

Accepted Manuscript

Fertilizer drawn forward osmosis process for sustainable water reuse to grow hydroponic lettuce using commercial nutrient solution

Laura Chekli, Jung Eun Kim, Ibrahim El Saliby, Youngjin Kim, Sherub Phuntsho, Sheng Li, Noreddine Ghaffour, TorOve Leiknes, Ho Kyong Shon

PII: S1383-5866(17)30104-1
DOI: <http://dx.doi.org/10.1016/j.seppur.2017.03.008>
Reference: SEPPUR 13594

To appear in: *Separation and Purification Technology*

Received Date: 10 January 2017
Revised Date: 8 March 2017
Accepted Date: 9 March 2017

Please cite this article as: L. Chekli, J. Eun Kim, I. El Saliby, Y. Kim, S. Phuntsho, S. Li, N. Ghaffour, T. Leiknes, H. Kyong Shon, Fertilizer drawn forward osmosis process for sustainable water reuse to grow hydroponic lettuce using commercial nutrient solution, *Separation and Purification Technology* (2017), doi: <http://dx.doi.org/10.1016/j.seppur.2017.03.008>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Fertilizer drawn forward osmosis process for sustainable water reuse to grow hydroponic lettuce using commercial nutrient solution

Laura Chekli¹, Jung Eun Kim¹, Ibrahim El Saliby², Youngjin Kim^{1,3}, Sherub Phuntsho¹, Sheng Li⁴, Noredine Ghaffour⁴, TorOve Leiknes⁴ and Ho Kyong Shon^{1*}

¹ School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), City Campus, Broadway, NSW 2007, Australia

² Botanic Gardens and Centennial Parklands, Mrs Macquarie Road, Sydney, NSW 2000, Australia

³ School of Civil, Environmental and Architectural Engineering, Korea University, Seongbuk-gu, Seoul, Republic of Korea

⁴ King Abdullah University of Science and Technology (KAUST), Water Desalination and Reuse Center (WDRC), Division of Biological & Environmental Science & Engineering (BESE), Thuwal 23955-6900, Saudi Arabia

* Corresponding author: Tel.: (+61) 02 9514 2629; email: Hokyong.Shon-1@uts.edu.au

ACCEPTED MANUSCRIPT

Abstract

This study investigated the sustainable reuse of wastewater using fertilizer drawn forward osmosis (FDFO) process through osmotic dilution of commercial nutrient solution for hydroponics, a widely used technique for growing plants without soil. Results from the bench-scale experiments showed that the commercial hydroponic nutrient solution (i.e. solution containing water and essential nutrients) exhibited similar performance (i.e., water flux and reverse salt flux) to other inorganic draw solutions when treating synthetic wastewater. The use of hydroponic solution is highly advantageous since it provides all the required macro- (i.e., N, P and K) and micronutrients (i.e., Ca, Mg, S, Mn, B, Zn and Mo) in a single balanced solution and can therefore be used directly after dilution without the need to add any elements. After long-term operation (i.e. up to 75% water recovery), different physical cleaning methods were tested and results showed that hydraulic flushing can effectively restore up to 75% of the initial water flux while osmotic backwashing was able to restore the initial water flux by more than 95%; illustrating the low-fouling potential of the FDFO process. Pilot-scale studies demonstrated that the FDFO process is able to produce the required nutrient concentration and final water quality (i.e., pH and conductivity) suitable for hydroponic applications. Coupling FDFO with pressure assisted osmosis (PAO) in the later stages could help in saving operational costs (i.e., energy and membrane replacement costs). Finally, the test application of nutrient solution produced by the pilot FDFO process to hydroponic lettuce showed similar growth pattern as the control without any signs of nutrient deficiency.

Keywords: Forward osmosis, commercial fertilizers, wastewater reuse, hydroponics.

1 Introduction

With increasing pressure on natural resources due to rapid and extensive urbanization and industrialization, freshwater resources are becoming limited, particularly in arid, semi-arid and coastal areas. On the other hand, the agricultural sector consumes about 70% of the accessible freshwater with about 15-35% of water being used unsustainably (i.e., wasted) [1-3]. Besides, in arid regions, agriculture is not only hindered by the limited freshwater resources but also by the scarcity of fertile lands. Hydroponics, a subset of hydroculture, is being increasingly used in commercial greenhouse vegetable production worldwide because it provides a substantial degree of control of the environment surrounding the roots [4]. In fact, being a soilless process, it eliminates all the problems associated with soil culture (e.g. poor drainage, soil pollution or soil-borne pathogens) and offers the possibility of using areas typically unsuitable for conventional farming such as arid regions [5]. However, this technique requires nutrient solutions (i.e. solution that provides water and nutrients to the plants) to grow plants and therefore also consumes a large amount of freshwater, although the water efficiency is much higher compared to open farming in the soil. In fact, nutrient (or hydroponic) solutions are usually made by mixing freshwater with a concentrated solution of mixed nutrients [6]. This water-food nexus has become a critical issue in most arid regions and therefore, the development of technologies to sustain water and food security must be explored [7].

Wastewater reuse for irrigation of plants and crops has gradually become a common practice worldwide since it represents a viable alternative water source [8]. However, wastewater effluent from a typical biologically treated effluent is generally not suitable for direct application due to the presence of pathogens (e.g. E-coli, faecal coliform, *Giardia* and *Cryptosporidium*, viruses etc.), organic and inorganic pollutants (e.g. heavy metals and micro pollutants) which are detrimental to both plants and human health [9, 10]. Therefore, advanced treatment processes (e.g. membrane technologies) are essential to eliminate any health risks which are usually done using ultrafiltration (UF), reverse osmosis (RO) or both [11, 12].

The fertilizer drawn forward osmosis (FDFO) process has received increased interest since its concept relies on the natural osmotic dilution of a fertilizer draw solution (DS) which can

then be applied directly for irrigation without the need of a DS recovery process as for most FO applications [13-16]. Although previous FDFO studies focused on the desalination of either brackish water or seawater, the relatively low salinity of most impaired waters makes them a suitable feed solution candidate for the FDFO process [17]. In fact, due to the limit posed by the osmotic equilibrium between the feed and the draw solutions, which will ultimately affect the final nutrient concentration, using a feed solution having a lower salinity (i.e., lower osmotic pressure) will help in meeting the standard requirements for irrigation. In fact, in a recent review paper on FO [18], it was emphasized that one of the few viable applications of FO is the use of impaired water sources to dilute a concentrated fertilizer; a concept which was already developed four decades ago but never applied on any scale. Besides, because irrigation is the largest water consumer, FDFO could have a significant contribution to the development of arid regions when applied to low-quality source such as seawater, brackish water or impaired waters. Finally, it has been demonstrated that FO alone can be effective for the treatment of impaired waters, especially for the removal of emerging pollutants such as persistent trace organic compounds (TrOCs) or boron, making it a suitable technology for wastewater reuse [19]. However, it has to be noted that the rejection of TrOCs by FO, although substantial, is not complete, especially for small, uncharged or hydrophobic compounds [19].

