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**Selection of suitable fertilizer draw solute for a novel fertilizer-drawn forward
osmosis-anaerobic membrane bioreactor hybrid system**

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Abstract

In this study, a protocol for selecting suitable fertilizer draw solute for anaerobic fertilizer-drawn forward osmosis membrane bioreactor (AnFDFOMBR) was proposed. Among eleven commercial fertilizer candidates, six fertilizers were screened further for their FO performance tests and evaluated in terms of water flux and reverse salt flux. Using selected fertilizers, bio-methane potential experiments were conducted to examine the effect of fertilizers on anaerobic activity due to reverse diffusion. Mono-ammonium phosphate (MAP) showed the highest biogas production while other fertilizers exhibited an inhibition effect on anaerobic activity with solute accumulation. Salt accumulation in the bioreactor was also simulated using mass balance simulation models. Results showed that ammonium sulphate and MAP were the most appropriate for AnFDFOMBR since they demonstrated less salt accumulation, relatively higher water flux, and higher dilution capacity of draw solution. Given toxicity of sulphate to anaerobic microorganisms, MAP appears to be the most suitable draw solution for AnFDFOMBR.

Keywords: Fertilizer-drawn forward osmosis; Anaerobic osmotic membrane bioreactor; Bio-methane potential; OMBR simulation; Draw solution selection

1. Introduction

Freshwater resources are getting scarcer due to the impacts of global warming, and rapid and extensive industrialization and urbanization (Rijsberman, 2006). Moreover, agricultural sector still consumes about 70% of the accessible freshwater with about 15-35% of water being used unsustainably (Clay, 2004). Therefore, countries such as in the Mediterranean region, which are stressed by water shortage, have considered wastewater reuse as a viable alternative water resource for agricultural purposes (Angelakis et al., 1999). Adequate treatment of wastewater before reuse as irrigation is essential not only to protect the human health from consumption and plant health but also enhance the value of the crops grown through wastewater reuse. Many researchers have studied the feasibility of wastewater reuse for irrigation by using a variety of treatment methods (Alderson et al., 2015; Ferro et al., 2015).

For wastewater reuse, however, advanced treatment processes (e.g., reverse osmosis (RO), nanofiltration (NF) or advanced oxidation) are generally required as a post-treatment process since wastewater could contain pollutants which are not removed by conventional treatment processes such as heavy metals, pharmaceuticals and trace organic contaminants (Ahluwalia & Goyal, 2007). Anaerobic membrane bioreactor (AnMBR) has been studied to treat wastewater and has several advantages including complete rejection of suspended solids, low sludge production, high organic rejection and biogas production (Stuckey, 2012). Moreover, both AnMBR and post-treatment (e.g., RO and NF) exhibit high fouling issues which ultimately increase energy requirements since these processes are driven by the hydraulic pressure as a driving force (Kim et al., 2014). To overcome these issues,

osmotic membrane bioreactor (OMBR) has been proposed by integrating AnMBR with forward osmosis (FO) instead of conventional pressurized membrane processes (Achilli et al., 2009; Chekli et al., 2016; Wang et al.). OMBR can provide high rejection of contaminants, low fouling propensity and high fouling reversibility but also has limitations that pure water should be extracted from draw solution and reversely transported draw solute can be toxic or inhibit the biological processes (Achilli et al., 2009).

Lately, fertilizer-drawn forward osmosis (FDFO) has received increased interest since the diluted draw solution can be used directly for irrigation purposes and therefore no recovery process is required (Phuntsho et al., 2011; Phuntsho et al., 2012). In FDFO, fertilizers are used as draw solution and the fertilizer solution is continuously diluted during operation (Phuntsho et al., 2011). In the early studies, only single fertilizers, which didn't provide sufficient nutrient composition for direct application, were examined. Thus, blended fertilizers were investigated for targeted crops (Phuntsho et al., 2012). However, the final nutrient concentration was still high and the final fertilizer solution required substantial dilution for direct fertigation. To solve this problem, NF was adopted as post-treatment and the produced fertilizer solution by NF could meet the water quality requirements for fertigation since it has lower rejection rates (i.e., 80-90%) than RO (Phuntsho et al., 2013). Nevertheless, high energy consumption is still an issue since NF is a pressurized desalting process and should overcome osmotic pressure of diluted fertilizer solution. Finally, pressure-assisted fertilizer-drawn forward osmosis (PAFDFO) was recently developed for enhancing final dilution of fertilizer draw solution without beyond the point of osmotic equilibrium between the draw and feed solutions (Sahebi et al., 2015).

In this study, we propose for the first time a FDFO-AnMBR hybrid system (AnFDFOMBR) for simultaneous wastewater treatment for greenhouse hydroponic application based on the concept described in Fig. S1 of the supporting information. This hybrid system consists of two parts (i.e., AnMBR and FDFO). In conventional AnMBR, microfiltration (MF) or ultrafiltration (UF) are employed to separate the treated wastewater from the anaerobic sludge. In this study, a FO membrane is used instead and submerged into the bioreactor. In addition, the FO process is here driven by fertilizers (FDFO process) and thus the treated water drawn from the wastewater is used to dilute the fertilizer solution which can then be directly used for fertigation. In this system, raw municipal wastewater will be utilized as influent and a highly concentrated fertilizer solution will be used as draw solution for the AnFDFOMBR process. The diluted fertilizer solution can then be obtained and supplied to greenhouse hydroponics irrigation.

The main objective of this study is to investigate a protocol for selecting the optimum draw solution for the novel AnFDFOMBR process. For selecting a suitable fertilizer as draw solute, FO performance was first investigated in terms of water flux and reverse salt flux (RSF). Bio-methane potential (BMP) was then measured to evaluate the potential effect of the fertilizer due to reverse diffusion on inhibiting the microbial activity in the bioreactor for methane production. Finally, salt accumulation in the AnFDFOMBR was simulated based on theoretical models derived from mass balance.

