

Six different recovery rates were tested in this study (i.e. 0%, 20%, 40%, 60%, 80% and 95%) and the concentrated synthetic wastewater was prepared accordingly. 50 mL of each solution was then mixed with 700 mL of digested sludge. All bottles were purged with nitrogen gas, and connected to the biogas collecting equipment. The BMP experiment was carried out until the methane production stopped.

2.3 Bench-scale FO system

The performance of the FO process was conducted in a closed-loop bench-scale FO system (Figure S1, Supporting Information) in which detailed characteristics can be found elsewhere (Lee, Boo et al., 2010; Kim, Lee et al., 2015). This lab-scale FO unit has an effective membrane area of 20.02 cm² with a channel dimension of 77 mm long, 26 mm wide, and 3 mm deep. The FO cell had two symmetric channels on both sides of the membrane for co-current flows of feed and draw solutions. Variable speed gear pumps (Cole-Parmer, USA)
were used to pump the liquid in a closed loop. The DS tank was placed on a digital scale and the weight changes were measured by a computer in real time to determine water flux. Conductivity and pH meters (HaCH, Germany) were connected to a computer to monitor the reverse salt flux (RSF) of draw solutes in the FS tank.

FO experiments were conducted in the FO mode where the active layer is facing the FS. Before each performance experiment, the FO membrane was stabilized for 30 minutes with DI water as FS and fertilizer solution as DS. Once stabilized, the water flux was measured continuously throughout the experiment with a 3 minutes time interval. All experiments were conducted at a cross-flow velocity of 8.5 cm/s, and a constant temperature of 25 ºC.

### 2.3.1 Short-term FO performance experiments – Initial Screening

The performance of each fertilizer (Table 1) as DS was assessed with either DI water (for RSF experiments) or with synthetic wastewater simulating municipal wastewater (Table 2) as FS. In all experiments, a concentration of 1M was used for each fertilizer DS, unless otherwise stated. For the RSF experiment, the FS was collected after 2 hours operation and RSF was determined by analysing the components of each tested DS. The experiments, using synthetic wastewater as FS, were carried out for one day (i.e. 24 hours) during which the water flux was measured continuously (i.e. one measurement every three minutes). At the end of the experiments, the final recovery rate and nutrient(s) concentration were calculated. The water flux, RSF, recovery rate and final nutrient composition were used to determine the optimum fertilizers to carry out long-term experiments (i.e. four days). The effect of DS concentration was also investigated by running experiments at 2M fertilizer DS concentration. Finally, this study also evaluate the performance of selected blended fertilizers (based on (Phuntsho, Shon et al., 2012b)) at 1M:1M ratio.

**Table 2**

### 2.3.2 Long term FO performance experiments

Long-term experiments were carried out with the optimum DS selected during the first stage screening and synthetic wastewater as FS. These experiments were run for four days during which the water flux was monitored continuously. At the end of the experiment, the final recovery rate and nutrients concentration were calculated.
A new FO membrane was used for each experiment, and the initial baseline flux of the virgin membrane was obtained using 1M NaCl as DS and DI water as FS under the operating conditions described earlier (i.e. cross-flow velocity of 8.5 cm/s, and a constant temperature of 25 °C). At the end of the long-term experiments, physical membrane cleaning was performed to evaluate the water flux recovery. The DS and FS were replaced with DI water, and the FO process was operated at triple cross-flow rate (i.e. 1,200 mL/min) for 15 minutes. Following this physical cleaning, the flux recovery was assessed by measuring the flux under the same conditions as the baseline experiment (i.e. 1M NaCl as DS and DI water as FS). The percentage ratio of the recovered flux after cleaning to initial virgin baseline flux (normalised) was assessed as the water flux recovery.

3 Results and Discussion

3.1 Bio-methane potential measurements

Bio-methane potential (BMP) measurements were carried out for 11 days to determine the effect of water recovery/osmotic concentration of wastewater in the FDFO process on the anaerobic biological process. Figure 1a shows the influence of water recovery achieved in the FDFO process on biogas production by activated sludge. It is clear from these results that biogas production increased with increasing recovery rate. In fact, 95% water recovery showed the highest cumulative biogas production, almost three times higher than the results obtained with 80% water recovery. It has been demonstrated previously that municipal wastewater usually needs to be concentrated five to ten times before reaching an acceptable level, in terms of chemical oxygen demand (COD), for subsequent anaerobic treatment and energy recovery via biogas production (Verstraete and Vlaeminck, 2011; Burn, Muster et al., 2014). Results in Figure 1b confirmed that there is a strong (i.e. R² = 0.9953) linear correlation between the final volume of biogas produced and the COD in wastewater. For example, from 0% water recovery to 20% recovery, the increase in COD value is not very significant (i.e. from 390 mg/L to 487.5 mg/L) which explains the very low biogas production for these two samples. However, from 0% water recovery to 40% water recovery, the COD in the concentrated wastewater increases by 1.7 times and similarly the final volume of biogas produced increases by 1.8 times. Therefore the COD contribution is crucial to promote a fast and adequate rate of methane production as it was already demonstrated in
previous research (Grobicki and Stuckey, 1989; Ansari, Hai et al., 2015). For these reasons, 95% was chosen as the optimum recovery rate to achieve for the wastewater via osmotic concentration in the FDFO process.

Figure 1

3.2 Performance of single fertilizers as draw solution

3.2.1 Water flux, water recovery and reverse salt flux

The performance of single fertilizers was initially evaluated in terms of water flux, water recovery and reverse salt flux; three essential criteria for agriculture and water reuse applications. In fact, a high water flux is desirable for the economic viability of the process since it will affect the total membrane area and thus the capital cost. Then, a high water recovery/wastewater concentration (i.e. target of 95% as discussed in the previous section) will ensure optimum biogas production in the subsequent AnMBR process and also help in achieving the required final nutrient concentration in the diluted DS. Finally, a low reverse salt flux is preferable since the accumulation of DS in the feed water due to its reverse movement can have detrimental effect on the anaerobic microbial activity in the post-AnMBR process (Ansari, Hai et al., 2015). Based on those criteria and previous studies on the FDFO process (Phuntsho, Shon et al., 2011; Phuntsho, Shon et al., 2012b), nine different fertilizers were selected for this study. The thermodynamic properties of the selected DS are gathered in Table 1 and were determined using OLI Stream Analyzer 3.2 (OLI System Inc., Morris Plains, NJ, USA). Diammonium phosphate (DAP) showed the highest osmotic pressure (i.e. 50.6 atm) followed by Ca(NO$_3$)$_2$ and ammonium sulphate (SOA) while NH$_4$Cl has the highest diffusivity ($1.85 \times 10^{-9} \text{ m}^2/\text{s}$) followed by KCl and KNO$_3$. The performance tests were carried out for one day (i.e. 24 hours) using synthetic wastewater (cf. Table 2) or DI water as FS under similar operating conditions at 1M DS concentration and the results are gathered in Table 3.

Table 3

Similarly to earlier studies on the FDFO process (Phuntsho, Shon et al., 2011; Phuntsho, Shon et al., 2012b), KCl showed the highest initial water flux (i.e. 21.1 LMH) together with NH$_4$Cl and followed by KNO$_3$ while KH$_2$PO$_4$ and DAP had the lowest among the different
tested fertilizers (i.e. 13.2 LMH and 13.3 LMH respectively). Theoretically, since the osmotic pressure difference across the membrane is the main driving force in the FO process, the water flux trend among the fertilizers should follow the same trend as the osmotic pressure. However, results in both Table 1 and Table 3 show that there is no direct correlation between the osmotic pressure of the DS and the water flux. For instance, while DAP generated the highest osmotic pressure, this fertilizer showed one of the lowest water flux. This is due to the concentration polarization (CP) effects and more importantly to the extent of internal CP (ICP) effects induced by the solute resistance (K) inside the membrane support layer facing the DS (McCutcheon, McGinnis et al., 2006; McCutcheon and Elimelech, 2007). The solute resistance is, in fact, a function of the diffusivity of the solute and thus, a DS having a high diffusivity will have a low K value and therefore generate a high water flux. This is confirmed by the results obtained in this study as data showed a fairly good correlation (i.e. $R^2 = 0.8077$) between the water flux generated by a DS and its diffusivity (Figure S2, Supporting Information).

The recovery rate after 1-day operation shows similar trend to the initial water flux (i.e. linear correlation, $R^2 = 0.8397$, Figure S3, Supporting Information) with NH$_4$Cl and KCl having the highest water recovery (i.e. 42.2% and 38.6% respectively). Comparing the results with the FDFO desalination studies using either seawater or brackish water as FS, the water flux obtained in this study (i.e. using synthetic wastewater as FS) is much higher, up to 80% (Table S1). In fact, the osmotic pressure of the synthetic wastewater used in this study (i.e. 0.149 atm) is considerably lower than, for instance, the brackish water used in Phuntsho, Shon et al., (2012b) (i.e. 3.9 atm) and therefore the initial difference in osmotic pressure across the membrane (i.e. which is the driving force of the FO process) is significantly higher, resulting in a higher initial water flux. This suggests that, if available, low-strength wastewater might be a more suitable FS for the FDFO process when targeting high water flux and water recovery. However, it should be noted that a different membrane has been employed in this study (i.e. Toray TFC PA membrane instead of HTI CTA membrane) so the increase in water flux might also be partially related to the better performance of this novel membrane.