To date, several inorganic fertilizer salts have been tested as a potential DS either separately or in blended form [13, 16]. However, by using single or blended salts as fertilizers, the final diluted DS does not have the required balanced nutrients (i.e., macronutrients and micronutrients) for plant growth. Therefore, two recent bench-scale studies (i.e., targeting greenwall and conventional soil irrigation) have suggested the use of commercial fertilizers containing all essential nutrients with the required balanced ratio [20, 21]. Although these preliminary bench-scale studies showed promising results and demonstrated the potential feasibility of water recovery by the FO process using commercial liquid fertilizers, the response of plants grown in nutrient solution produced by the FDFO process has not been assessed. Hydroponic nutrient solutions are the most versatile medium where plants can grow with little care. They can be easily prepared, modified, and replaced. The production of lettuce (*Lactuca sativa* L.) in hydroponic systems is well studied under different conditions and scenarios [22-24].

Therefore, the main objective of the present study is to demonstrate, for the first time, the feasibility of the FDFO process, at laboratory and pilot scales, to produce a nutrient solution suitable for hydroponics via osmotic dilution of synthetic wastewater effluent using commercial hydroponic nutrient solution as DS. Bench-scale experiments were firstly conducted to evaluate the performance of the commercial hydroponic nutrient solution in comparison to standard single inorganic DS (i.e. NaCl). Pilot-scale operation of the FDFO process was then carried out to investigate the potential of the FDFO process to produce a nutrient solution suitable for hydroponic application. Finally, the response (i.e., growth performance) of hydroponic lettuce plants grown in nutrient solutions produced by the pilot FDFO process was tested and compared with standard hydroponic formulation. To the authors' knowledge, this is the first time that the FDFO produced nutrient solution is tested on plants to provide substantial evidence on the suitability of wastewater reuse via the FDFO process.

2 Materials and Methods

2.1 Bench-scale FO experiments

2.1.1 FO membranes and commercial hydroponic nutrient solution

A commercially available thin-film composite (TFC) polyamide (PA) FO membrane (Toray Industry Inc.) was used for all the bench-scale experiments. This membrane was obtained from a spiral wound 8040 TFC FO membrane module, similar to the one used for the subsequent pilot-scale experimental studies, to ensure data consistency. The pure water permeability coefficient (A value) and salt rejection rate of the TFC PA FO membrane were determined based on the previous experimental protocol [25], and found as follow: $A = 8.9 \pm 0.14 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ and salt rejection of 85% (using 1.2 g/L Red Sea salt as initial feed solution).

The commercial hydroponic nutrient solution (Optimum Grow - twin pack hydroponic nutrient) used in this study as DS was obtained from Fernland Agencies Pty Ltd (Queensland, Australia). This is a hydroponic nutrient solution usually employed in plant nurseries and commercial greenhouses. This commercial nutrient solution consists of two concentrated solutions, namely "Part A" and "Part B" which is typical of any hydroponic recipes [26]. In

fact, as shown in Table 1, Part A contains calcium while Part B includes phosphates and sulphates which can both form insoluble precipitates with calcium if mixed in the concentrated form [27]. This also indicates that, Part A and B solutions have to be processed by the FDFO process separately either in a parallel stage or using only one of the solutions as DS while the other can be later mixed in dilute form. Table 1 also shows that the commercial nutrient solution contains a significant concentration of organics which usually comes from humic-like materials or organic chelating agents such as ethylenediaminetetraacetic acid (EDTA) used to facilitate nutrient uptake or urea as a source of nitrogen. The impact of the presence of organics in the DS on the FO performance (i.e., water flux and reverse salt flux) remains largely unknown and therefore requires further insights. Bench-scale experiments to determine the effect of the presence of organics in the DS will be detailed in the next section (i.e. 2.1.3.).

Bench-scale and pilot-scale FO experiments were conducted with Part B only since it contains all essential macronutrients (i.e., N, P, K) as well as other important micronutrients (i.e., Mg, S, Mn, B, Zn and Mo). Besides, Part A contains a high concentration of calcium (Table 1) which can cause severe membrane fouling if it diffuses to the feed solution via bridging mechanisms with organic compounds such as humic acid [28-31], by complexation to bacterial extracellular polymeric substances [32] or by enhancing the scaling potential of the osmotically concentrated feed solution [33]. For the hydroponic experiments, Part A was simply added, at the required ratio, and mixed to the final nutrient solution produced by the FDFO pilot.

Table 1

2.1.2 Bench-scale FO setup

Although the present study is application-oriented; fundamental studies assessing the basic performance of the commercial hydroponic nutrient solution are crucial. In fact, bench-scale studies using commercial nutrient solutions (i.e. complex mixture of organic and inorganic compounds essential for plant growth) as draw solution in the FDFO process are very limited [20, 21]. Besides, all commercial nutrient solutions have their own specific composition and therefore are expected to behave differently in the FDFO process in terms of water flux, RSF and fouling especially.

The performance of the FO process was first evaluated in a batch mode of FO operation, similar to the one used in previous studies [34, 35]. The FO cell has two symmetric channels on each side of the membrane and the system was operated under co-current flow mode. The cell has internal dimensions of 7.7 cm length, 2.6 cm width and 0.3 cm depth (i.e., effective membrane area of 0.002 m²). Variable speed gear pumps (Cole Parmer, USA) were employed to circulate the feed and DSs. The DS tank was placed on a digital scale connected to a computer to enable the determination of the water flux by measuring the weight changes over time. A conductivity and pH meter (Hach, Germany) was connected to the feed tank to record the variation of pH and electrical conductivity in the feed solution.

The experiments were conducted under the active layer facing the feed solution (AL-FS) mode. A new membrane was used for each experiment and the FO membrane was stabilised for 30 minutes using DI water on both sides of the membrane prior to the start of the experiment. Once stabilised, the feed and DSs were replaced and the water flux was measured continuously every 3 minute. All experiments were conducted at a cross-flow velocity of 8.5 cm/s, and a constant temperature of 25 °C maintained with the help of temperature control bath connected to a heating/chilling unit.

2.1.3 Short and long term performance

Preliminary short-term experiments (i.e., up to 25% water recovery) were conducted to evaluate the basic performance (i.e., water flux and RSF) of the commercial hydroponic nutrient solution (Part B only) against NaCl, a widely used standard DS. NaCl solution was prepared at 1.4 M concentration, corresponding to an osmotic pressure of 66 bar, similar to the one of Part B fertilizer (Table 1). The osmotic pressure was calculated using ROSA software (Version 9.1, Filmtech Dow Chemicals, USA). Experiments using 1.4 M NaCl with 1.8 g/L humic acid (i.e., corresponding to 500 mg/L of total organic carbon (TOC) or 500 mgC/L, similar to the concentration measured in Part B solution) as DS were also conducted to evaluate the effect of organics in the DS on the FO performance (i.e., water flux, RSF and reverse organic compounds flux). These short-term experiments were conducted with DI water as the feed solution. Water flux was measured continuously and the average water flux obtained after 25% water recovery was reported. Reverse salts and organic compounds fluxes were quantified by analysing their concentration in the feed solution at the beginning and end

of each experiment. Samples from the feed solution were taken at the start and completion of each experiment for inorganic and organic compounds analysis.