2. Materials and methods

2.1 FO membrane

The FO membrane used in this study was provided by Hydration Technology Innovations (Albany, OR, USA). This membrane is made of cellulose-based polymers with an embedded polyester mesh for mechanical strength. Detailed characteristics of this commercial membrane can be found elsewhere (Tiraferri et al., 2013).

2.2 Draw solutions

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 S1. Osmotic pressure and diffusivity were obtained by OLI Stream Analyzer 3.2 (OLI System Inc., Morris Plains, NJ, USA).

2.3 Lab-scale FO system

2.3.1 FO membrane characterization

Properties of FO membrane are commonly classified into the water permeability coefficient (A) and the salt permeability coefficient (B) of the active layer, and the structure parameter (S) of the support layer. The mathematical method (Tiraferri et al., 2013) which can simultaneously measure three parameters under the non-pressurized condition was used in this study. Experimental measurements were conducted in a lab-scale FO unit with an effective membrane area of 20.02 cm^2 . Operating temperature was 25°C and the cross-flow velocities of both the solutions were maintained at 25 cm/s . The methods to determine the A ,

B and *S* parameters (see Table S2) are described elsewhere in detail (Tiraferri et al., 2013; Yip & Elimelech, 2013).

2.3.2 FO performance experiments

FO performance experiments were carried out using a lab-scale FO system similar to the one described elsewhere (Kim et al., 2015b; Lee et al., 2015). The FO cell had two symmetric channels on both sides of the membrane each for the feed and draw solutions. Variable speed gear pumps (Cole-Parmer, USA) were used to provide crossflows under co-current directions at a crossflow rate of 8.5 cm/s and solution temperature of 25°C and the solutions were recirculated in a loop resulting in a batch mode of process operation. The draw solution tank was placed on a digital scale and the weight changes were recorded by a computer in real time to determine the water flux. Conductivity and pH meters (HACH, Germany) were connected to a computer to monitor RSF of draw solutes in the feed tank.

FO experiments were conducted in the FO mode with the active layer facing the feed solution. The fertilizer draw solution concentrations were fixed at 1 M for all the experiments. Before each performance experiment, the FO membrane was stabilized for 30 minutes with DI water as feed solution and 1 M fertilizer solution as draw solution. Once stabilized, the water flux was measured continuously throughout the experiment every 3 minutes time interval. After 1 hour of operation, the feed solution was collected and then RSF was measured by analyzing its composition.

2.4 Selection of suitable fertilizer draw solution for anaerobic fertilizer-drawn forward osmosis membrane bioreactor process

2.4.1 Determination of reverse salt concentration in a bioreactor based on a dilution factor

When considering a typical submerged AnFDFOMBR as depicted in Fig. S2, salt accumulation will take place in the bioreactor from both the influent and draw solution. This is due to wastewater continuously being fed into the bioreactor and the FO membrane rejecting almost 100% of ionic compounds and the back diffusion of the draw solution. Salt concentration will continuously increase and therefore may affect the microbial activity of the anaerobic bacteria as well as FO performances. This salt concentration in the bioreactor can be calculated through the solute mass balance with the assumption of no change of water flux and RSF during operation. In this study, no sludge discharge is also assumed since AnFDFOMBR is usually operated under high solids retention time (SRT) (Qiu & Ting, 2014), and the concept of dilution factor (DF), which is defined as a ratio of final volume to initial volume, was adopted since total permeate volume will be different for each fertilizer at a similar operation time. Thus, an equation for salt concentration induced by RSF in the bioreactor can be obtained as Eq. (1).

$$C_{R,RSF} = \frac{1}{(J_w/J_{s,RSF})} \frac{V_{D,i}}{V_R} (DF - 1) \quad (1)$$

where, $C_{R,RSF}$ is the bioreactor concentration caused by RSF, J_w and $J_{s,RSF}$ is the water flux and RSF in FO, respectively, $V_{D,i}$ is the initial volume of draw solution, V_R is the bioreactor volume, and DF is the dilution factor.

2.4.2 Bio-methane potential experiments

BMP experiments, which can be utilized to simulate the anaerobic process in batch mode to assess the bio-methane production potential from different substrates (Ansari et al., 2015), were carried out using the BMP apparatus depicted in Fig. S3 to investigate the effect of RSF on the performance of the AnFDFOMBR. The BMP apparatus consisted of 7 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 1000 mL plastic mass cylinders submerged in the water bath filled with 1 M NaOH solution to collect and measure the biogas. 1 M NaOH solution plays an important role to remove CO₂ and H₂S from biogas to evaluate only CH₄ production potential. Air volume in each mass cylinder was recorded 2 times per a day. Detailed description of BMP apparatus used in this study is given elsewhere (Ansari et al., 2015).

To determine the amount of fertilizer chemicals to be added to the digested sludge, Eq. (1) was used on the assumption that the bioreactor volume is 6 L, the initial volume of draw solution is 2 L, and draw solution is diluted 9 times (i.e., DF is 9 by the end of the experiment). The determined amount of each fertilizer salt was dissolved in 50 mL of DI water and then mixed with 700 mL of digested sludge. For the control, 700 mL of digested sludge mixed with 50 mL of DI water was prepared. All bottles were purged with nitrogen gas, and connected to the biogas collecting equipment. The substrate in each bottle was characterized in terms of total solids (TS), mixed liquor suspended solids (MLSS), pH, and chemical oxygen demand (COD). pH was measured using pH meter (Hach, Germany), and COD was determined using a COD cell test kit (Merck Millipore, Germany) following the

standard method (DIN ISO 15705). TS and MLSS were measured using standard methods (Federation & Association, 2005).