After one day of operation, both KNO$_3$ and KCl showed the highest flux decline (i.e. 55.4% and 49.2%, respectively) while the water flux generated by DAP, mono-ammonium
phosphate (MAP) and KH$_2$PO$_4$ only decreased by less than 20%. This trend can be explained by the fact that an initial higher water flux level can generally be coupled with elevated rate of RSF resulting in more severe fouling (Hancock and Cath, 2009; Phillip, Yong et al., 2010; Tang, She et al., 2010). Besides, both KCl and KNO$_3$ have ionic species with small hydrated diameter (i.e. K$^+$, Cl$^-$ and NO$_3^-$) which will therefore readily diffuse through the membrane compared to fertilizers having larger-sized hydrated anions (i.e. SO$_4^{2-}$ and PO$_4^{3-}$) regardless of the paired cations (Achilli, Cath et al., 2010). It is well established that a greater rate of RSF will significantly affect the feed water chemistry which may cause more severe fouling (She, Wang et al., 2016).

Reverse salt flux selectivity (RSFS = $J_w/J_s$), which represents the ratio of the forward water flux ($J_w$) to the RSF ($J_s$), was also calculated and results are displayed in Table 3. This ratio is very useful to estimate how much salts from the DS are lost through RSF during the FO process operation. It is usually preferable to have a DS with a high RSFS in terms of replenishment cost but also for sustainable FO operation (Achilli, Cath et al., 2010). Table 3 shows that MAP, SOA and KH$_2$PO$_4$ exhibited the highest RSFS suggesting that all three DS can produce the highest volume of permeate per gram of lost draw salts. This is very crucial in our study since the target is to produce a highly diluted DS for possible direct hydroponic application while concentrating the wastewater with minimum reverse diffusion from the DS to minimize the impact on the microbial activity in the subsequent AnMBR process. Because for hydroponics, one of the most important parameters to evaluate is the final nutrient concentration, the RSF in the FDFO process has also been evaluated in terms of loss of essential nutrients (i.e. N, P and K) per unit volume of water extracted from the FS as described in Phuntsho, Shon et al., (2012b). Results in Table 3 showed that KNO$_3$, KCl and NH$_4$NO$_3$ had the highest loss of nutrient which correlates with the RSF data for these three fertilizers. SOA, MAP and KH$_2$PO$_4$ exhibited the lowest loss of nutrient by reverse diffusion for N, P and K, respectively. In fact, these fertilizers have divalent ions (i.e. SO$_4^{2-}$, PO$_4^{3-}$) which display significantly lower loss through RSF due to their larger hydrated ions.

### 3.2.2 Final nutrient concentration after 1-day operation

Figure 2 presents the final nutrient (i.e. N, P and K) concentrations in the final diluted DS after 1-day operation for all nine tested fertilizers. Based on earlier FDFO studies (Phuntsho,
Shon et al., 2012b), the final NPK concentration is highly dependent on the feed water (i.e. seawater, brackish water, wastewater) as well as the percentage of a particular nutrient in the DS and the final recovery rate. In fact, by comparing MAP and DAP fertilizers, which have the same counter ion (i.e. $\text{PO}_4^{2-}$) but a different percentage of N (i.e. 12.2% and 21.2 %, respectively), the final diluted DS contained 10.8 and 21.5 g/L of N, respectively. The lowest nutrient concentration for N was observed for $\text{NH}_4\text{Cl}$ (i.e. 9.8 g/L) which generated one of the highest water flux and recovery rate (Table 3). All DS containing either P or K resulted in similar final concentration in the diluted DS after 1-day and this concentration remained fairly high (i.e. about 24 g/L for P and 30 g/L for K).

Figure 2

However, the results presented in Figure 2 indicate that the final nutrient concentration after 1-day operation remains significantly higher than the standards for hydroponics. In fact, depending on the crop types and growth stages, the required nutrient concentration varies significantly with a maximum recommended concentration of 200 mg/L for N, 50 mg/L for P and 300 mg/L for K (Resh, 2012). Taking tomatoes as an example, the nutritional requirement for hydroponics varies from 70-150 mg/L for N, 50 mg/L for P (i.e. no variation during the different growth periods) and 120-200 mg/L for K (Hochmuth and Hochmuth, 2001). It is clear from these data that the results obtained in Figure 2 after 1-day operation are significantly higher than the standards for hydroponics suggesting that the final DS still requires a substantial dilution before being applied to hydroponic crops. Additional post-treatment (e.g. nanofiltration) or alternative process configuration (e.g. use of blended fertilizers or pressure-assisted osmosis) might help in obtaining the desired nutrient concentration as demonstrated in previous FO studies (Tan and Ng, 2010; Phuntsho, Shon et al., 2012b; Zhao, Zou et al., 2012; Phuntsho, Hong et al., 2013; Sahebi, Phuntsho et al., 2015).

3.2.3 Effect of fertilizer draw solution concentration

Short-term experiments were also carried out at 2.0 M DS concentration since higher water flux has been generally observed at higher fertiliser concentrations. Results for this study are presented in Table 4 (i.e. water flux and recovery rate) and Figure 3 (i.e. final NPK concentrations). With the exception of $\text{KH}_2\text{PO}_4$ which has a maximum solubility of 1.8 M, all
fertilizer DS generated a higher water flux at 2.0 M concentration (Table 4). However, the improvement ratio (i.e. percentage increase in water flux from 1.0 M to 2.0 M concentration) is different among the tested fertilizers. In fact, previous studies have already shown that DS concentration influences the FO process performance (Seppälä and Lampinen, 2004; McCutcheon, McGinnis et al., 2006; Achilli, Cath et al., 2009; Choi, Choi et al., 2009; Hancock and Cath, 2009; Xu, Peng et al., 2010). It was demonstrated that the relationship between DS concentration and water flux is not linear and different among the DS types, especially at high DS concentration where the relation has been found logarithmic. This has been attributed to ICP effects in the membrane support layer which become more important at higher permeate flux resulting in less effective water flux improvement (Tan and Ng, 2010). The lower improvement ratio for MAP and DAP (i.e. less than 5%) suggests that the percentage of the bulk osmotic pressure effectively available did not improve significantly when increasing the solute concentration (Phuntsho, Hong et al., 2013).

Table 4

The recovery rate after 1-day operation also increased with the increase in DS concentration, with the exception of NH₄Cl and MAP. However, the improvement ratio (i.e. percentage increase) in comparison with the results obtained with 1.0 M DS concentration is quite heterogeneous among the tested fertilizers. In fact, it has been previously demonstrated that, although the increase in DS concentration can increase the initial water flux, it can also exacerbate membrane fouling due to the greater hydraulic drag force promoting more foulant deposition on the membrane (Mi and Elimelech, 2008; Zou, Gu et al., 2011; She, Jin et al., 2012) as well as an increase in the solute reverse diffusion from the DS (Hancock and Cath, 2009; Phillip, Yong et al., 2010). Besides, it is evident that the membrane fouling behaviour and especially the foulant-membrane interactions, are closely dependent on the type of DS (i.e. diffusivity, solubility, molecular weight, soluble species, etc.) and therefore, different fertilizer DS will have different impacts on membrane fouling resulting in different water flux trends (i.e. and thus final recovery rate) which explains the results obtained in Table 4.

The final nutrient (i.e. NPK) concentrations for all DS (i.e. except KH₂PO₄) are shown in Figure 3. Considering the negligible improvement in terms of water flux and more importantly in terms of recovery rate, it is not surprising that the final NPK concentrations, using 2.0 M initial DS concentration, are almost twice for the values obtained with 1.0 M DS.
concentration. This result suggests that increasing the initial DS concentration might not be the best approach to achieve lower nutrient concentration in the final diluted DS.

Figure 3

3.3 Performance of blended fertilizers as draw solution

A previous FDFO study (Phuntsho, Shon et al., 2012b) demonstrated that blending two or more fertilizers as DS can help in reducing the final nutrient (i.e. NPK) concentration compared to the use of single fertilizer. Based on this finding, four different combinations of two fertilizers (i.e. at 1 M: 1 M ratio) were selected since they already exhibited good performance among all the blended solutions tested. Results, in terms of water flux, recovery rate and final NPK concentration are gathered in Table 5.