Long-term experiments (i.e., up to 75% water recovery) were then conducted using the liquid fertilizer (Part B) as DS and synthetic wastewater simulating municipal wastewater effluent (Table 2) as feed solution. Upon completion of the experiments, different physical cleaning methods were tested to evaluate their effectiveness on water flux recovery. Membrane surface flushing (or hydraulic flushing) was conducted by replacing both the solutions with DI water and recirculating for 30 minutes at triple crossflow velocity (i.e., 25.5 cm/s). Osmotic backwashing was also employed during which the feed solution was replaced with 1M NaCl and DS with DI water to create a negative water flux. Osmotic backwashing was conducted at crossflow rates of 8.5 cm/s for 30 minutes. After physical cleaning or osmotic backwashing, the initial feed and draw solutions (i.e., synthetic wastewater and commercial liquid fertilizer) were switched back to the system and water flux was monitored for an additional 2 hours after which the water flux recovery rates were calculated.

Table 2

2.1.4 Analytical methods

Macro- and micronutrients (i.e., N-NH_4^+ , N-NO_3^- , N-NO_2^- , TN, P-PO_4^{3-} , K^+ , SO_4^{2-} , Mg^{2+} and Ca^{2+}) concentrations were determined using Merck cell tests and spectrophotometer (Spectroquant NOVA 60; Merck, Germany). The total organic content of the feed solution was measured using a TOC analyser (TOC-VCPH, TNM-1, Shimadzu, Japan).

The surface of virgin, fouled and cleaned membranes were analysed by scanning electron microscopy (SEM, Zeiss Supra 55VP, Carl Zeiss AG, Germany). Samples were first dried under air purging and then lightly coated with Au/Pd. The SEM imaging was performed at an accelerating voltage of 10 kV at different magnifications and at various points.

2.2 Operation of pilot-scale FDFO unit

Figure 1 illustrates the layout of the pilot-scale FO unit operated in this study and more details on its design and control are provided in our previous study [36]. Here, an 8" spiral wound thin-film composite (TFC) FO membrane module with a total membrane area of 15.3

m² (Toray Industries, Korea) was used. All experimental studies were conducted in the FO mode or AL-FS mode. Feed and draw solutions flow rates were maintained at 70 and 6 L/min, respectively, throughout the experiments. The feed and draw solutions were the same during the bench-scale tests (i.e., synthetic wastewater and commercial liquid fertilizer Part B). The feed solution was kept constant throughout the experiments (i.e., conductivity was measured at frequent intervals and adjusted when necessary with tap water) to maintain the same osmotic pressure on the feed side of the membrane while the DS was continuously diluted.

The system was operated under a combination of FO and pressure assisted osmosis (PAO) modes [37]. In FO mode (referred as stage 1), water flux was generated solely by the osmotic driving force of the DS, and FO unit was operated until the DS tank (1,000 L) was full with the diluted fertilizer DS. The diluted DS from stage 1 was then used as the DS in PAO operations (referred as stage 2 and stage 3). For PAO operations, hydraulic pressure (i.e., 2 bar) was applied on the feed side of the membrane module and used as an additional driving force to enhance water flux [37]. In order to achieve the targeted fertilizer dilution for direct hydroponic application (i.e., 250 times dilution as indicated by the manufacturer) two stages of PAO was necessary at an applied pressure of 2 bar (i.e., maximum pressure rating of the feed pump). The first PAO experiment (i.e., stage 2) was continued until the DS tank was full with the diluted fertilizer DS and this solution was in turn used as the DS for the second PAO experiment (stage 3). The pilot operation was stopped when the targeted dilution factor (i.e., recommended by the manufacturer) was achieved. At the end of the experiments, the diluted DS (i.e., Part B) was mixed with the required ratio of Part A solution (Table 1) and stored in 200 L tanks for the subsequent hydroponic experiments. About 120 L of nutrient solution was delivered to the Royal Botanic Gardens (Sydney, Australia) every week for hydroponic testing. All containers were initially disinfected using 70% ethanol solution and rinsed with MQ water to avoid bacterial growth. Conductivity and pH were measured twice a week to ensure both parameters remain within the acceptable range for hydroponics (i.e., pH 6.0-6.5 and conductivity 1.5-2.0 mS/cm) and hydrogen peroxide (50% v/v) was applied once a week at a rate of 2 mL per 10 L of nutrient solution to prevent microorganism growth in the tanks. The same treatment (i.e. initial disinfection of the containers followed by weekly treatment with hydrogen peroxide) was applied to the tanks containing the commercial hydroponic

nutrient solution diluted with DI water.

Figure 1

2.3 Preliminary economic analysis

A critical optimisation aspect of this hybrid FO-PAO process relies on the determination of the optimal contribution of both processes. In other words, it is crucial to determine the optimal point at which we should apply PAO (i.e. at which DS osmotic dilution). In order to do so, a preliminary assessment of the capital and operational costs (CAPEX and OPEX) has been carried out for the FO, PAO and different FO-PAO configuration processes.

The total capital costs determination was based on the following assumptions: a) plant availability of 0.95, b) a 6% interest rate, c) a 20-year lifetime for the plant [38]. The total capital cost was calculated based on the data provided by the manufacturer on a single module and the capacity for each module. Based on this data, the total membrane area required to produce 100,000 m³/day can be estimated. Total capital costs include the construction and equipment costs. The construction cost includes pressure vessels, pumps, piping and others (i.e., civil engineering, intakes, working capital and contingencies) while the equipment cost includes membranes and materials [38]. FO feed brine is assumed to be treated by a separate wastewater treatment plant and thus the capital costs associated to the disposal facility are not considered. Amortised capital cost is calculated based on:

$$\text{CAPEX amortisation (AUD, m}^3\text{)} = \frac{\text{total capital cost} \times i}{1 - (1 + i)^{-n}} \times \frac{1}{\text{plant capacity} \times 365}$$

where i is the interest rate, n is the plant lifetime and the plant capacity is 100,000 m³/day, and 365 is the number of days in a year.

Yearly operating costs were calculated based on the reported percentages of membrane replacement, electrical cost, chemical cleaning and others such as repairs, laboratory fees, labour and insurance [38]. The cost of FO module was assumed to be AUD \$ 1,250 and the cost of electricity (i.e. AUD \$0.29/kWh) was based on the current price in New South Wales, Australia [39].

2.4 Hydroponic lettuce plants

2.4.1 Nutrient film technique (NFT) and experimental procedures

Different types of hydroponic systems are used for the production of lettuce and include solution hydroponics, substrate hydroponics with recirculating solution and the nutrient film technique (NFT), the latter being the most popular system was selected for this study. In NFT, the plants are supported in a gently sloping (about 1.5-2.0°) shallow gully in which the roots are suspended in a flowing stream containing the nutrient solution, as shown in Figure S1 (Supporting Information). This marginal slope allows the nutrient solution to flow back into the recirculation tank from which it is pumped to the top of the gully making it a closed loop. The circulation of the nutrient solution down the gullies also helps in making the solution sufficiently aerated. The NFT units typically used in Australia consist of PVC channels having rectangular base and fitted with plastic covers containing plant holes. The NFT units used in this study have been purchased from Sage Horticultural (Hallam, Vic., Australia).