2.5 Models for salt accumulation in anaerobic fertilizer-drawn forward osmosis membrane bioreactor

2.5.1 Water flux

Many studies have reported that experimental water flux is significantly lower than the ideal water flux obtained by using bulk osmotic pressure difference (Chekli et al., 2012; McCutcheon & Elimelech, 2006). This significant difference is caused by concentration polarization when feed salt is accumulated near the active layer in the salt rejecting membrane process, which is referred to as concentrative external concentration polarization (ECP), and draw salt is diluted across the support layer, which is referred to as dilutive internal concentration polarization (ICP). McCutcheon and Elimelech (McCutcheon & Elimelech, 2006) derived the simplified equation for water flux in FO as follows, taking into account both the dilutive ICP and concentrative ECP under the FO mode of membrane orientation:

$$J_w = A[\pi_{D,b} \exp(-J_w K) - \pi_{F,b} \exp(J_w/k)] \quad (2)$$

where, A is the water permeability coefficient, K is the mass transfer resistance in the support layer, k is the mass transfer coefficient in the feed solution, and $\pi_{F,b}$ and $\pi_{D,b}$ are bulk osmotic pressures of feed and draw solutions, respectively.

In this study, we assumed the bioreactor as a completely stirred reactor tank where the mass transfer coefficient is infinite ($k \rightarrow \infty$), and thus ECP can be ignored ($\exp(J_w/k) \rightarrow 1$). Therefore, Eq. (2) can be modified as:

$$J_w = A[\pi_{D,b} \exp(-J_w K) - \pi_{F,b}] \quad (3)$$

The mass transfer resistance, K , is obtained by dividing the membrane structure parameter by the solute diffusion coefficient.

$$K = \frac{S}{D} \quad (4)$$

Reverse solute flux selectivity (RSFS) is defined as the ratio of water flux to RSF in FO as presented in Eq. (5). The RSFS is independent of membrane support layer properties and can quantitatively describe FO membrane performance.

$$\frac{J_w}{J_s} = \frac{A}{B} n R_g T \quad (5)$$

where, n is the number of species that draw solute dissociates into $n = 2$ for NaCl, and R_g is the gas constant, and T is the absolute temperature.

2.5.2 Salt accumulation

In AnMBR, microfiltration or ultrafiltration is utilized for separating water from feed solution, but both processes have low rejection rates for ionic solutes. To enhance the produced water quality, FO can be integrated with AnMBR since it has high rejection rate of all compounds including ions. At the same time however, the rejected salts can accumulate in the bioreactor. In addition, RSF from draw solution can also cause an increase of salt concentration in the bioreactor. In order to understand AnFDFOMBR, it is important to determine salt accumulation in the bioreactor as a function of time based on solute mass balance in terms of both feed and draw solutes since draw solutes may be different from feed solutes in real applications. Mass balance for water can be written as Eq. (6) since the reactor volume is constant.

$$Q_{in} = Q_{out} + J_w A_m \quad (6)$$

The mixed liquor salt concentration can be separated into two solute components: salt concentrations induced by feed solution ($C_{R,feed}$) and draw solution ($C_{R,RSF}$). Mass balance for feed solutes in AnFDFOMBR can be written in the form of Eq. (7). As shown in Fig. S2, $J_{s,feed}$ indicates the forward solute flux (FSF) through FO membrane, and this term can be neglected assuming perfect salt rejection of the FO membrane due to the hindrance effect of RSF on FSF (Kim et al., 2012; Xie et al., 2012). Thus, Eq. (7) can be modified as Eq. (8).

$$\left(\frac{\partial C_{R,feed}}{\partial t}\right) V_R = Q_{in} C_{in,feed} - J_{s,feed} A_m - Q_{out} C_{R,feed} \quad (7)$$

$$\frac{\partial C_{R,feed}}{\partial t} = \frac{(Q_{out} + J_w A_m)}{V_R} C_{in,feed} - \frac{Q_{out}}{V_R} C_{R,feed} \quad (8)$$

where, $C_{R,feed}$ is the accumulated solute concentration in the bioreactor rejected from the influent flow or feed solution by the FO membrane, $C_{in,feed}$ is the influent or feed solution solute concentration, and $J_{s,feed}$ is the FSF to draw solution.

Mass balance for draw solutes in the AnFDFOMBR can be represented using Eq. (9). In this equation, the term ($C_{in,RSF}$) can be neglected since influent does not contain any draw solute. Thus, Eq. (9) can be modified as Eq. (10) by substituting Eq. (5) into Eq. (9).

$$\left(\frac{\partial C_{R,RSF}}{\partial t}\right) V_R = Q_{in} C_{in,RSF} + J_{s,RSF} A_m - Q_{out} C_{R,RSF} \quad (9)$$

$$\frac{\partial C_{R,RSF}}{\partial t} = \frac{1}{V_R} \left(\frac{B_{RSF}}{AnR_g T} \right) J_w A_m - \frac{Q_{out}}{V_R} C_{R,RSF} \quad (10)$$

where, B_{RSF} is the salt permeability coefficient of draw solutes.

2.5.3 Draw solution dilution

To obtain the variations of water flux over time, the change in the volume and concentration of the draw solution in the draw solution tank should be determined via mass balance equations as follows.

$$\frac{\partial V_D}{\partial t} = J_w A_m \quad (11)$$

$$\frac{\partial C_D}{\partial t} = -\frac{1}{V_D} \left(\frac{B}{AnR_gT} \right) J_w A_m - \frac{C_D}{V_D} \frac{dV_D}{dt} \quad (12)$$

where, V_D is the draw solution volume and C_D is the concentrations of draw solution.