Similarly to the previous FDFO study on blended fertilizers, all four blended solutions generated a higher water flux than the individual fertilizers but it was still lower than the sum of the water fluxes obtained with the two single fertilizers. This was previously explained as a result of complex interactions occurring between the ions and counterions of the two fertilizers leading to a decreased number of formed species in the final solution (Phuntsho, Shon et al., 2012b). The coexistence of two different species in the same solution was also found to affect the diffusivity of a specific compound which will indirectly affect the internal CP (ICP) effects and thus the water flux in the FO process (Gray, McCutcheon et al., 2006; McCutcheon and Elimelech, 2006; Tan and Ng, 2008; Tang, She et al., 2010).

Table 5

The highest water flux and recovery rate were generated by the NH₄NO₃ + NH₄Cl blend while NH₄NO₃ combined with KH₂PO₄ produced the lowest water flux and recovery rate. In most cases, the final NPK concentration was slightly lower than with single fertilizers but the difference was not significant, especially when considering the increase in cost when using an additional fertilizer. For instance, when NH₄NO₃ and KH₂PO₄ were used individually, the final NPK concentration in the final diluted DS was 21.1/0/0 mg/L and 0/24.1/30.4 mg/L, respectively but when mixed together, the final NPK concentration only reduced to 21.1/23.3/29.4 mg/L. This suggests that blended fertilizers at 1 M: 1 M ratio might not be the best strategy to reduce the final NPK concentration. In fact, a better approach would be to prepare blended fertilizers (i.e. two or more) with different NPK grade (i.e. percentage of
each nutrient in the blended solution) to target specific crop requirement. For instance, if the targeted crop is tomato which has a maximum NPK requirement of 150/50/200 mg/L then the initial NPK grade for the blended fertilizers could be 15/5/20. This approach has already shown the promising results for the FDFO desalination process when the DS was prepared by mixing four different fertilizers (i.e. NaNO$_3$, SOA, KCl and KH$_2$PO$_4$) at targeted NPK grade (Phuntsho, Shon et al., 2012b). Further studies are needed in this area and should focus on finding the optimum blended fertilizers solution according to the type of crops and feed waters. This will significantly help in achieving the required final NPK concentration for direct agriculture application and thus potentially eliminate the need for further post-treatment or additional dilution.

3.4 Long-term experiments – Maximum water recovery, fouling behaviour and final NPK concentration

Based on the results obtained in section 3.2, SOA, MAP and KH$_2$PO$_4$ were selected for longer-term operation (i.e. 4 days) due to their high RSFS combined with low nutrient loss by reverse diffusion. Besides, because of their low RSF, these three fertilizers present a relatively low inhibition impact on anaerobic activity (i.e. biogas production) due to lower salt accumulation inside the bioreactor (Chen, Cheng et al., 2008; Chen, Ortiz et al., 2014).

The performance of the selected fertilizers, in terms of water flux, water recovery rate and water flux recovery after hydraulic cleaning is presented in Table 6. Among the three selected fertilizers, SOA showed the best performance in terms of initial water flux (i.e. 17.2 LMH) and final recovery rate (i.e. 76.2%). In fact, it was already demonstrated in the previous FDFO studies (Phuntsho, Shon et al., 2011; Phuntsho, Hong et al., 2013) that SOA generates one of the highest water flux combined with a relatively low RSF and was therefore employed in pilot-scale investigations of the FDFO process (Kim, Phuntsho et al., 2013; Kim, Phuntsho et al., 2015). In terms of fouling behaviour, all three fertilizers showed severe flux decline (i.e. about 70%) along the 4-day operation. However, since flux decline was fairly similar among all three tested fertilizers, this suggests that it might most likely be related to the continuous osmotic dilution of the DS resulting in the reduction of the osmotic pressure difference across the membrane (i.e. the driving force of the FO process) rather than the intrinsic properties of the DS. Nevertheless, since membrane fouling is a rather complex
phenomenon, it is very likely that flux decline was also associated with foulant-membrane interactions, CP effects and reverse diffusion of the draw solutes (She, Wang et al., 2016). For instance, both MAP and KH₂PO₄ exhibited low flux decline (i.e. less than 20%) during short-term experiments (Table 3). However, after 4-day operation, results in Table 6 showed severe flux decline for both fertilizers. This is most likely related to the osmotic concentration of the feed water combined with the back-diffusion of PO₄ which can cause membrane scaling on the feed side (i.e. formation of calcium phosphate) resulting in much severe flux decline (Greenberg, Hasson et al., 2005; Phuntsho, Lotfi et al., 2014). In fact, Figure 4 (i.e. SEM images of membrane surface) and Table 7 (i.e. EDX results) showed higher scaling for both MAP and KH₂PO₄ after long-term operation and EDX results revealed a higher concentration of phosphate on the active layer of the membrane during long-term operation.

**Table 6**

**Figure 4**

**Table 7**

After the 4-day experiments, physical cleaning (i.e. membrane surface flushing by enhancing the shear force – triple cross flow – along the membrane surface) was performed to remove the deposited foulants. In fact, this method has already been proved to be very effective against membrane fouling in the FO process (Mi and Elimelech, 2010; Arkhangelsky, Wicaksana et al., 2012). However, results in Table 6 and Figure S4 (i.e. pictures of membrane surface after physical cleaning) show a partial membrane cleaning and water flux recovery varying from 47.0% for MAP to 75.1% for KH₂PO₄. This result clearly indicates that internal fouling within the support layer (i.e. due to ICP effects) occurred during the operation since the membrane surface flushing was not effective in restoring the original water flux (Arkhangelsky, Wicaksana et al., 2012). Besides, the extent of internal fouling varied among the fertilizers with MAP having the lowest water flux recovery (i.e. 47.0%) and thus had potentially the highest internal fouling which can be likely related to its molecular weight, being the lowest among the three tested fertilizers. In order to mitigate internal fouling, many researchers have suggested the use of osmotic backwashing to remove the foulants blocked within the support layer (Boo, Elimelech et al., 2013; Valladares Linares, Li et al., 2013; Yip and Elimelech, 2013). This membrane cleaning technique can thus be adopted in the present FDFO process as a more efficient way to reduce fouling during continuous operation.
The final NPK concentration after four days operation is shown in Figure 5a. Compared to the results obtained in section 3.2.2. (i.e. short-term operation), there is a slight reduction in the final nutrient concentrations of about 20-25% depending on the nutrient and the fertilizer DS. This reduction was found higher with SOA (i.e. 27% reduction for N compared to 22% for MAP) since it achieved the highest initial water flux and final water recovery. However, for all three fertilizers, the final nutrient concentrations were still not suitable for hydroponics and yet required substantial dilution (i.e. about 100 times if targeting tomato crops) before application.

Figure 5b shows the estimated final NPK concentrations if the process is operated until the bulk osmotic equilibrium between the fertilizer DS and wastewater FS is reached (i.e. when the osmotic pressure of the fertilizer DS equals that of the wastewater FS (0.149 atm) as described in Phuntsho et al. (2012b). Osmotic pressure of the different fertilizer DS as a function of molar concentrations was predicted using OLI Stream Analyser 3.1 (OLI Inc, USA) at 25°C and data are displayed in the Supporting Information (Figure S5). Results indicate that, at the point of osmotic equilibrium, the final nutrient concentrations are considerably reduced, even below the standard requirements for both N and K nutrients (i.e. if considering tomato as the targeted crop). This clearly emphasizes the benefit of using a low-salinity feed water such as municipal wastewater in the FDFO process to meet the nutrient standard requirements for hydroponics. However, for both MAP and KH₂PO₄, the final P nutrient concentration still exceeded the acceptable threshold (i.e. 50 mg/L), suggesting that further dilution or post-treatment may be required. Besides, as discussed previously by Phuntsho et al. (2012b), operating the FDFO process until the osmotic equilibrium might not be an economically viable solution considering the significant reduction in water flux due to the continuous osmotic dilution of the fertilizer DS.

Figure 5

4 Conclusions

This study investigated the potential of the FDFO process to achieve simultaneous water reuse from wastewater and sustainable agriculture application. Results showed that 95% was the optimum water recovery to achieve in the FDFO process for further AnMBR treatment. The performance of different fertilizers (i.e. single and blended) as DS was assessed in terms
of water flux, reverse salt flux, water recovery and final nutrient concentration. While KCl and NH$_4$Cl showed the highest water flux and water recovery, MAP, KH$_2$PO$_4$ and SOA demonstrated the lowest RSF and thus loss of nutrient through back diffusion. The use of wastewater effluent instead of brackish or seawater as FS in the FDFO process proved to be beneficial in terms of reducing the final nutrient concentration. In fact, the water fluxes obtained with wastewater as FS was substantially higher than those obtained with high salinity FS (i.e. up to 80% higher). Increasing the DS concentration or blending fertilizers at equal ratio (i.e. 1 M: 1 M) did not provide significant improvement in terms of water flux and final NPK concentration. Finally, although high recovery rate can be achieved during long-term operations (i.e. up to 76.2% for SOA after 4-day operation), the final diluted DS still required substantial dilution (i.e. up to 100 times depending on the targeted crop) before meeting the nutrient standard requirements for hydroponics.