The experiment was conducted in a controlled environment greenhouse at the Royal Botanic Garden nursery in Sydney from April to June 2016. The diluted nutrient solution obtained from the pilot FDFO unit was used to grow lettuce in NFT units. The experiment consisted of three different treatments: i) T1: Optimum Grow nutrient solution diluted through the FDFO process; ii) T2: Optimum Grow nutrient solution diluted with distilled water; and iii) T3: Half-strength Hoagland's solution, a standard hydroponic nutrient solution tailored for lettuce [40] used as control (Table 3). Therefore, T1 and T2 can be compared to directly evaluate the loss of nutrients during the FO operations while T1 and T3 can be compared to identify if the loss of some specific nutrients can be detrimental for the lettuce since the Hoagland's solution contains all the essential nutrients for lettuce growth.

Table 3

2.4.2 Response of hydroponic lettuce plants: Growth performance

Lettuce seeds (*Lactuca sativa* L. 'Green Mignonette', Mr. Fothergill's Seeds Pty Ltd.) were first sown on Rockwool cells in a germination glasshouse under controlled temperature (18-27 °C) and grown for three weeks. A total of 57 seeds (Figure S2, SI) were germinated in

individual cells within trays filled with Optimum nutrient solution (EC = 700 $\mu\text{s}/\text{cm}$ and pH = 6.0). After three weeks, seedlings were then transferred to the NFT units and grown for eight weeks under the three aforementioned treatments (19 plants per treatment, Figure S3, SI). All nutrient solutions were prepared to an EC of 1100 $\mu\text{s}/\text{cm}$ and a pH of 6 adjusted with distilled water, phosphoric acid and potassium hydroxide, respectively. At the end of the experiment (Figure S4, SI), five plants were randomly selected and analysed on different growth parameters such as fresh biomass production (i.e., aerial parts and roots) and dried biomass (i.e., oven dried at 60 °C for 72 h).

3 Results and Discussion

3.1 Bench-scale performance of commercial fertilizer

3.1.1 Short-term studies and comparison with single inorganic fertilizer

The performance of the commercial fertilizer in terms of water flux, final TOC concentration in the feed solution and reverse solute flux (RSF) is presented in Figure 2. At similar initial driving force (i.e., initial osmotic pressure of 66.3 bar), the average water flux produced by the commercial fertilizer was slightly lower than the one obtained with NaCl (i.e., 15.9 ± 0.7 LMH against 19.7 ± 0.9 LMH for the commercial fertilizer and 1.4 M NaCl, respectively). Although, theoretically, the osmotic pressure difference across the membrane is the main driving force in the FO process, it has been shown previously that the extent of internal concentration polarization (ICP) effects inside the membrane support layer facing the DS will have significant impact on the water flux [41, 42]. Therefore, a DS having a higher diffusivity (e.g. NaCl) will generate a high water flux because of the lower ICP effects inside the membrane support layer. The presence of multiple solutes in the commercial fertilizer including those solutes with lower diffusivities probably lowers the average diffusivity of the DS thereby resulting in slightly lower water flux [16]. Figure 2a and 2d show that the presence of humic acid (HA) (i.e., 500 mg/L of carbon or mgC/L) in the DS did not affect the FO water flux performance. In fact, there was no significant difference in the average water flux (Figure 2a) which indicates that HA did not accumulate on the membrane support layer to induce a potential fouling layer which would have created an additional resistance to the water flux. This is in accordance with previous studies showing that the water permeation

drag (i.e., from the feed to the DS) prevents the accumulation of HA on the support layer [20, 43, 44].

At similar initial TOC content (i.e., 500 mgC/L) there were more organic compounds diffusing to the feed solution with the commercial fertilizer compared with 1.4 M NaCl with HA (Figure 2b). This clearly demonstrates that the commercial fertilizer contains other organic compounds beside HA, which can diffuse easily through the membrane towards the DS. Other sources of organics in the commercial fertilizer solution can include chelating agents or urea, as a source of nitrogen. Chelating agents, such as EDTA, have large molecular weight (e.g. molecular weight of EDTA is 292.24 g/mol) so it is very unlikely that these organic compounds will diffuse to the feed solution. However, the high reverse solute transport of urea has already been demonstrated [16] attributed to its low molecular size (60.06 g/mol) combined with the fact that it remains neutral in solution, increasing its reverse diffusion through the FO membrane [45]. This hypothesis is further confirmed by the high reverse diffusion of N compounds from the commercial fertilizer (Figure 2c). However, urea is TOC-neutral since it rapidly hydrolyses to ammonia and carbon dioxide. Because the samples are acid-hydrolysed and purge before TOC analysis, the carbon dioxide present in urea is removed. Therefore, the increase in TOC in the feed solution is originated from another organic compound present in the DS. One possibility could be acetate; which is often used to increase the plant foliar uptake. Besides, acetate has a relatively low molecular weight (i.e. 59.04 g/mol) so it is very likely that this compound diffused through the FO membrane, thereby increasing the TOC content in the feed solution [46].

The loss of nutrients from the commercial fertilizer by reverse diffusion during its osmotic dilution is an important factor that needs to be evaluated since it will affect the final nutrient concentration available to the plants. A well-balanced macro- and micronutrients solution is essential to ensure favourable plant growth and health. Figure 2c shows the reverse permeation of the different nutrients present in the commercial fertilizer. First, it can be seen that the solutes having the lower hydrated solute radii (i.e., K^+ , NH_4^+ and NO_3^-) had the highest RSF while the solutes having the larger solute radii (i.e., PO_4^{3-} , SO_4^{2-} and Mg^{2+}) showed the lowest reverse permeation, indicating that steric hindrance played a role in the reverse diffusion of nutrients [47, 48]. Phosphate and sulphate ions, besides having a relatively high hydrated radius, possess negatively charged multivalent ions and are thus

subjected to electrostatic repulsion resulting in lower RSF. The difference of RSF amongst the solute ions can also be explained based on their initial concentration. In fact, previous studies have shown that RSF increases with the increase in draw solutes concentration [49, 50]. Potassium had the highest concentration (36.8 g/L) while NH_4^+ ions had the lowest (1.4 g/L) followed by NO_3^- (8.7 g/L) in the commercial liquid fertilizer DS. Based on their hydrated radii and diffusivity [51], these solutes may appear to have similar reverse diffusion transport behaviour. However, results in Figure 2c show that the reverse diffusion of K^+ was significantly higher than for NH_4^+ and NO_3^- which may be related to their differences in the initial concentration. Another explanation for the difference in RSF between K^+ , NH_4^+ and NO_3^- could be ion pairing. For instance, NH_4Cl and $\text{NH}_4\text{H}_2\text{PO}_4$ both contain NH_4^+ which can easily diffuse through the membrane [52]. However, NH_4Cl will have a higher RSF since both NH_4^+ and Cl^- will readily and equally diffuse through the membrane. On the other hand, $\text{NH}_4\text{H}_2\text{PO}_4$ will have a lower RSF because the diffusion of NH_4^+ will be limited since the corresponding anion (i.e., HPO_4^{2-}) has a much larger hydrated radius, reducing its reverse permeation. In this case, the limited diffusion of NH_4^+ is necessary in order to maintain electroneutrality. Therefore, depending on their associated ions, the reverse transport of different solutes will be different.