3. Results and discussion

3.1 Draw solution selection protocol for anaerobic fertilizer-drawn forward osmosis membrane bioreactor and initial screening

A flow diagram for selecting the best fertilizer as draw solute for AnFDFOMBR is illustrated in Fig. S4. A comprehensive list of fertilizer chemicals was initially screened based on solubility in water, osmotic pressure, their popularity as fertilizers, and their potential toxicity to the microorganisms in the bioreactor. For the application of draw solution, fertilizer chemicals should be highly soluble in water and also should generate higher osmotic pressure than target feed solution. In addition, the draw solution should not react with the feed solutes to form precipitates and membrane scaling during the reverse diffusion of draw solutes (Chekli et al., 2012). Based on this preliminary screening, a total of eleven different fertilizers were finally selected for further study. Their thermodynamic properties listed in Table S1 were obtained by using OLI Stream Analyzer 3.2 (OLI System Inc., Morris Plains, NJ, USA). In terms of osmotic pressure, di-ammonium phosphate (DAP) has the highest value (132.1 atm) followed by $\text{Ca}(\text{NO}_3)_2$, ammonium sulphate (SOA), mono-ammonium phosphate (MAP), and NH_4Cl . In terms of diffusivity, NH_4Cl has

the highest value ($1.85 \times 10^{-9} \text{ m}^2/\text{s}$) followed by KCl, KNO_3 , NH_4NO_3 , and NaNO_3 .

These fertilizers are commonly used for fertigation (Phuntsho et al., 2011; Phuntsho et al., 2012). We excluded volatile fertilizers such as ammonium carbonate and ammonia carbonate due to the handling problem although they have sufficient water solubility and osmotic pressure. The eleven selected fertilizers candidates were further screened by conducting FO performance experiments measured in terms of water flux and RSF, and then finally six fertilizers were chosen and further evaluated for bio-methane production (BMP) experiments and AnFDFOMBR simulation. Based on these approaches of evaluation, the most suitable fertilizers as draw solute was finally determined.

3.2 FO performance

In order to evaluate the performance of each fertilizer draw solution, FO process performance experiments were carried out using 1 M concentration draw solution and DI water as feed solution, and their water flux measured (see Fig. 1a). Results showed that KCl has the highest water flux ($11.13 \text{ Lm}^{-2}\text{h}^{-1}$) followed by NH_4Cl , NH_4NO_3 , and KNO_3 , while urea has the lowest water flux ($2.12 \text{ Lm}^{-2}\text{h}^{-1}$). However, the osmotic pressure of fertilizers shows a different trend compared to water flux. In fact, DAP shows the highest osmotic pressure (50.6 atm) followed by $\text{Ca}(\text{NO}_3)_2$, SOA, and MAP. This difference in water flux between fertilizers is explained from the variations of the extent of ICP effects induced by the mass transfer resistance (K) within the membrane support layer (McCutcheon & Elimelech, 2006; Phuntsho et al., 2011). As shown by Eq. (4), mass transfer resistance refers to the ratio between the S parameter and diffusivity of draw solution, and thus a draw solute with higher diffusion coefficient has low mass transfer resistance and should have

high water flux. Even though draw solution has low mass transfer resistance, however, it is possible to have low water flux if it has low osmotic pressure.

RSF of the fertilizer was also measured at 1 M draw solution concentration to evaluate the suitability of the fertilizer candidates (see Fig. 1b) since RSF can be a useful indicator of the extent of draw solute that can be lost during the FO process. Results showed that urea has the highest RSF ($257.68 \text{ g/m}^2/\text{h}$) followed by KNO_3 , NH_4NO_3 , and $\text{Ca}(\text{NO}_3)_2$. On the other hand, MAP has the lowest RSF ($1.15 \text{ g/m}^2/\text{h}$) followed by SOA, KH_2PO_4 , and DAP. Unlike water flux which increased at higher diffusivity however, the trend for RSF with diffusivity was quite different. This is because RSF is theoretically a function of not only the effective concentration gradient between the draw and feed solutions at the active layer surface of the FO membrane but also the salt rejecting properties of the membrane characterised by the salt permeability coefficient (B value) which varies with each fertilizer (Kim et al., 2015b) as shown in Table S3. The high RSF of urea could be explained because of the high B parameter which is likely due to very low diffusivity (in fact lowest amongst all the fertilizer solutes) which could induce high ICP effects. Besides, urea has low molecular size and low hydrated diameter and also forms a neutral solution in water which accelerated its permeation through the FO membrane resulting in significantly higher RSF compared to other fertilizer solutes (Phuntsho et al., 2011). On the other hand, SOA showed low ICP and low RSF which could be due to its low B parameter value. A lower RSF could be preferable for AnFDFOMBR since the accumulation of inorganic salt ions in the active bioreactor could potentially inhibit the anaerobic microbial activity (Ansari et al., 2015).

For efficient and sustainable operation of the FO process, high RSFS is therefore desirable (Achilli et al., 2010). For example, RSFS of 6 L/g indicates that 6 L of permeate can be produced per gram of a draw solute lost by RSF. Results showed that MAP has the highest RSFS (5.98 L/g) followed by SOA, KH_2PO_4 , and DAP (see Fig. 1c), which means that MAP can produce the highest permeate per gram of lost draw solute. As mentioned previously, low RSF can be beneficial for the anaerobic process. However, since RSFS is the ratio of water flux and RSF, high RSFS means high water flux or low RSF. Therefore, when evaluating draw solution, both water flux and RSF should be considered.

Two parameters (i.e., water flux and RSF) were used to evaluate the performance of fertilizer as draw solution. These parameters were normalized to find out the optimum fertilizer as shown in Table 1. In case of water flux, each value of fertilizers was divided by the highest value and the ratios ($J_w/J_{w,Highest}$) were obtained for each fertilizer chemical. Similarly, the ratio ($J_s/J_{s,Lowest}$) for RSF was also determined by dividing RSF by the lowest RSF. In terms of water flux, KCl, NH_4Cl , and NH_4NO_3 ranked high, while in terms of RSF, MAP, SOA, and KH_2PO_4 ranked high.