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References:


Evaluation of fertilizer-drawn forward osmosis for sustainable agriculture and water reuse in arid regions

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ABSTRACT

Recently, increased attention has been received on the concept of fertiliser-drawn forward osmosis (FDFO) process. In this process, the fertilizer draw solution is continuously diluted and can then be directly used for fertigation as it contains the essential nutrients for plant growth. The relatively low salinity of most wastewaters makes them good candidates for such dilution purposes. The concentrated wastewater from the FO process can then be sent to an anaerobic membrane bioreactor (AnMBR) for further treatment and biogas production. The present study focused on the performance of the FDFO process to achieve simultaneous water reuse from wastewater and production of nutrient solution for hydroponic application. Bio-methane potential (BMP) measurements were firstly carried out to determine the effect of osmotic concentration of wastewater achieved in the FDFO process on the anaerobic activity. Results showed that 95% water recovery from the FDFO process is the optimum value for further AnMBR treatment. Nine different fertilizers were then tested based on their FO performance (i.e. water flux, water recovery and reverse salt flux) and final nutrient concentration. From this initial screening, ammonium phosphate monobasic (MAP), ammonium sulfate (SOA) and mono-potassium phosphate were selected for long term experiments to investigate the maximum water recovery achievable. After the experiments, hydraulic membrane cleaning was performed to assess the water flux recovery. SOA showed the highest water recovery rate, up to 76% while KH₂PO₄ showed the highest water flux recovery, up to 75% and finally MAP showed the lowest final
nutrient concentration. However, substantial dilution was still necessary to comply with the standards for fertigation even if the recovery rate was increased.

**Keywords:** Forward osmosis, fertilizer draw solution, hydroponic, nutrient, water reuse.
1 Introduction

Freshwater resources are getting scarcer, particularly in arid, semi-arid and coastal areas, while agricultural sector consumes about 70% of the accessible freshwater with about 15-35% of water being used unsustainably (Assessment, 2005; Clay, 2013). In arid regions, the development of agriculture is not only hindered by the limited freshwater resources but also by the scarcity of fertile lands. Hydroponics is a subset of hydroculture with several advantages over conventional soil culture. In fact, it is a soilless process using synthetic mineral solution to grow crops (Jensen, 1997). As such, it eliminates the problems associated with soil culture; i.e. poor soil culture, poor drainage, soil pollution and soil-borne pathogens. Therefore, hydroponics has been widely used in commercial greenhouse vegetable production around the world. However, hydroponics requires a nutrient solution to fertilize the plants under a controlled environment (e.g., concentration, flow rate, temperature). As a result, this process also consumes a large amount of fresh water to prepare the fertilizer solution. This water-food nexus is becoming a critical issue in most arid regions and therefore, sustainable solutions to assure water and food security must be explored.

Recently, increased consideration has been given to the concept of fertilizer drawn forward osmosis (FDFO) process. In fact, the novelty of the concept relies on the low-energy osmotic dilution of the fertilizer draw solution (DS) which can then be applied directly for irrigation since it contains the essential nutrients required for plant growth. Although early studies on FDFO (Phuntsho, Shon et al., 2011; Phuntsho, Shon et al., 2012a) demonstrated that most fertilizers can be suitable DS, the limit posed by the osmotic equilibrium between the feed and the draw solutions will dictate the final nutrient concentration, which, in most cases, was found to exceed the standards for irrigation. This means that the final DS still requires additional dilution which is not acceptable, especially in the context of freshwater scarcity. To circumvent this issue, nanofiltration (NF) was proposed as pre or post-treatment for FDFO with the aim of reducing the nutrient concentration in the final product water (Phuntsho, Hong et al., 2013). Results from this study showed that the product water was suitable for direct application when NF was used as post-treatment and when brackish water with low TDS (i.e. < 4000 mg/L) was employed as feed solution (FS). However, the use of an additional process will increase the energy consumption of the system and thus the final cost of produced water especially because NF is a pressure-driven membrane process. Recently,
pressure-assisted forward osmosis (PAFO) was tested as an alternative solution to eliminate the need for NF post-treatment (Sahebi, Phuntsho et al., 2015). The PAFO process used an additional hydraulic driving force to simultaneously enhance the water flux and dilute the draw solution DS beyond the point of osmotic equilibrium. In this study, it was concluded that the use of PAFO instead of NF can further dilute the fertilizer draw solution DS, thereby producing permeate water that meets the acceptable nutrient concentrations for direct fertigation.

To date, all the FDFO studies have either used brackish water (Phuntsho, Hong et al., 2013; Phuntsho, Lotfi et al., 2014; Raval and Koradiya, 2016), treated coalmine water with a TDS of about 2.5 g/L (Phuntsho, Kim et al., 2016), or seawater (Phuntsho, Shon et al., 2011; Phuntsho, Shon et al., 2012a; Phuntsho, Shon et al., 2012b; Phuntsho, Sahebi et al., 2013) have been employed as the feed solution FS. However, the relatively low salinity of most impaired waters makes them potentially suitable candidate for such dilution (Lew, Hu et al., 2005). Besides, drawing the water from impaired sources to produce nutrient solution for hydroponic culture seems a very promising and sustainable approach to solve the freshwater scarcity issue in most arid regions. This concept can be further extended if the concentrated impaired water from the FDFO process is sent to an anaerobic membrane bioreactor (AnMBR) for additional treatment and biogas production to supply energy to the hybrid process.

The main objective of this study is therefore to evaluate the potential of FDFO process for simultaneous water reuse and sustainable agriculture. The optimum recovery rate for feeding the AnMBR process will be first determined through bio-methane potential measurements. Then, bench-scale FO experiments will be carried out to optimize the fertilizer formula and process configuration in order to simultaneously achieve the optimum recovery rate and favourable nutrient supply for hydroponics.

2 Materials and Methods

2.1 FO membrane and draw solutions

The FO membrane used in this study was a commercial thin film composite (TFC) polyamide (PA) FO membrane (Toray Industry Inc.).
All chemical fertilizers used in this study were reagent grade (Sigma Aldrich, Australia). Draw solutions were prepared by dissolving fertilizer chemicals in deionized (DI) water. Detail information of fertilizer chemicals are provided in Table 1. Osmotic pressure and diffusivity were obtained by OLI Stream Analyzer 3.1 (OLI System Inc., Morris Plains, NJ, USA).

Table 1

2.2 Bio-methane potential experiments

The bio-methane potential (BMP) experiment was carried out using the BMP apparatus described in our previous study (Kim, Chekli et al., 2016) to investigate the effect of water recovery in the FO process on the performance of the post-AnMBR process. The BMP apparatus consisted of 6 fermentation bottles submerged in a water bath connected to a temperature control device to maintain a temperature of 35±1 ºC. These bottles were connected to an array of inverted 1,000 mL plastic mass cylinders submerged in the water bath filled with 1 M NaOH solution to collect and measure the biogas. The NaOH solution plays an important role to sequester both CO₂ and H₂S to evaluate only CH₄ production potential. Air volume in each mass cylinder was recorded twice a day. Detailed description of BMP apparatus used in this study is given elsewhere (Nghiem, Nguyen et al., 2014; Ansari, Hai et al., 2015).

Six different recovery rates were tested in this study (i.e. 0%, 20%, 40%, 60%, 80% and 95%) and the concentrated synthetic wastewater was prepared accordingly. 50 mL of each solution was then mixed with 700 mL of digested sludge. All bottles were purged with nitrogen gas, and connected to the biogas collecting equipment. The BMP experiment was carried out until the methane production stopped.

2.3 Bench-scale FO system

The performance of the FO process was conducted in a closed-loop bench-scale FO system (Figure S1, Supporting Information) in which detailed characteristics can be found elsewhere (Lee, Boo et al., 2010; Kim, Lee et al., 2015). This lab-scale FO unit has an effective membrane area of 20.02 cm² with a channel dimension of 77 mm long, 26 mm wide, and 3 mm deep. The FO cell had two symmetric channels on both sides of the membrane for co-
current flows of feed and draw solutions. Variable speed gear pumps (Cole-Parmer, USA) were used to pump the liquid in a closed loop. The draw solution DS tank was placed on a digital scale and the weight changes were measured by a computer in real time to determine water flux. Conductivity and pH meters (HaCH, Germany) were connected to a computer to monitor the reverse salt flux (RSF) of draw solutes in the feed FS tank.