Figure 2

3.1.2 Long-term studies with synthetic wastewater: Fouling behaviour and water flux recovery

The long-term FDFO operation was carried out to achieve a wastewater feed recovery of up to 75% using commercial hydroponic nutrient solution as DS in a batch process and the performance assessed in terms of water flux, reverse solute flux and water flux recovery after hydraulic flushing and osmotic backwashing (Figure 3 and Figures S5 and S6, SI). Figure S5 shows that the water flux was initially fairly stable up to 25% recovery rate and then the flux significantly decreased to about 85% on reaching recovery rate of 75%. The water flux decline is mostly due to continuous decrease of the osmotic pressure driving force (i.e., dilution of the fertilizer DS and concentration of the feed solution in a batch mode of operation) and also likely due to the deposition of foulants on the membrane surface, increasing the resistance to water permeation through the membrane. In fact, visual observation of the membrane surface after the experiment showed a brownish cake layer

formed with a loose structure (Figure S6, SI).

At the end of each FDFO performance experiment, two physical cleaning methods (i.e., hydraulic flushing and osmotic backwashing) were adopted to remove the deposited foulants and recover the initial water flux. Results in Figure 3a show a partial water flux recovery of only about 75% after the hydraulic flushing, which may be explained by the surface structure of the TFC FO membrane. In fact, the membrane surface of TFC is much rougher than that of CTA which lowers the efficacy of physical washing [29]. Osmotic backwashing, however, was able to restore up to 95% of the initial water flux (Figure 3a). In fact, this cleaning method was employed in previous studies and showed better performance for the removal of foulants within the support layer [43, 53, 54]. Figure S5 (SI) shows the SEM images of the virgin membrane, the fouled membrane and the membrane surface after hydraulic flushing and osmotic backwashing. It can be clearly seen that the surface of the membranes after both cleaning methods is very similar to the virgin membrane, indicating that most of the foulants deposited on the membrane surface were easily removed by physical hydraulic flushing. However, after the hydraulic flushing, a partial fouling layer can still be observed which was probably attached strongly on the membrane surface and not easily removed by simple hydraulic flushing.

The reverse nutrient diffusion during long-term operation using synthetic wastewater as feed showed a similar trend but slightly lower values compared to the results obtained during the short-term experiments using DI water as feed. This can be attributed to the formation of the organic foulant cake layer that reduced the reverse solute transport through the membrane. In fact, it has been previously demonstrated that the formation of organic fouling layer rendered the membrane surface negatively charged which reduces the reverse transport of negatively charged solutes (e.g. HPO_4^{2-}) by enhanced electrostatic repulsion by the fouling layer. Thus, to maintain the electrical neutrality of the DS, the reverse diffusion of the coupled positive ions also improves [20, 55].

Figure 3

3.2 Performances of pilot-scale FDFO operations

According to the manufacturer, the commercial hydroponic solution used in this study must

be diluted 250 times while the final pH and conductivity must fall within the range of 6.0-6.5 and 1.5-2.0 mS/cm, respectively. The osmotic dilution using synthetic wastewater as feed was carried out for the commercial fertilizer Part B only in three stages as described in Section 2.2. The first stage was performed in FO mode (i.e., using osmotic driving force only) while the second and third stages were carried out under PAO mode (i.e., using osmotic driving force combined with an applied hydraulic pressure at 2 bar). These 3 stages were necessary as the pilot-scale FO process has to be operated in a batch mode and hence the desired dilution could not be achieved in a single stage. In fact, a recent FDFO study [37] demonstrated that the additional hydraulic driving force not only enhances the permeate flux when the osmotic driving force is significantly reduced (i.e., the osmotic pressure of the diluted DS approaches the feed solution one) but also could further dilute the DS beyond the point of osmotic equilibrium which is not possible under the FO mode of operation alone. Therefore, PAO could eliminate the need for an additional post-treatment process such as nanofiltration (NF) for enhancing the fertilizer dilution [15] and thus reduce the overall process footprint and cost. Besides, this study [37] also demonstrated that the effective gain in water flux was higher when the DS concentration becomes closer to the osmotic equilibrium when the osmotic driving force approaches zero. This is also one of the reasons why PAO was applied in the second and third stages in this study and not in the first stage.

3.2.1 FDFO performance: Water flux and reverse salt flux

The results from the pilot-scale investigations are gathered in Figure 4. Figure 4a and 4b show the water flux, the osmotic pressure of the commercial fertilizer and the accumulated permeate volume during the three different stages of pilot operation. During stage 1 (i.e., FO mode), the gradual decrease in water flux is related to the continuous dilution of the commercial fertilizer since both the water flux and the DS osmotic pressure are following the same trend (Figures 4a and 4b). At the end of stage 1, the osmotic pressure from the commercial hydroponic solution fell down to 5.5 bar (corresponding to a conductivity of 8.6 mS/cm) while the water flux decreased to 5.9 LMH. The additional 2 bar pressure applied during stage 2 of the FO operation increased the initial water flux by 57%. It is interesting to note that, at the beginning of stage 3, a small water flux increase (i.e., 18%) was observed; although the driving force was similar to the one at the end of stage 2. This increase in water flux could have been due to cake relaxation caused by the interruption of operation between

the two stages. Another possible reason behind this water flux improvement could be due to the feed solution by-pass valve that needs to be closed at the beginning of the experiment; generating temporarily an increase in the feed flow rate which can act as a small hydraulic flushing.

A recent PAO study [56] showed that the application of hydraulic pressure contributes positively on the water flux but also resulted in more severe CP effects affecting the efficiency of the osmotic pressure, especially when the hydraulic pressure contribution becomes predominant. Figure 4d shows that, at the beginning of stage 2, the contribution of the osmotic pressure is still predominant over the hydraulic pressure (i.e., 5.5 bar for the diluted DS with a conductivity of 8.6 mS/cm against 2 bar applied pressure), however, at the beginning of stage 3, the osmotic pressure of the diluted DS was only 0.4 bar (i.e., which corresponding to a conductivity of 1.2 mS/cm), which is very close to the osmotic pressure of the synthetic wastewater feed (i.e., 0.14 bar) and much lower than the additional 2 bar pressure. Therefore, CP effects were most likely more prominent towards the end of stage 2, limiting the expected flux enhancement. Another likely explanation for the lower than expected water flux improvement can be the enhanced membrane fouling due to PAO operation. In fact, it has been explained in previous studies [56-58] that in PAO, both fouling layer compaction and cake-enhanced osmotic pressure are expected to occur, resulting in a slightly higher fouling propensity compared to FO (where only cake-enhanced osmotic pressure occurred). It is very likely that, under the 2 PAO stages, a more compact fouling layer has been formed on the membrane surface leading to an additional barrier for water permeation. Previous studies on FO (no pressure), RO (high pressure) and low-pressure ultrafiltration (0.5 to 1 bar) directly correlated the fouling layer thickness and foulant volume to the applied pressure [58, 59]. In those studies, it was found that, for the same amount of deposited matter, the deposit thickness was lower at higher applied pressure; suggesting a more compact fouling layer at increasing applied pressure.