From these results, it is evident that MAP, SOA, KH_2PO_4 , KCl, NH_4NO_3 and NH_4Cl could be ranked high and thus could be considered as the most suitable fertilizers in terms of FO performance. These selected fertilizers can be divided into two groups. The first group (i.e., MAP, SOA, and KH_2PO_4) is a group with low RSF with moderate water flux, and the second group (i.e., KCl, NH_4NO_3 , and NH_4Cl) with higher water flux with relatively high RSF. Therefore, the comparison of two different groups is expected to provide useful information. Consequently, these six selected fertilizers will be examined for

their influence on the performance of AnFDFOMBR measured in terms of anaerobic activity on BMP due to salt accumulation.

3.3 Bio-methane potential measurements

For BMP experiments, concentrations of fertilizer in the AnFDFOMBR were estimated using Eq. (1) with the assumption of 9 dilution factor and the draw and reactor volumes of 2 L and 6 L, respectively. As shown in Table S4, high RSFS resulted in low concentration of fertilizer in the reactor since the equation derived in this study was reversely related to RSFS.

To investigate the effect of selected fertilizers on the anaerobic biological process, BMP experiments were carried out at determined fertilizer concentrations (see Table S4) during 4 days of operation. The substrate characteristics after BMP experiments were analyzed and shown in Table S5. Results showed that MAP has the highest bio-methane production among six fertilizers as shown in Fig. 2a but all fertilizers had lower bio-methane production compared to the control (DI water addition) thereby indicating that these inorganic chemical fertilizers could inhibit anaerobic microbial activity even at their low concentrations (Ansari et al., 2015; Chen et al., 2008). The results in Fig. 2b further confirm that the biogas production linearly decreases as the fertilizer concentration due to RSF increases in the bioreactor except for MAP which did not fit it within the regression line. This likely shows that the presence of MAP in the bioreactor is likely to have a significantly different influence on the AnMBR compared to the other fertilizers. For the fertilizer group with high concentration (i.e., KCl, NH_4NO_3 , and NH_4Cl), they exhibited

lower biogas production (i.e., 122 mL, 66 mL, and 84 mL, respectively) than the fertilizer group with low concentrations.

The lower concentration group (i.e., MAP, SOA, and KH_2PO_4) showed significantly different behaviours in the biogas production. The difference in the biogas production between KH_2PO_4 and MAP was 313 mL after 4 days, while their difference in molar concentration was only 5.7 mM. This result indicates that KH_2PO_4 and SOA have higher inhibition impact on anaerobic activity than MAP. In the case of SOA, the sulphate reducing bacteria (SRB) can reduce sulphate to sulphide in the presence of sulphate ions. Thus, in the presence of sulphate ions, the SRB have to compete with methanogen bacteria for common organic and inorganic resources. In addition, reduced sulphide ion is toxic to other bacteria groups thereby likely inhibiting or killing certain bacterial species useful for the BMP (Chen et al., 2014; Chen et al., 2008). In the case of KH_2PO_4 , the presence of potassium ions could also inhibit the anaerobic process since high potassium concentration can lead to a passive influx of potassium ions which neutralize the membrane potential (Chen et al., 2008). However, in this study, potassium concentration was under 250 mg/L and thus KH_2PO_4 is expected to have less inhibition effect based on the previous study (Chen et al., 2008). Therefore in order to understand more about the influence of the potassium ions using KH_2PO_4 , further study would be required.

3.4 Salt accumulation in anaerobic fertilizer-drawn forward osmosis membrane bioreactor

Fig. S5 shows the modelled water flux versus the experimental water flux for all the eleven fertilizer initially selected for this study. The theoretical model used in this study

was derived by accounting ECP effect on the feed side of the active layer and ICP effect in the support layer (McCutcheon & Elimelech, 2006). Results showed that the modelled water flux reasonably agreed with the experimental data. Therefore, the models for salt accumulation by feed and draw solutes in the bioreactor were derived based on this basic water flux model as presented in Section 2.5.

Based on the salt accumulation models, time-dependent water flux and reactor concentration were determined under the simulation conditions shown in Table S6, and the effect of fertilizer chemicals on salt accumulation was investigated. FO mode of membrane orientation was adopted since PRO mode previously showed severe fouling potential in the support layer (Kim et al., 2015a). Influent solute concentration was determined as 10 mM NaCl. SRT was determined for 10 days to see how much sludge waste can affect salt accumulation. Initial hydraulic retention time (HRT) used in this study was determined based on the initial water fluxes of fertilizer draws solutions. To simulate the OMBR integrated with FDFO, we assumed that the draw solution is diluted unlike usual OMBR that constant draw concentration is applied since diluted draw solution is recovered by post-treatment (e.g., RO, NF, membrane distillation, etc.). A set of ordinary differential equations (ODEs) described in Section 2.5 were numerically solved to simulate AnFDFOMBR.