FO experiments were conducted in the FO mode where the active layer is facing the feed solution FS. Before each performance experiment, the FO membrane was stabilized for 30 minutes with DI water as feed solution FS and fertilizer solution as draw solution DS. Once stabilized, the water flux was measured continuously throughout the experiment with a 3 minutes time interval. All experiments were conducted at a cross-flow velocity of 8.5 cm/s, and a constant temperature of 25 ºC.

2.3.1 Short-term FO performance experiments – Initial Screening

The performance of each fertilizer (Table 1) as DS was assessed with either DI water (for RSF experiments) or with synthetic wastewater simulating municipal wastewater (Table 2) as feed FS. In all experiments, a concentration of 1M was used for each fertilizer DS, unless otherwise stated. For the RSF experiment, the feed solution FS was collected after 2 hours operation and RSF was determined by analysing the components of each tested DS. The experiments, using synthetic wastewater as feed solution FS, were carried out for one day (i.e. 24 hours) during which the water flux was measured continuously (i.e. one measurement every three minutes). At the end of the experiments, the final recovery rate and nutrient(s) concentration were calculated. The water flux, RSF, recovery rate and final nutrient composition were used to determine the optimum fertilizers to carry out long-term experiments (i.e. four days). The effect of DS concentration was also investigated by running experiments at 2M fertilizer DS concentration. Finally, this study also evaluate the performance of selected blended fertilizers (based on (Phuntsho, Shon et al., 2012b)) at 1M:1M ratio.

Table 2

2.3.2 Long term FO performance experiments

Long-term experiments were carried out with the optimum DS selected during the first stage
screening and synthetic wastewater as feed FS. These experiments were run for four days during which the water flux was monitored continuously. At the end of the experiment, the final recovery rate and nutrients concentration were calculated.

A new FO membrane was used for each experiment, and the initial baseline flux of the virgin membrane was obtained using 1M NaCl as DS and DI water as FS under the operating conditions described earlier (i.e. cross-flow velocity of 8.5 cm/s, and a constant temperature of 25 °C). At the end of the long-term experiments, physical membrane cleaning was performed to evaluate the water flux recovery. The DS and FS were replaced with DI water, and the FO process was operated at triple cross-flow rate (i.e. 1,200 mL/min) for 15 minutes. Following this physical cleaning, the flux recovery was assessed by measuring the flux under the same conditions as the baseline experiment (i.e. 1M NaCl as DS and DI water as FS). The percentage ratio of the recovered flux after cleaning to initial virgin baseline flux (normalised) was assessed as the water flux recovery.

3 Results and Discussion

3.1 Bio-methane potential measurements

Bio-methane potential (BMP) measurements were carried out for 11 days to determine the effect of water recovery/osmotic concentration of wastewater in the FDFO process on the anaerobic biological process. Figure 1a shows the influence of water recovery achieved in the FDFO process on biogas production by activated sludge. It is clear from these results that biogas production increased with increasing recovery rate. In fact, 95% water recovery showed the highest cumulative biogas production, almost three times higher than the results obtained with 80% water recovery. It has been demonstrated previously that municipal wastewater usually needs to be concentrated five to ten times before reaching an acceptable level, in terms of chemical oxygen demand (COD), for subsequent anaerobic treatment and energy recovery via biogas production (Verstraete and Vlaeminck, 2011; Burn, Muster et al., 2014). Results in Figure 1b confirmed that there is a strong (i.e. $R^2 = 0.9953$) linear correlation between the final volume of biogas produced and the COD in wastewater. For example, from 0% water recovery to 20% recovery, the increase in COD value is not very significant (i.e. from 390 mg/L to 487.5 mg/L) which explains the very low biogas...
production for these two samples. However, from 0% water recovery to 40% water recovery, the COD in the concentrated wastewater increases by 1.7 times and similarly the final volume of biogas produced increases by 1.8 times. Therefore the COD contribution is crucial to promote a fast and adequate rate of methane production as it was already demonstrated in previous research (Grobicki and Stuckey, 1989; Ansari, Hai et al., 2015). For these reasons, 95% was chosen as the optimum recovery rate to achieve for the wastewater via osmotic concentration in the FDFO process.

Figure 1

3.2 Performance of single fertilizers as draw solution

3.2.1 Water flux, water recovery and reverse salt flux

The performance of single fertilizers was initially evaluated in terms of water flux, water recovery and reverse salt flux; three essential criteria for agriculture and water reuse applications. In fact, a high water flux is desirable for the economic viability of the process (e.g. since it will affect the total membrane area and thus the capital cost). Then, a high water recovery/wastewater concentration (i.e. target of 95% as discussed in the previous section) will ensure optimum biogas production in the subsequent AnMBR process and also help in achieving the required final nutrient concentration in the diluted DS. Finally, a low reverse salt flux is preferable since the accumulation of DS in the feed water due to its reverse movement can have detrimental effect on the anaerobic microbial activity in the post-AnMBR process (Ansari, Hai et al., 2015). Based on those criteria and previous studies on the FDFO process (Phuntsho, Shon et al., 2011; Phuntsho, Shon et al., 2012b), nine different fertilizers were selected for this study. The thermodynamic properties of the selected DS are gathered in Table 1 and were determined using OLI Stream Analyzer 3.2 (OLI System Inc., Morris Plains, NJ, USA). Diammonium phosphate (DAP) showed the highest osmotic pressure (i.e. 50.6 atm) followed by Ca(NO\(_3\))\(_2\) and ammonium sulphate (SOA) while NH\(_4\)Cl has the highest diffusivity (1.85 \times 10^{-9} m^2/s) followed by KCl and KNO\(_3\). The performance tests were carried out for one day (i.e. 24 hours) using synthetic wastewater (cf. Table 2) or DI water as feed solution under similar operating conditions at 1M DS concentration and the results are gathered in Table 3.
Similarly to earlier studies on the FDFO process (Phuntsho, Shon et al., 2011; Phuntsho, Shon et al., 2012b), KCl showed the highest initial water flux (i.e. 21.1 LMH) together with NH₄Cl and followed by KNO₃ while KH₂PO₄ and DAP had the lowest among the different tested fertilizers (i.e. 13.2 LMH and 13.3 LMH respectively). Theoretically, since the osmotic pressure difference across the membrane is the main driving force in the FO process, the water flux trend among the fertilizers should follow the same trend as the osmotic pressure. However, results in both Table 1 and Table 3 show that there is no direct correlation between the osmotic pressure of the DS and the water flux. For instance, while DAP generated the highest osmotic pressure, this fertilizer showed one of the lowest water flux. This is due to the concentration polarization (CP) effects and more importantly to the extent of internal CP (ICP) effects induced by the solute resistance (K) inside the membrane support layer facing the DS (McCutcheon, McGinnis et al., 2006; McCutcheon and Elimelech, 2007). The solute resistance is, in fact, a function of the diffusivity of the solute and thus, a DS having a high diffusivity will have a low K value and therefore generate a high water flux. This is confirmed by the results obtained in this study as data showed a fairly good correlation (i.e. \( R^2 = 0.8077 \)) between the water flux generated by a DS and its diffusivity (Figure S2, Supporting Information). The recovery rate after 1-day operation shows similar trend to the initial water flux (i.e. linear correlation, \( R^2 = 0.8397 \), Figure S3, Supporting Information) with NH₄Cl and KCl having the highest water recovery (i.e. 42.2% and 38.6% respectively). Comparing the results with the FDFO desalination studies using either seawater or brackish water as feedFS, the water flux obtained in this study (i.e. using synthetic wastewater as feedFS) is much higher, up to 80% (Table S1). In fact, the osmotic pressure of the synthetic wastewater used in this study (i.e. 0.149 atm) is considerably lower than, for instance, the brackish water used in Phuntsho, Shon et al. (2012b) (i.e. 3.9 atm) and therefore the initial difference in osmotic pressure across the membrane (i.e. which is the driving force of the FO process) is significantly higher, resulting in a higher initial water flux. This suggests that, if available, low-strength wastewater might be a more suitable feed solutionFS for the FDFO process when targeting high water flux and water recovery. However, it has to be noted that a different membrane has been employed in this study (i.e. Toray TFC PA membrane instead...
of HTI CTA membrane) so the increase in water flux might also be partially related to the better performance of this novel membrane.

After one day of operation, both KNO₃ and KCl showed the highest flux decline (i.e. 55.4% and 49.2%, respectively) while the water flux generated by DAP, mono-ammonium phosphate (MAP) and KH₂PO₄ only decreased by less than 20%. This trend can be explained by the fact that an initial higher water flux level can generally be coupled with elevated rate of reverse salt flux (RSF) resulting in more severe fouling (Hancock and Cath, 2009; Phillip, Yong et al., 2010; Tang, She et al., 2010). Besides, both KCl and KNO₃ have ionic species with small hydrated diameter (i.e. K⁺, Cl⁻ and NO₃⁻) which will therefore readily diffuse through the membrane compared to fertilizers having larger-sized hydrated anions (i.e. SO₄²⁻ and PO₄³⁻) regardless of the paired cations (Achilli, Cath et al., 2010). It is well established that a greater rate of RSF will significantly affect the feed water chemistry which may cause more severe fouling (She, Wang et al., 2016).