Finally, Figure 4c shows the RSF results at the end of each pilot stage. During stage 1 (FO mode), the reverse nutrients transport was quite similar to the values obtained during the bench-scale experiments with synthetic wastewater as feed. However, during both stage 2 and 3 under the PAO mode of operations, the RSF was significantly reduced, unlike in the FO process where a higher concentration difference leads to a more severe RSF and an increase

in the water flux. In the PAO process, however, the enhanced water permeation increases the dilutive ICP that reduces the draw solute concentration at the membrane interface which results in lower RSF [56].

Figure 4

3.2.2 Preliminary assessment of energy and capital costs

Combining the FDFO process with PAO could help in saving the overall operating costs (i.e., energy and membrane costs) compared to applying FDFO or PAO alone. However, in order for this hybrid FDFO-PAO process to be economically feasible, a trade-off between membrane and energy costs (i.e., from the additional pressure) has to be determined. Figure 5 displays the capital and operational expenses (i.e. CAPEX and OPEX) for different process configurations (i.e., FDFO alone, FDFO coupled with PAO at different DS osmotic dilution and PAO alone). It is clear from this figure that using osmotic dilution alone will result in higher CAPEX due to the higher required membrane elements, pressure vessels as well as equipment and associated materials (Figure 5a). On the other hand, using PAO only will result in higher OPEX due to higher energy requirements as well as higher chemical and repair and maintenance costs (Figure 5b). To optimise this hybrid process, it is therefore necessary to find out at which stage (i.e., DS concentration) PAO should be applied. Although previous studies have found that applying PAO at lower DS concentration (i.e. at higher FO recovery rate) is more beneficial in terms of water flux enhancement (e.g. [37]), this also means that the initial feed concentration for PAO operation will be higher due to increased recovery rates. The draw solute concentration in the feed stream due to RSF will be also much higher. Both these increased solute concentrations increases the need for a higher applied pressure thereby increasing the energy consumption of the PAO feed pump (i.e. energy component in Figure 5b is higher at higher FO recovery rate) to achieve similar final DS concentration [60]. At the same time, Figure 5 shows that if the FO process is operated at lower recovery rate, then the contribution of applied pressure (PAO) to the water flux gain will be lower (i.e. because the osmotic pressure of the DS will still be significant) which will in turn increase the total membrane area (Figure 5a) and thus the membrane replacement cost (Figure 5b). Further studies are therefore needed in this area in order to find the optimum process configurations for this hybrid FDFO-PAO system.

Figure 5

3.2.3 Final water quality: Suitable for hydroponics?

Finally, Table 4 presents the water quality of the diluted fertilizer at each stage of the pilot-scale operation as well as the final nutrient solution (i.e., diluted part B mixed with Part A). It is clear from the results that the concentration of nutrients is decreasing at each stage due to the continuous dilution of the fertilizer DS. The pH and conductivity of the final product complied with the hydroponic requirements (i.e., pH 6.0-6.5 and conductivity 1.5-2.0 mS/cm), demonstrating the feasibility of the FDFO-PAO process to produce nutrient solution suitable for hydroponics application. The pH of hydroponic solutions should usually fall between 5.5 and 6.5 since previous studies have shown that nutrient deficiencies can occur outside this acceptable range because the pH can greatly affect the availability of fertilizer salts [6, 61].

A diluted fertilizer solution was also separately prepared with distilled water in order to remove the presence of draw solutes from reverse diffusion and obtain the correct nutrients concentration following the manufacturer's guidelines for hydroponic solution, presented in brackets in Table 4. It can be seen that the use of the FDFO process to prepare the hydroponic solution resulted in a loss of some essential nutrients to variable extent. Nutrient deficiencies can greatly affect the plant health and growth and typical symptoms generally include reduced plant growth, yellowing and/or scorching of leaves and growing tips as depicted in Table S1 (SI). The type of symptoms and their extent on plant growth and health will depend on the nutrient(s) being deficient [6, 61]. For instance, nitrogen deficiency will lead to severe stunting while potassium deficiency will lead to yellowing and scorching of old leaves, highlighting the importance of these macronutrients. Table S2 (SI) shows the hydroponic formulation of two standard recipes (i.e., Huett and Hoagland hydroponic formulations [40, 62]) and the nutrients concentration in the final FDFO solution are within the range of these two standard hydroponic solutions, suggesting that nutrient deficiencies should not be expected for the hydroponic lettuce.

Table 5

3.3 Response of hydroponic lettuce plants grown in FDFO nutrient solutions

The response of hydroponic plants grown using different nutrient solutions obtained from the FDFO process has been assessed in terms of different growth parameters, including fresh biomass production (aerial parts and roots) and dried biomass (oven dried at 60 °C for 72 h). Growth performance results gathered in Figure 6 show similar growth patterns between the selected treatments indicating that the FDFO nutrient solution can be applicable to any hydroponic applications using different plant species. The fresh and dry weights of aerial parts and roots were also comparable to other reports [23, 63]. Plants grown in T2 (i.e., Optimum Grow - same hydroponic nutrient solution used as DS in FO experiments) revealed the highest biomass production followed by plants grown in T1 (i.e., FDFO nutrient solution) and then T3 (i.e., Half-strength Hoagland's solution). Fresh and dry biomass data displayed in Figure 6 show that the fresh weight of aerial parts was 158.53 g (\pm 14.9 g), 160.32 g (\pm 20.45 g), and 105.33 g (\pm 14.42 g) for T1, T2 and T3, respectively. The difference in yield between T1, T2 and T3 could be due to cooler and warmer air movement around the first two treatments which created more plant transpiration, then higher photosynthesis and consequently biomass. Lettuce plants fed with FDFO nutrient solution showed no signs of nutrient deficiency (cf. Table S1, SI) indicating the suitability of growing lettuce in NFT system with the prescribed conditions.

Figure 6

4 Conclusions

This study investigated the potential of the FDFO process to produce nutrient solutions for hydroponics through the osmotic dilution of a commercial hydroponic fertilizer solution using wastewater as a sustainable alternative water source. Preliminary bench-scale experiments demonstrated good performance of the commercial liquid fertilizer in terms of water flux and reverse salt flux. The main advantage of using a commercial fertilizer as DS, compared to inorganic salts, relies on its well-balanced macro- and micronutrients composition. The presence of organic nitrogen such as urea can, however, be detrimental to the FDFO process in terms of nutrient loss by reverse diffusion towards the feed water. Physical cleaning was observed adequate to recover the initial water flux by up to 75% while osmotic backwashing was able to recover flux by 95%, highlighting the low-fouling potential

of the FDFO process. Pilot-scale experiments were carried out in different stages incorporating PAO mode of operations in order to achieve the required dilution for hydroponics. The hybrid FDFO-PAO system was able to produce a suitable hydroponic solution in terms of nutrient concentration, pH and conductivity. Future works are still required to further improve this hybrid system in order to find the optimum trade-off between process footprint (FO) and energy costs (PAO). Finally, the diluted nutrient solution produced by the pilot FDFO process was tested to grow hydroponic lettuce plants and growth pattern was compared with plants grown using standard hydroponic formulations. Growth performance results indicate that the lettuce growth pattern with FDFO diluted fertilizer solution showed similar trends with the standard hydroponic treatments and their biomass were comparable to previous reports. These results are very promising for the future of the FDFO process for hydroponic applications to grow any types of crops.