To investigate the effect of the presence of fertilizer salts on the performance of OMBR, water flux, HRT and salt concentrations in the bioreactor and the draw tank solution was simulated over time. Results showed that water flux for all the fertilizers severely declined with time as shown in Fig. 3a since draw and feed solutions in FO were

continuously diluted and concentrated with time. After 240 hours of operation, SOA exhibited the highest water flux ($1.58 \text{ L/m}^2/\text{h}$) followed by MAP and KH_2PO_4 despite the fact that NH_4Cl had the highest initial water flux ($10.33 \text{ L/m}^2/\text{h}$) followed by KCl and SOA. This different flux decline behaviour of each fertilizer was likely due to the differences in the salt accumulation rate by RSF as shown in Fig. 3b. In the case of NH_4NO_3 , it had not only high water flux ($10.21 \text{ L/m}^2/\text{h}$) but also high RSF ($42.01 \text{ g/m}^2/\text{h}$). Therefore, a significant amount of draw solutes moved from draw solution to the bioreactor and thus the concentration gradient was significantly reduced. On the contrary for MAP, it had low water flux ($6.86 \text{ L/m}^2/\text{h}$) but also low RSF ($1.15 \text{ g/m}^2/\text{h}$) and thus only small amount of draw solutes were expected to move to the bioreactor. Although it has the lowest final salt concentration (42.37 mM) in the bioreactor, MAP exhibited the second highest final water flux ($1.55 \text{ L/m}^2/\text{h}$) following by SOA which had lower K parameter ($0.071 \text{ m}^2\text{h/kg}$) and higher osmotic pressure (46.1 atm) than MAP. Besides bioreactor concentration, change in the draw concentration also affects the change in the water flux based on Eq. (3).

Results (see Figs. 3b & 3c) show that NH_4Cl had the lowest final draw concentration (0.13 M) followed by KCl and NH_4NO_3 by the end of the experimental duration of 240 hours despite the fact that SOA had the highest dilution capacity (i.e., DF 6.83) which is an important factor in the FDFO process to supply diluted fertilizer solution for the agricultural purpose (Phuntsho et al., 2013). This variation in the dilution trend between draw concentration and draw volume is due to the differences in their salt accumulation rates of each fertilizer draw solution. Since fertilizers with high initial water flux showed more severe flux decline and also high RSF, their average water flux became

lower than fertilizers having lower initial water flux and RSF and thus dilution capacity also became lower. However, the loss of draw solutes due to RSF also played an important role in reducing the draw concentration with time. In the case of NH_4Cl , it had the fourth highest average water flux but also resulted in the highest solute concentration in the bioreactor. Therefore, NH_4Cl could achieve the lowest final draw concentration at the end of the operation but, as shown in Fig. 2, it is possible for higher inhibition potential on the anaerobic microbial activity due to high RSF and hence high solute accumulation rate. From these results, it can be concluded that the draw solution should have low RSF for the stable long-term operation of the AnFDFOMBR.

The rate of solute accumulation in the bioreactor caused by feed and draw solutes is separately simulated and presented in Fig. 4. As shown in Fig. 4a, the solute concentration in the bioreactor caused due to rejection of influent feed solutes continuously increased over time although the rate of accumulation decreased at the later stages of the operation time. This slight decrease in the rate of feed solute accumulation in the bioreactor is due to decrease in the water flux with time as a result of the cumulative dilution of the draw solution with time when operated in a batch process. Similarly, the accumulation of draw solutes in the bioreactor increases continuously with time but gradually the rate of accumulation gradually decreased over time beyond certain operation time which is also due to reduction in the draw solution concentration with the cumulative dilution of the draw solution in the tank. As evident in Fig. 4b, the first group of fertilizer (KCl , NH_4NO_3 and NH_4Cl) with high RSF exhibited significantly higher concentration of accumulated draw solute while the second group (SOA , MAP , KH_2PO_4) showed significantly lower

concentration of accumulated draw solute. Interestingly, fertilizers with high RSF (first group) exhibited slower rate of salt accumulation in the bioreactor after 180 hours of operation compared to the second group which showed a continuous and rather linear rate of accumulation. This decrease in the rate of draw solute accumulation in the bioreactor for the first group is attributed to the reduction in the RSF due to cumulative decrease in the draw solution concentration with time. From these results, it can be concluded that draw solution for the AnFDFOMBR should have desirably low RSF for stable operation.

Comparing Fig. 4a and 4b shows that the rate of feed solute accumulation is not significantly affected by the types of fertilizer draw solution while the rate of draw solute accumulation is highly influenced by the types of draw solution used. This is because the rate of feed solute accumulation mostly depends on the feed solute rejection rate of the FO membrane. The differences in the water flux generated by each fertilizer also slightly influences the accumulation rates in the batch process as it affects the influent flow rate and hence the mass of the feed solutes that reaches the bioreactor.

3.5 Most suitable fertilizer draw solution for anaerobic fertilizer-drawn forward osmosis membrane bioreactor

Among eleven pre-screened fertilizer candidates, the fertilizer chemicals which ranked particularly high in terms of the water flux are NH_4NO_3 , KCl , and NH_4Cl , while the fertilizer chemicals which ranked best in terms of RSF are MAP, SOA, and KH_2PO_4 .

Considering both the criteria, six fertilizers (i.e., MAP, SOA, KH_2PO_4 , KCl , NH_4Cl , and NH_4NO_3) are ranked high for further investigation. Since all fertilizer chemicals are

inorganic salts which can inhibit the biological activities of the anaerobic microorganisms, low RSF is therefore desirable for the biological application as well as for maintaining stable operation and reducing salinity build-up in the bioreactor. In terms of BMP, MAP exhibited better potential as draw solution for AnFDFOMBR than other fertilizers. In addition, in terms of salt accumulation, MAP and SOA ranked best considering the water flux sustainability and salinity build-up by draw solution. Thus, MAP is projected as likely the best draw solution for the AnFDFOMBR process.