Specific reverse salt flux selectivity ($\text{SRSF} = \frac{J_s}{J_w}$), which represents the ratio of the forward water flux ($J_w$) to the RSF ($J_s$), was also calculated and results are displayed in Table 3. This ratio is very useful to estimate how much salts from the DS are lost through RSF during the FO process operation. It is usually preferable to have a DS with a high SRSF in terms of replenishment cost but also for sustainable FO operation (Achilli, Cath et al., 2010). Table 3 shows that MAP, SOA and KH₂PO₄ exhibited the highest SRSF suggesting that all three DS can produce the highest volume of permeate per gram of lost draw salts. This is very crucial in our study since the target is to produce a highly diluted DS for possible direct hydroponic application while concentrating the wastewater with minimum reverse diffusion from the DS to minimize the impact on the microbial activity in the subsequent AnMBR process. Because for hydroponics, one of the most important parameters to evaluate is the final nutrient concentration, the RSF in the FDFO process has also been evaluated in terms of loss of essential nutrients (i.e. N, P and K) per unit volume of water extracted from the feed FS as described in Phuntsho, Shon et al., (2012b). Results in Table 3 showed that KNO₃, KCl and NH₄NO₃ had the highest loss of nutrient which correlates with the RSF data for these three fertilizers. SOA, MAP and KH₂PO₄ exhibited the lowest loss of nutrient by reverse diffusion for N, P and K, respectively. In fact, these fertilizers have divalent ions (i.e. SO₄²⁻, PO₄³⁻).
PO₄³⁻) which display significantly lower loss through RSF due to their larger hydrated ions.

3.2.2 Final nutrient concentration after 1-day operation

Figure 2 presents the final nutrient (i.e. N, P and K) concentrations in the final diluted DS after 1-day operation for all nine tested fertilizers. Based on earlier FDFO studies (Phuntsho, Shon et al., 2012b), the final NPK concentration is highly dependent on the feed water (i.e. seawater, brackish water, wastewater) as well as the percentage of a particular nutrient in the DS and the final recovery rate. In fact, by comparing MAP and DAP fertilizers, which have the same counter ion (i.e. PO₄³⁻) but a different percentage of N (i.e. 12.2% and 21.2 %, respectively), the final diluted DS contained 10.8 and 21.5 g/L of N, respectively. The lowest nutrient concentration for N was observed for NH₄Cl (i.e. 9.8 g/L) which generated one of the highest water flux and recovery rate (Table 3). All DS containing either P or K resulted in similar final concentration in the diluted DS after 1-day and this concentration remained fairly high (i.e. about 24 g/L for P and 30 g/L for K).

Figure 2

However, the results presented in Figure 2 indicate that the final nutrient concentration after 1-day operation remains significantly higher than the standards for hydroponics. In fact, depending on the crop types and growth stages, the required nutrient concentration varies significantly with a maximum recommended concentration of 200 mg/L for N, 50 mg/L for P and 300 mg/L for K (Resh, 2012). Taking tomatoes as an example, the nutritional requirement for hydroponics varies from 70-150 mg/L for N, 50 mg/L for P (i.e. no variation during the different growth periods) and 120-200 mg/L for K (Hochmuth and Hochmuth, 2001). It is clear from these data that the results obtained in Figure 2 after 1-day operation are significantly higher than the standards for hydroponics suggesting that the final DS still requires a substantial dilution before being applied to hydroponic crops. Additional post-treatment (e.g. nanofiltration) or alternative process configuration (e.g. use of blended fertilizers or pressure-assisted osmosis) might help in obtaining the desired nutrient concentration as demonstrated in previous FO studies (Tan and Ng, 2010; Phuntsho, Shon et al., 2012b; Zhao, Zou et al., 2012; Phuntsho, Hong et al., 2013; Sahebi, Phuntsho et al., 2015).
3.2.3 Effect of fertilizer draw solution concentration

Short-term experiments were also carried out at 2.0 M DS concentration since higher water flux has been generally observed at higher fertiliser concentrations. Results for this study are presented in Table 4 (i.e. water flux and recovery rate) and Figure 3 (i.e. final NPK concentrations). With the exception of $\text{KH}_2\text{PO}_4$ which has a maximum solubility of 1.8 M, all fertilizer DS generated a higher water flux at 2.0 M concentration (Table 4). However, the improvement ratio (i.e. percentage increase in water flux from 1.0 M to 2.0 M concentration) is different among the tested fertilizers. In fact, previous studies have already shown that DS concentration influences the FO process performance (Seppälä and Lampinen, 2004; McCutcheon, McGinnis et al., 2006; Achilli, Cath et al., 2009; Choi, Choi et al., 2009; Hancock and Cath, 2009; Xu, Peng et al., 2010). It was demonstrated that the relationship between DS concentration and water flux is not linear and different among the DS types, especially at high DS concentration where the relation has been found logarithmic. This has been attributed to ICP effects in the membrane support layer which become more important at higher permeate flux resulting in less effective water flux improvement (Tan and Ng, 2010). The lower improvement ratio for MAP and DAP (i.e. less than 5%) suggests that the percentage of the bulk osmotic pressure effectively available did not improve significantly when increasing the solute concentration (Phuntsho, Hong et al., 2013).

Table 4
The recovery rate after 1-day operation also increased with the increase in DS concentration, with the exception of $\text{NH}_4\text{Cl}$ and MAP. However, the improvement ratio (i.e. percentage increase) in comparison with the results obtained with 1.0 M DS concentration is quite heterogeneous among the tested fertilizers. In fact, it has been previously demonstrated that, although the increase in DS concentration can increase the initial water flux, it can also exacerbate membrane fouling due to the greater hydraulic drag force promoting more foulant deposition on the membrane (Mi and Elimelech, 2008; Zou, Gu et al., 2011; She, Jin et al., 2012) as well as an increase in the solute reverse diffusion from the DS (Hancock and Cath, 2009; Phillip, Yong et al., 2010). Besides, it is evident that the membrane fouling behaviour and especially the foulant-membrane interactions, are closely dependent on the type of DS (i.e. diffusivity, solubility, molecular weight, soluble species, etc.) and therefore, different fertilizer DS will have different impacts on membrane fouling resulting in different water flux
trends (i.e. and thus final recovery rate) which explains the results obtained in Table 4.

The final nutrient (i.e. NPK) concentrations for all DS (i.e. except KH$_2$PO$_4$) are shown in Figure 3. Considering the negligible improvement in terms of water flux and more importantly in terms of recovery rate, it is not surprising that the final NPK concentrations, using 2.0 M initial DS concentration, are almost twice for the values obtained with 1.0 M DS concentration. This result suggests that increasing the initial DS concentration might not be the best approach to achieve lower nutrient concentration in the final diluted DS.

### 3.3 Performance of blended fertilizers as draw solution

A previous FDFO study (Phuntsho, Shon et al., 2012b) demonstrated that blending two or more fertilizers as DS can help in reducing the final nutrient (i.e. NPK) concentration compared to the use of single fertilizer. Based on this finding, four different combinations of two fertilizers (i.e. at 1 M: 1 M ratio) were selected since they already exhibited good performance among all the blended solutions tested. Results, in terms of water flux, recovery rate and final NPK concentration are gathered in Table 5.

Similarly to the previous FDFO study on blended fertilizers, all four blended solutions generated a higher water flux than the individual fertilizers but it was still lower than the sum of the water fluxes obtained with the two single fertilizers. This was previously explained as a result of complex interactions occurring between the ions and counterions of the two fertilizers leading to a decreased number of formed species in the final solution (Phuntsho, Shon et al., 2012b). The coexistence of two different species in the same solution was also found to affect the diffusivity of a specific compound which will indirectly affect the internal CP (ICP) effects and thus the water flux in the FO process (Gray, McCutcheon et al., 2006; McCutcheon and Elimelech, 2006; Tan and Ng, 2008; Tang, She et al., 2010).