Acknowledgements

The research reported in this paper is part of a collaborative project between the King Abdullah University of Science and Technology (KAUST) and the University of Technology Sydney (UTS) and funded through a SEED Fund provided by KAUST. Support was also provided to HKS by the Australian Research Council (ARC) through Future Fellowship (FT140101208).

References:

- [1] M.E. Assessment, *Ecosystems and human well-being*, Island Press Washington, DC, 2005.
- [2] J. Clay, *World agriculture and the environment: a commodity-by-commodity guide to impacts and practices*, Island Press, Washington, DC, 2013.
- [3] X. Cai, M.W. Rosegrant, 10 *World Water Productivity: Current Situation and Future Options*, *Water productivity in agriculture: limits and opportunities for improvement*, 1 (2003) 163.
- [4] J.B. Jones Jr, *Hydroponics: its history and use in plant nutrition studies*, *Journal of plant Nutrition*, 5 (1982) 1003-1030.
- [5] M.H. Jensen, *Hydroponics worldwide*, in: *International Symposium on Growing Media and Hydroponics*, 1997, pp. 719-730.
- [6] S. Parks, *Nutrient management of Asian vegetables*, Horticulture Australia, 2011.
- [7] M. Qadir, B.R. Sharma, A. Bruggeman, R. Choukr-Allah, F. Karajeh, *Non-conventional water resources and opportunities for water augmentation to achieve food security in water scarce countries*, *Agricultural water management*, 87 (2007) 2-22.
- [8] A. Angelakis, M.M. Do Monte, L. Bontoux, T. Asano, *The status of wastewater reuse practice in the Mediterranean basin: need for guidelines*, *Water Research*, 33 (1999) 2201-2217.
- [9] U.S. EPA, *Guidelines for water reuse*, Environmental Protection Agency, Municipal Support Division Office of Wastewater Management Office of Water Washington, DC. Agency for International Development Washington DC, EPA/625/R-04/108, Cincinnati, OH US EPA/625/R-04/108, (2012).
- [10] X. Wang, V.W. Chang, C.Y. Tang, *Osmotic membrane bioreactor (OMBR) technology for wastewater treatment and reclamation: Advances, challenges, and prospects for the future*, *Journal of Membrane Science*, 504 (2016) 113-132.
- [11] G. Ferro, A. Fiorentino, M.C. Alferez, M.I. Polo-López, L. Rizzo, P. Fernández-Ibáñez, *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 (2015) 65-73.
- [12] S.S. Ahluwalia, D. Goyal, *Microbial and plant derived biomass for removal of heavy metals from wastewater*, *Bioresource technology*, 98 (2007) 2243-2257.
- [13] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, *A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: evaluating the performance of fertilizer draw solutions*, *Journal of Membrane Science*, 375 (2011) 172-181.
- [14] S. Phuntsho, H.K. Shon, S. Hong, S. Lee, S. Vigneswaran, J. Kandasamy, *Fertiliser drawn forward osmosis desalination: the concept, performance and limitations for fertigation*, *Reviews in Environmental Science and Bio/Technology*, 11 (2012) 147-168.
- [15] S. Phuntsho, S. Hong, M. Elimelech, H.K. Shon, *Forward osmosis desalination of brackish groundwater: Meeting water quality requirements for fertigation by integrating nanofiltration*, *Journal of Membrane Science*, 436 (2013) 1-15.
- [16] S. Phuntsho, H.K. Shon, T. Majeed, I. El Saliby, S. Vigneswaran, J. Kandasamy, S. Hong, S. Lee, *Blended fertilizers as draw solutions for fertilizer-drawn forward osmosis desalination*, *Environmental Science & Technology*, 46 (2012) 4567-4575.
- [17] C. Lew, J. Hu, L. Song, L. Lee, S. Ong, W. Ng, H. Seah, *Development of an integrated membrane process for water reclamation*, *Water Science and Technology*, 51 (2005) 455-463.
- [18] B. Van der Bruggen, P. Luis, *Forward osmosis: understanding the hype*, *Reviews in Chemical Engineering*, 31 (2015) 1-12.
- [19] B.D. Coday, B.G. Yaffe, P. Xu, T.Y. Cath, *Rejection of trace organic compounds by forward osmosis membranes: a literature review*, *Environmental Science & Technology*, 48 (2014) 3612-3624.
- [20] M. Xie, M. Zheng, P. Cooper, W.E. Price, L.D. Nghiem, M. Elimelech, *Osmotic dilution for sustainable greenwall irrigation by liquid fertilizer: Performance and implications*, *Journal of Membrane Science*, 494 (2015) 32-38.
- [21] S. Zou, Z. He, *Enhancing wastewater reuse by forward osmosis with self-diluted commercial fertilizers as draw solutes*, *Water Research*, 99 (2016) 235-243.

- [22] D.S. Domingues, H.W. Takahashi, C.A. Camara, S.L. Nixdorf, Automated system developed to control pH and concentration of nutrient solution evaluated in hydroponic lettuce production, *Computers and electronics in agriculture*, 84 (2012) 53-61.
- [23] S. Smoleń, I. Kowalska, W. Sady, Assessment of biofortification with iodine and selenium of lettuce cultivated in the NFT hydroponic system, *Scientia Horticulturae*, 166 (2014) 9-16.
- [24] J. Park, J.-h. Yoon, S. Depuydt, J.-W. Oh, Y.-m. Jo, K. Kim, M.T. Brown, T. Han, The sensitivity of an hydroponic lettuce root elongation bioassay to metals, phenol and wastewaters, *Ecotoxicology and Environmental Safety*, 126 (2016) 147-153.
- [25] T.Y. Cath, M. Elimelech, J.R. McCutcheon, R.L. McGinnis, A. Achilli, D. Anastasio, A.R. Brady, A.E. Childress, I.V. Farr, N.T. Hancock, Standard methodology for evaluating membrane performance in osmotically driven membrane processes, *Desalination*, 312 (2013) 31-38.
- [26] J.B. Jones Jr, *Hydroponics: a practical guide for the soilless grower*, CRC press, 2016.
- [27] N.S. Mattson, C. Peters, *A recipe for hydroponic success*, Inside Grower. Ball Publishing, Chicago, IL, (2014) 16-19.
- [28] S. Lee, M. Elimelech, Relating organic fouling of reverse osmosis membranes to intermolecular adhesion forces, *Environmental Science & Technology*, 40 (2006) 980-987.
- [29] B. Mi, M. Elimelech, Organic fouling of forward osmosis membranes: fouling reversibility and cleaning without chemical reagents, *Journal of Membrane Science*, 348 (2010) 337-345.
- [30] B. Mi, M. Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, *Journal of Membrane Science*, 320 (2008) 292-302.
- [31] Q. She, R. Wang, A.G. Fane, C.Y. Tang, Membrane fouling in osmotically driven membrane processes: a review, *Journal of Membrane Science*, 499 (2016) 201-233.
- [32] M. Xie, E. Bar-Zeev, S.M. Hashmi, L.D. Nghiem, M. Elimelech, Role of reverse divalent cation diffusion in forward osmosis biofouling, *Environmental Science & Technology*, 49 (2015) 13222-13229.
- [33] M. Zhang, D. Hou, Q. She, C.Y. Tang, Gypsum scaling in pressure retarded osmosis: experiments, mechanisms and implications, *Water Research*, 48 (2014) 387-395.
- [34] S. Lee, C. Boo, M. Elimelech, S. Hong, Comparison of fouling behavior in forward osmosis (FO) and reverse osmosis (RO), *Journal of Membrane Science*, 365 (2010) 34-39.
- [35] Y. Kim, S. Lee, H.K. Shon, S. Hong, Organic fouling mechanisms in forward osmosis membrane process under elevated feed and draw solution temperatures, *Desalination*, 355 (2015) 169-177.
- [36] J.E. Kim, S. Phuntsho, F. Lotfi, H.K. Shon, Investigation of pilot-scale 8040 FO membrane module under different operating conditions for brackish water desalination, *Desalination and Water Treatment*, 53 (2015) 2782-2791.
- [37] S. Sahebi, S. Phuntsho, J. Eun Kim, S. Hong, H. Kyong Shon, Pressure assisted fertiliser drawn osmosis process to enhance final dilution of the fertiliser draw solution beyond osmotic equilibrium, *Journal of Membrane Science*, 481 (2015) 63-72.
- [38] R. Valladares Linares, Z. Li, V. Yangali-Quintanilla, N. Ghaffour, G. Amy, T. Leiknes, J.S. Vrouwenvelder, Life cycle cost of a hybrid forward osmosis – low pressure reverse osmosis system for seawater desalination and wastewater recovery, *Water Research*, 88 (2016) 225-234.
- [39] AEMC, Final Report: 2013 Residential Electricity Price Trends, Australian Energy Market Commission (AEMC), (2013).
- [40] D.R. Hoagland, D.I. Arnon, The water-culture method for growing plants without soil, *Circular. California Agricultural Experiment Station*, 347 (1950).
- [41] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia-carbon dioxide forward osmosis: influence of draw and feed solution concentrations on process performance, *Journal of Membrane Science*, 278 (2006) 114-123.
- [42] J.R. McCutcheon, M. Elimelech, Modeling water flux in forward osmosis: implications for improved membrane design, *AIChE journal*, 53 (2007) 1736-1744.
- [43] C. Boo, M. Elimelech, S. Hong, Fouling control in a forward osmosis process integrating seawater desalination and wastewater reclamation, *Journal of Membrane Science*, 444 (2013) 148-156.