The other criterion which must be considered while selecting a suitable fertilizer draws solution candidate is the influence of the draw solute on the fouling and scaling potential during the AnFDFOMBR process. Based on the earlier studies (Phuntsho et al., 2014), MAP has been observed to have low scaling or fouling potential compared to other fertilizers. DAP has been reported to have very high scaling potential especially when feed water contains calcium and magnesium ions (Phuntsho et al., 2014). The presence of scaling precursor ions such as Ca^{2+} and PO_4^{3-} on the membrane surface may exceed its solubility limits of inorganic minerals such as CaCO_3 (calcite) and $\text{Ca}_3(\text{PO}_4)_2$ (tricalcium phosphate) (Greenberg et al., 2005) resulting in the formation of scales on the membrane surface thereby reducing the water flux. In addition to scaling, fertilizers containing multivalent cations such as Ca^{2+} or Mg^{2+} can induce severe membrane fouling. The reverse diffusion of draw solute cations could promote foulant-membrane and foulant-foulant interactions thereby enhancing membrane fouling (She et al., 2012; Xie et al., 2015).

4. Conclusions

Primary findings drawn from this study are summarized as follows:

- A selection procedure of fertilizers as draw solution for novel AnFDFOMBR was investigated.
- From preliminary screening and FO experiments, six fertilizers (i.e., MAP, SOA, KH_2PO_4 , KCl, NH_4NO_3 , and NH_4Cl) were selected.
- MAP exhibited the highest biogas production since other fertilizers exhibited the inhibition effect on the anaerobic activity under determined concentrations.
- Simulation results showed that SOA and MAP were appropriate to OMBR integrated with FDFO since they had less salt accumulation and relatively higher water flux.
- For these reasons, MAP can be the most suitable draw solution for AnFDFOMBR.

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References

1. Achilli, A., Cath, T.Y., Childress, A.E. 2010. Selection of inorganic-based draw solutions for forward osmosis applications. *Journal of Membrane Science*, **364**(1–2), 233–241.

2. Achilli, A., Cath, T.Y., Marchand, E.A., Childress, A.E. 2009. The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes. *Desalination*, **239**(1–3), 10-21.
3. Ahluwalia, S.S., Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource Technology*, **98**(12), 2243-2257.
4. Alderson, M.P., dos Santos, A.B., Mota Filho, C.R. 2015. Reliability analysis of low-cost, full-scale domestic wastewater treatment plants for reuse in aquaculture and agriculture. *Ecological Engineering*, **82**, 6-14.
5. Angelakis, A.N., Marecos Do Monte, M.H.F., Bontoux, L., Asano, T. 1999. The status of wastewater reuse practice in the Mediterranean basin: need for guidelines. *Water Research*, **33**(10), 2201-2217.
6. Ansari, A.J., Hai, F.I., Guo, W., Ngo, H.H., Price, W.E., Nghiem, L.D. 2015. Selection of forward osmosis draw solutes for subsequent integration with anaerobic treatment to facilitate resource recovery from wastewater. *Bioresource Technology*, **191**, 30-36.
7. Chekli, L., Phuntsho, S., Kim, J.E., Kim, J., Choi, J.Y., Choi, J.-S., Kim, S., Kim, J.H., Hong, S., Sohn, J., Shon, H.K. 2016. A comprehensive review of hybrid forward osmosis systems: Performance, applications and future prospects. *Journal of Membrane Science*, **497**, 430-449.
8. Chekli, L., Phuntsho, S., Shon, H.K., Vigneswaran, S., Kandasamy, J., Chanan, A. 2012. A review of draw solutes in forward osmosis process and their use in modern applications. *Desalination and Water Treatment*, **43**(1-3), 167-184.
9. Chen, J.L., Ortiz, R., Steele, T.W.J., Stuckey, D.C. 2014. Toxicants inhibiting anaerobic digestion: A review. *Biotechnology Advances*, **32**(8), 1523-1534.

10. Chen, Y., Cheng, J.J., Creamer, K.S. 2008. Inhibition of anaerobic digestion process: A review. *Bioresource Technology*, **99**(10), 4044-4064.
11. Clay, J. 2004. *World Agriculture and the Environment: A Commodity-by-Commodity Guide to Impacts and Practices*. Island Press.
12. Federation, W.E., Association, A.P.H. 2005. Standard methods for the examination of water and wastewater. *American Public Health Association (APHA): Washington, DC, USA*.
13. Ferro, G., Fiorentino, A., Alferez, M.C., Polo-López, M.I., Rizzo, L., Fernández-Ibáñez, P. 2015. Urban wastewater disinfection for agricultural reuse: effect of solar driven AOPs in the inactivation of a multidrug resistant E. coli strain. *Applied Catalysis B: Environmental*, **178**, 65-73.
14. Greenberg, G., Hasson, D., Semiat, R. 2005. Limits of RO recovery imposed by calcium phosphate precipitation. *Desalination*, **183**(1-3), 273-288.
15. Kim, C., Lee, S., Shon, H.K., Elimelech, M., Hong, S. 2012. Boron transport in forward osmosis: Measurements, mechanisms, and comparison with reverse osmosis. *Journal of Membrane Science*, **419-420**, 42-48.
16. Kim, D.I., Kim, J., Shon, H.K., Hong, S. 2015a. Pressure retarded osmosis (PRO) for integrating seawater desalination and wastewater reclamation: Energy consumption and fouling. *Journal of Membrane Science*, **483**, 34-41.
17. Kim, J., Shin, J., Kim, H., Lee, J.-Y., Yoon, M.-h., Won, S., Lee, B.-C., Song, K.G. 2014. Membrane fouling control using a rotary disk in a submerged anaerobic membrane sponge bioreactor. *Bioresource Technology*, **172**, 321-327.
18. Kim, Y., Lee, S., Shon, H.K., Hong, S. 2015b. Organic fouling mechanisms in forward osmosis membrane process under elevated feed and draw solution temperatures. *Desalination*, **355**, 169-177.