### Table 5

The highest water flux and recovery rate were generated by the NH$_4$NO$_3$ + NH$_4$Cl blend while NH$_4$NO$_3$ combined with KH$_2$PO$_4$ produced the lowest water flux and recovery rate. In most cases, the final NPK concentration was slightly lower than with single fertilizers but the difference was not significant, especially when considering the increase in cost when using an
additional fertilizer. For instance, when NH$_4$NO$_3$ and KH$_2$PO$_4$ were used individually, the final NPK concentration in the final diluted DS was 21.1/0/0 mg/L and 0/24.1/30.4 mg/L, respectively but when mixed together, the final NPK concentration only reduced to 21.1/23.3/29.4 mg/L. This suggests that blended fertilizers at 1 M: 1 M ratio might not be the best strategy to reduce the final NPK concentration. In fact, a better approach would be to prepare blended fertilizers (i.e. two or more) with different NPK grade (i.e. percentage of each nutrient in the blended solution) to target specific crop requirement. For instance, if the targeted crop is tomato which has a maximum NPK requirement of 150/50/200 mg/L then the initial NPK grade for the blended fertilizers could be 15/5/20. This approach has already shown the promising results for the FDFO desalination process when the DS was prepared by mixing four different fertilizers (i.e. NaNO$_3$, SOA, KCl and KH$_2$PO$_4$) at targeted NPK grade (Phuntsho, Shon et al., 2012b). Further studies are needed in this area and should focus on finding the optimum blended fertilizers solution according to the type of crops and feed waters. This will significantly help in achieving the required final NPK concentration for direct agriculture application and thus potentially eliminate the need for further post-treatment or additional dilution.

3.4 Long-term experiments – Maximum water recovery, fouling behaviour and final NPK concentration

Based on the results obtained in section 3.2, SOA, MAP and KH$_2$PO$_4$ were selected for longer-term operation (i.e. 4 days) due to their high SRSE-RSFS combined with low nutrient loss by reverse diffusion. Besides, because of their low RSF, these three fertilizers present a relatively low inhibition impact on anaerobic activity (i.e. biogas production) due to lower salt accumulation inside the bioreactor (Chen, Cheng et al., 2008; Chen, Ortiz et al., 2014).

The performance of the selected fertilizers, in terms of water flux, water recovery rate and water flux recovery after hydraulic cleaning is presented in Table 6. Among the three selected fertilizers, SOA showed the best performance in terms of initial water flux (i.e. 17.2 LMH) and final recovery rate (i.e. 76.2%). In fact, it was already demonstrated in the previous FDFO studies (Phuntsho, Shon et al., 2011; Phuntsho, Hong et al., 2013) that SOA generates one of the highest water flux combined with a relatively low RSF and was therefore employed in pilot-scale investigations of the FDFO process (Kim, Phuntsho et al., 2013;
Kim, Phuntsho et al., 2015). In terms of fouling behaviour, all three fertilizers showed severe flux decline (i.e. about 70%) along the 4-day operation. However, since flux decline was fairly similar among all three tested fertilizers, this suggests that it might most likely be related to the continuous osmotic dilution of the DS resulting in the reduction of the osmotic pressure difference across the membrane (i.e. the driving force of the FO process) rather than the intrinsic properties of the DS. Nevertheless, since membrane fouling is a rather complex phenomenon, it is very likely that flux decline was also associated with foulant-membrane interactions, CP effects and reverse diffusion of the draw solutes (She, Wang et al., 2016). For instance, both MAP and KH$_2$PO$_4$ exhibited low flux decline (i.e. less than 20%) during short-term experiments (Table 3). However, after 4-day operation, results in Table 6 showed severe flux decline for both fertilizers. This is most likely related to the osmotic concentration of the feed water combined with the back-diffusion of PO$_4$ which can cause membrane scaling on the feed side (i.e. formation of calcium phosphate) resulting in much severe flux decline (Greenberg, Hasson et al., 2005; Phuntsho, Lotfi et al., 2014). In fact, Figure 4 (i.e. SEM images of membrane surface) and Table 7 (i.e. EDX results) showed higher scaling for both MAP and KH$_2$PO$_4$ after long-term operation and EDX results revealed a higher concentration of phosphate on the active layer of the membrane during long-term operation.

Table 6

Table 7

After the 4-day experiments, physical cleaning (i.e. membrane surface flushing by enhancing the shear force – triple cross flow – along the membrane surface) was performed to remove the deposited foulants. In fact, this method has already been proved to be very effective against membrane fouling in the FO process (Mi and Elimelech, 2010; Arkhangelsky, Wicaksana et al., 2012). However, results in Table 6 and Figure S3-S4 (i.e. pictures of membrane surface after physical cleaning) show a partial membrane cleaning and water flux recovery varying from 47.0% for MAP to 75.1% for KH$_2$PO$_4$. This result clearly indicates that internal fouling within the support layer (i.e. due to ICP effects) occurred during the operation since the membrane surface flushing was not effective in restoring the original water flux (Arkhangelsky, Wicaksana et al., 2012). Besides, the extent of internal fouling varied among the fertilizers with MAP having the lowest water flux recovery (i.e. 47.0%) and thus had potentially the highest internal fouling which can be likely related to its molecular
weight, being the lowest among the three tested fertilizers. In order to mitigate internal fouling, many researchers have suggested the use of osmotic backwashing to remove the foulants blocked within the support layer (Boo, Elimelech et al., 2013; Valladares Linares, Li et al., 2013; Yip and Elimelech, 2013). This membrane cleaning technique can thus be adopted in the present FDFO process as a more efficient way to reduce fouling during continuous operation.

The final NPK concentration after four days operation is shown in Figure 5a. Compared to the results obtained in section 3.2.2. (i.e. short-term operation), there is a slight reduction in the final nutrient concentrations of about 20-25% depending on the nutrient and the fertilizer DS. This reduction was found higher with SOA (i.e. 27% reduction for N compared to 22% for MAP) since it achieved the highest initial water flux and final water recovery. However, for all three fertilizers, the final nutrient concentrations were still not suitable for hydroponics and yet required substantial dilution (i.e. about 100 times if targeting tomato crops) before application.

Figure 5b shows the estimated final NPK concentrations if the process is operated until the bulk osmotic equilibrium between the fertilizer DS and wastewater $F_S^{feed}$ is reached (i.e. when the osmotic pressure of the fertilizer DS equals that of the wastewater feed-$F_S$ (0.149 atm)) as described in Phuntsho et al. (2012b). Osmotic pressure of the different fertilizer DS as a function of molar concentrations was predicted using OLI Stream Analyser 3.1 (OLI Inc, USA) at 25°C and data are displayed in the Supporting Information (Figure S4S5). Results indicate that, at the point of osmotic equilibrium, the final nutrient concentrations are considerably reduced, even below the standard requirements for both N and K nutrients (i.e. if considering tomato as the targeted crop). This clearly emphasizes the benefit of using a low-salinity feed water such as municipal wastewater in the FDFO process to meet the nutrient standard requirements for hydroponics. However, for both MAP and KH$_2$PO$_4$, the final P nutrient concentration still exceeded the acceptable threshold (i.e. 50 mg/L), suggesting that further dilution or post-treatment may be required. Besides, as discussed previously by Phuntsho et al. (2012b), operating the FDFO process until the osmotic equilibrium might not be an economically viable solution considering the significant reduction in water flux due to the continuous osmotic dilution of the fertilizer DS.
4 Conclusions

This study investigated the potential of the FDFO process to achieve simultaneous water reuse from wastewater and sustainable agriculture application. Results showed that 95% was the optimum water recovery to achieve in the FDFO process for further AnMBR treatment. The performance of different fertilizers (i.e. single and blended) as draw solution DS was assessed in terms of water flux, reverse salt flux, water recovery and final nutrient concentration. While KCl and NH₄Cl showed the highest water flux and water recovery, MAP, KH₂PO₄ and SOA demonstrated the lowest RSF and thus loss of nutrient through back diffusion. The use of wastewater effluent instead of brackish or seawater as feed solution FS in the FDFO process proved to be beneficial in terms of reducing the final nutrient concentration. In fact, the water fluxes obtained with wastewater as feed solution FS was substantially higher than those obtained with high salinity feed solution FS (i.e. up to 80% higher). Increasing the draw solution DS concentration or blending fertilizers at equal ratio (i.e. 1 M: 1 M) did not provide significant improvement in terms of water flux and final NPK concentration. Finally, although high recovery rate can be achieved during long-term operations (i.e. up to 76.2% for SOA after 4-day operation), the final diluted draw solution DS still required substantial dilution (i.e. up to 100 times depending on the targeted crop) before meeting the nutrient standard requirements for hydroponics.

Acknowledgements

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**List of Figure captions**

**Figure 1**: (a) Influence of water recovery in the FDFO process on biogas (i.e. methane) production by activated sludge and (b) relationship between the COD in wastewater and the final volume of biogas produced.

**Figure 2**: Final NPK nutrient concentration of fertilizer solution (Initial concentration: 1M) after one day operation of the FDFO process using synthetic wastewater as feed solution.

**Figure 3**: Final NPK nutrient concentration of fertilizer solution (Initial concentration: 2M) after one day operation of the FDFO process using synthetic wastewater as feed solution.

**Figure 4**: SEM images of membrane surface (active layer) after short-term (i.e. 1 day) and long-term (i.e. 4 days) FDFO operations using KH$_2$PO$_4$ and MAP as fertilizer DS and synthetic wastewater as feed.