19. Lee, S., Kim, Y., Kim, A.S., Hong, S. 2015. Evaluation of membrane-based desalting processes for RO brine treatment. *Desalination and Water Treatment*, 1-8.
20. McCutcheon, J.R., Elimelech, M. 2006. Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. *Journal of Membrane Science*, **284**(1-2), 237-247.
21. Phuntsho, S., Hong, S., Elimelech, M., Shon, H.K. 2013. Forward osmosis desalination of brackish groundwater: Meeting water quality requirements for fertigation by integrating nanofiltration. *Journal of Membrane Science*, **436**, 1-15.
22. Phuntsho, S., Lotfi, F., Hong, S., Shaffer, D.L., Elimelech, M., Shon, H.K. 2014. Membrane scaling and flux decline during fertiliser-drawn forward osmosis desalination of brackish groundwater. *Water Research*, **57**, 172-182.
23. Phuntsho, S., Shon, H.K., Hong, S., Lee, S., Vigneswaran, S. 2011. A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions. *Journal of Membrane Science*, **375**(1-2), 172-181.
24. Phuntsho, S., Shon, H.K., Majeed, T., El Saliby, I., Vigneswaran, S., Kandasamy, J., Hong, S., Lee, S. 2012. Blended Fertilizers as Draw Solutions for Fertilizer-Drawn Forward Osmosis Desalination. *Environmental Science & Technology*, **46**(8), 4567-4575.
25. Qiu, G., Ting, Y.-P. 2014. Direct phosphorus recovery from municipal wastewater via osmotic membrane bioreactor (OMBR) for wastewater treatment. *Bioresource Technology*, **170**, 221-229.
26. Rijsberman, F.R. 2006. Water scarcity: Fact or fiction? *Agricultural Water Management*, **80**(1-3), 5-22.

27. Sahebi, S., Phuntsho, S., Eun Kim, J., Hong, S., Kyong Shon, H. 2015. Pressure assisted fertiliser drawn osmosis process to enhance final dilution of the fertiliser draw solution beyond osmotic equilibrium. *Journal of Membrane Science*, **481**, 63-72.
28. She, Q., Jin, X., Li, Q., Tang, C.Y. 2012. Relating reverse and forward solute diffusion to membrane fouling in osmotically driven membrane processes. *Water Research*, **46**(7), 2478-2486.
29. Stuckey, D.C. 2012. Recent developments in anaerobic membrane reactors. *Bioresource Technology*, **122**, 137-148.
30. Tiraferri, A., Yip, N.Y., Straub, A.P., Romero-Vargas Castrillon, S., Elimelech, M. 2013. A method for the simultaneous determination of transport and structural parameters of forward osmosis membranes. *Journal of Membrane Science*, **444**, 523-538.
31. Wang, X., Chang, V.W.C., Tang, C.Y. Osmotic membrane bioreactor (OMBR) technology for wastewater treatment and reclamation: Advances, challenges, and prospects for the future. *Journal of Membrane Science*.
32. Xie, M., Bar-Zeev, E., Hashmi, S.M., Nghiem, L.D., Elimelech, M. 2015. Role of Reverse Divalent Cation Diffusion in Forward Osmosis Biofouling. *Environmental Science & Technology*, **49**(22), 13222-13229.
33. Xie, M., Nghiem, L.D., Price, W.E., Elimelech, M. 2012. Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis. *Water Research*, **46**(8), 2683-2692.
34. Yip, N.Y., Elimelech, M. 2013. Influence of Natural Organic Matter Fouling and Osmotic Backwash on Pressure Retarded Osmosis Energy Production from Natural Salinity Gradients. *Environmental Science & Technology*, **47**(21), 12607-12616.

Figure Captions

Fig. 1. FO performance for different fertilizer draw solutions: (a) water fluxes, (b) reverse salt fluxes, and (c) reverse salt flux selectivity (RSFS). Performance ratio was determined by divided the experimental water flux with the theoretical water flux which was calculated by Eq. (4), and RSFS was obtained by using Eq. (7). Experimental conditions of performance experiments: 1 M fertilizer draw solution; cross-flow velocity of 25 cm/s; and temperature of 25 °C.

Fig. 2. Bio-methane potential results: (a) influence of fertilizers on the biogas production for 4 days of operation, and (b) comparison of biogas production with fertilizer concentration. Biogas production volumes with respect to fertilizers were determined after 4 days of operation. Experimental conditions: 700 mL of digested sludge with addition of 50 mL of each fertilizer solution; and temperature of 35 °C

Fig. 3. Simulated (a) water fluxes, (b) salt concentration in a bioreactor (left axis) and fertilizer concentration in draw tank (right axis), and (c) draw tank volume as a function of operation time.

Fig. 4. Influence of fertilizers on salt accumulation in the bioreactor: (a) induced by feed solutes rejected by the FO membrane and (b) induced by the back diffusion of draw solutes.

Table 1. Ratios between the best draw solution and the draw solution itself for water flux, performance ratio, and reverse salt flux. Each draw solution was evaluated at concentration of 1 M.

Fertilizers	Relative water flux	Relative reverse salt flux
	$(J_w)/(J_w)_{KCl}$	$((J_s)_{MAP}/J_s)$
NH₄NO₃	0.917	0.027
SOA	0.806	0.755
NH₄Cl	0.956	0.057
Ca(NO₃)₂	0.854	0.045
NaNO₃	0.788	0.061
KCl	1	0.051
MAP	0.616	1
DAP	0.607	0.181
KNO₃	0.906	0.024
Urea	0.19	0.004
KH₂PO₄	0.664	0.534

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Highlights

- A fertilizer draw solution selection protocol was proposed for AnFDFOMBR.
- Screening includes water flux, reverse salt flux, biogas potential and simulation.
- Reverse salt flux of fertilizers except MAP may inhibit methane production.
- Low reverse salt flux induced higher water flux and less salt accumulation.
- MAP could be the most suitable draw solution for AnFDFOMBR.

Graphical abstract