**Figure 5**: Final NPK nutrient concentration of fertilizer solution (Initial concentration: 1M) (a) after four days operation and (b) at the point of osmotic equilibrium of the FDFO process using synthetic wastewater as feed solution. The NPK limits were derived from [1].
References:

Figure 3

The diagram illustrates the nutrient concentration (g/L) for various compounds, including SOA, MAP, DAP, KCl, KNO₃, Ca(NO₃)₂, NH₄Cl, and NH₄NO₃, with concentrations represented in green (N), orange (P), and purple (K) bars.
List of Tables

Table 1: Properties of the fertilizer solutions used in this study. Thermodynamic properties were determined at 1 M concentration and 25 ºC by using OLI Stream Analyzer 3.2.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Formula</th>
<th>Molecular weight (g/mol)</th>
<th>Osmotic pressure (atm)</th>
<th>Diffusivity ($10^{-9}$ m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium nitrate</td>
<td>NH$_4$NO$_3$</td>
<td>80.04</td>
<td>33.7</td>
<td>1.65</td>
</tr>
<tr>
<td>Ammonium sulphate (SOA)</td>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>132.1</td>
<td>46.1</td>
<td>1.14</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>NH$_4$Cl</td>
<td>53.5</td>
<td>43.5</td>
<td>1.85</td>
</tr>
<tr>
<td>Calcium nitrate</td>
<td>Ca(NO$_3$)$_2$</td>
<td>164.1</td>
<td>48.8</td>
<td>1.01</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>74.6</td>
<td>44</td>
<td>1.79</td>
</tr>
<tr>
<td>Ammonium phosphate monobasic (MAP)</td>
<td>NH$_4$H$_2$PO$_4$</td>
<td>115.0</td>
<td>43.8</td>
<td>1.06</td>
</tr>
<tr>
<td>Ammonium phosphate dibasic (DAP)</td>
<td>(NH$_4$)$_2$HPO$_4$</td>
<td>132.1</td>
<td>50.6</td>
<td>0.912</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>KNO$_3$</td>
<td>101.1</td>
<td>37.2</td>
<td>1.78</td>
</tr>
<tr>
<td>Potassium phosphate monobasic</td>
<td>KH$_2$PO$_4$</td>
<td>136.09</td>
<td>36.5</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table 2: Composition and characteristics of the synthetic wastewater used in this study (based on [1]).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose (mg/L)</td>
<td>275</td>
</tr>
<tr>
<td>Peptone (mg/L)</td>
<td>100</td>
</tr>
<tr>
<td>Beef extract (mg/L)</td>
<td>100</td>
</tr>
<tr>
<td>Urea (mg/L)</td>
<td>10</td>
</tr>
<tr>
<td>NaHCO$_3$ (mg/L)</td>
<td>100</td>
</tr>
<tr>
<td>KH$_2$PO$_4$ (mg/L)</td>
<td>20</td>
</tr>
<tr>
<td>NH$_4$Cl (mg/L)</td>
<td>25</td>
</tr>
<tr>
<td>MgCl$_2$·6H$_2$O (mg/L)</td>
<td>10</td>
</tr>
<tr>
<td>CaCl$_2$·2H$_2$O (mg/L)</td>
<td>5</td>
</tr>
<tr>
<td>pH</td>
<td>6.58</td>
</tr>
<tr>
<td>Conductivity (mS/cm)</td>
<td>0.226</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>390</td>
</tr>
</tbody>
</table>
Table 3: Performance of single fertilizers as draw solution in the FDFO process using synthetic wastewater and DI water as feed solution

<table>
<thead>
<tr>
<th>Fertilizers</th>
<th>Osmotic pressure at 1M (bar)</th>
<th>Synthetic wastewater as feed solution</th>
<th>DI water as feed solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial flux (LMH)</td>
<td>Final flux (LMH)</td>
<td>Flux decline (%)</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>33.7</td>
<td>17.1</td>
<td>9.7</td>
</tr>
<tr>
<td>KNO₃</td>
<td>37.7</td>
<td>18.6</td>
<td>8.3</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>43.5</td>
<td>21.1</td>
<td>11.2</td>
</tr>
<tr>
<td>KCl</td>
<td>44.6</td>
<td>21.1</td>
<td>10.7</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>36.5</td>
<td>13.2</td>
<td>10.6</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>49.4</td>
<td>16.7</td>
<td>9.2</td>
</tr>
<tr>
<td>SOA</td>
<td>46.7</td>
<td>15.5</td>
<td>7.9</td>
</tr>
<tr>
<td>MAP</td>
<td>44.4</td>
<td>13.8</td>
<td>11.5</td>
</tr>
<tr>
<td>DAP</td>
<td>51.3</td>
<td>13.3</td>
<td>11.8</td>
</tr>
</tbody>
</table>

RSF: Reverse Salt Flux; RFS: Reverse Flux Selectivity. Recovery rate is the ratio between the accumulated volume of water transferred from the feed solution to the draw solution and the initial feed solution volume. Results obtained after 1-day operation.
Table 4: Effect of fertilizer draw solution concentration on water flux and recovery rate in the FDFO process using synthetic wastewater as feed solution.

<table>
<thead>
<tr>
<th>Fertilizer</th>
<th>Initial Water Flux (LMH)</th>
<th>Recovery Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1M</td>
<td>2M</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>17.1</td>
<td>22.2</td>
</tr>
<tr>
<td>KNO₃</td>
<td>18.6</td>
<td>21.2</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>21.1</td>
<td>26.6</td>
</tr>
<tr>
<td>KCl</td>
<td>21.1</td>
<td>26.4</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>13.1</td>
<td>Not measured – above max. solubility</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>16.7</td>
<td>21.1</td>
</tr>
<tr>
<td>SOA</td>
<td>15.5</td>
<td>19.5</td>
</tr>
<tr>
<td>MAP</td>
<td>13.8</td>
<td>14.1</td>
</tr>
<tr>
<td>DAP</td>
<td>13.3</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Table 5: Performance of selected blended fertilizers (1 M: 1 M ratio) as draw solution in the FDFO process using synthetic wastewater as feed solution.

<table>
<thead>
<tr>
<th>Fertilizer combinations (1M:1M)</th>
<th>Osmotic Pressure (bar)</th>
<th>Initial flux (LMH)</th>
<th>Recovery rate (%)</th>
<th>Final nutrient concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Cl : KH₂PO₄</td>
<td>80.0</td>
<td>21.5</td>
<td>38.2</td>
<td>N 10.1</td>
</tr>
<tr>
<td>MAP : KCl</td>
<td>89.0</td>
<td>22.6</td>
<td>38.0</td>
<td>N 10.1</td>
</tr>
<tr>
<td>NH₄NO₃ : KH₂PO₄</td>
<td>70.2</td>
<td>19.2</td>
<td>33.0</td>
<td>N 21.1</td>
</tr>
<tr>
<td>NH₄NO₃ : NH₄Cl</td>
<td>77.2</td>
<td>26.1</td>
<td>38.2</td>
<td>N 30.4</td>
</tr>
</tbody>
</table>

Table 6: Performance of selected single draw solution in the FDFO process during long-term (i.e. 4 days) operations.

<table>
<thead>
<tr>
<th>Fertilizers</th>
<th>Initial flux (LMH)</th>
<th>Flux decline (%) after 4 days</th>
<th>Recovery rate (%) after 4 days</th>
<th>Water flux recovery after hydraulic cleaning (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOA</td>
<td>17.2</td>
<td>68</td>
<td>76.2</td>
<td>60.5</td>
</tr>
<tr>
<td>MAP</td>
<td>13.3</td>
<td>70.7</td>
<td>66.1</td>
<td>47.0</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>12.6</td>
<td>71.4</td>
<td>66.8</td>
<td>75.1</td>
</tr>
</tbody>
</table>

Table 7: EDX results of membrane surface (active layer) after short-term (i.e. 1 day) and long-term (i.e. 4 days) FDFO operations using KH₂PO₄ and MAP as fertilizer DS and synthetic wastewater as feed.

<table>
<thead>
<tr>
<th>Atomic %</th>
<th>C</th>
<th>O</th>
<th>P</th>
<th>K</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>KH₂PO₄ – 1 day</td>
<td>57.55</td>
<td>38.7</td>
<td>2.61</td>
<td>1.14</td>
<td>N/D</td>
</tr>
<tr>
<td>KH₂PO₄ – 4 days</td>
<td>51.17</td>
<td>42.25</td>
<td>3.27</td>
<td>0.31</td>
<td>N/D</td>
</tr>
<tr>
<td>MAP – 1 day</td>
<td>44.56</td>
<td>34.97</td>
<td>2.37</td>
<td>1.14</td>
<td>16.95</td>
</tr>
<tr>
<td>MAP – 4 days</td>
<td>36.95</td>
<td>35.55</td>
<td>7.12</td>
<td>5.69</td>
<td>14.68</td>
</tr>
</tbody>
</table>
References:

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