- [44] D.I. Kim, J. Kim, H.K. Shon, S. Hong, Pressure retarded osmosis (PRO) for integrating seawater desalination and wastewater reclamation: energy consumption and fouling, *Journal of Membrane Science*, 483 (2015) 34-41.
- [45] N.T. Hancock, T.Y. Cath, Solute coupled diffusion in osmotically driven membrane processes, *Environmental Science & Technology*, 43 (2009) 6769-6775.
- [46] Z. Li, R.V. Linares, S. Bucs, C. Aubry, N. Ghaffour, J.S. Vrouwenvelder, G. Amy, Calcium carbonate scaling in seawater desalination by ammonia-carbon dioxide forward osmosis: Mechanism and implications, *Journal of Membrane Science*, 481 (2015) 36-43.
- [47] A.A. Alturki, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, M. Elimelech, Removal of trace organic contaminants by the forward osmosis process, *Separation and Purification Technology*, 103 (2013) 258-266.
- [48] R.V. Linares, V. Yangali-Quintanilla, Z. Li, G. Amy, Rejection of micropollutants by clean and fouled forward osmosis membrane, *Water Research*, 45 (2011) 6737-6744.
- [49] Q. Ge, J. Su, G.L. Amy, T.-S. Chung, Exploration of polyelectrolytes as draw solutes in forward osmosis processes, *Water Research*, 46 (2012) 1318-1326.
- [50] S. Phuntsho, S. Sahebi, T. Majeed, F. Lotfi, J.E. Kim, H.K. Shon, Assessing the major factors affecting the performances of forward osmosis and its implications on the desalination process, *Chemical Engineering Journal*, 231 (2013) 484-496.
- [51] E. Nightingale Jr, Phenomenological theory of ion solvation. Effective radii of hydrated ions, *The Journal of Physical Chemistry*, 63 (1959) 1381-1387.
- [52] B. Wishaw, R. Stokes, The diffusion coefficients and conductances of some concentrated electrolyte solutions at 25, *Journal of the American Chemical Society*, 76 (1954) 2065-2071.
- [53] N.Y. Yip, M. Elimelech, Influence of natural organic matter fouling and osmotic backwash on pressure retarded osmosis energy production from natural salinity gradients, *Environmental Science & Technology*, 47 (2013) 12607-12616.
- [54] R. Valladares Linares, Z. Li, V. Yangali-Quintanilla, Q. Li, G. Amy, Cleaning protocol for a FO membrane fouled in wastewater reuse, *Desalination and Water Treatment*, 51 (2013) 4821-4824.
- [55] M. Xie, L.D. Nghiem, W.E. Price, M. Elimelech, Impact of humic acid fouling on membrane performance and transport of pharmaceutically active compounds in forward osmosis, *Water Research*, 47 (2013) 4567-4575.
- [56] G. Blandin, A.R.D. Verliefdé, C.Y. Tang, A.E. Childress, P. Le-Clech, Validation of assisted forward osmosis (AFO) process: Impact of hydraulic pressure, *Journal of Membrane Science*, 447 (2013) 1-11.
- [57] T. Yun, Y.-J. Kim, S. Lee, S. Hong, G.I. Kim, Flux behavior and membrane fouling in pressure-assisted forward osmosis, *Desalination and Water Treatment*, 52 (2014) 564-569.
- [58] M. Xie, J. Lee, L.D. Nghiem, M. Elimelech, Role of pressure in organic fouling in forward osmosis and reverse osmosis, *Journal of Membrane Science*, 493 (2015) 748-754.
- [59] J. Mendret, C. Guigui, P. Schmitz, C. Cabassud, In situ dynamic characterisation of fouling under different pressure conditions during dead-end filtration: Compressibility properties of particle cakes, *Journal of Membrane Science*, 333 (2009) 20-29.
- [60] S. Phuntsho, J.E. Kim, M.A. Jahir, S. Hong, Z. Li, N. Ghaffour, T. Leiknes, H.K. Shon, Fertiliser drawn forward osmosis process: Pilot-scale desalination of mine impaired water for fertigation, *Journal of Membrane Science*, 508 (2016) 22-31.
- [61] M. Brechner, A. Both, C. Staff, *Hydroponic Lettuce Handbook*, Cornell Controlled Environment Agriculture.
- [62] D.O. Huett, Precise nutrient solution formulation and management for hydroponically grown crops, in: *Agricultural Science and Technology*, Food and Agriculture Organization of the United Nations, Alstonville (Australia), 1993.
- [63] D.C. Sikawa, A. Yakupitiyage, The hydroponic production of lettuce (*Lactuca sativa* L) by using hybrid catfish (*Clarias macrocephalus* × *C. gariepinus*) pond water: Potentials and constraints, *Agricultural water management*, 97 (2010) 1317-1325.

Figure Captions

Figure 1: Schematic diagram of the pilot-scale FO experimental set up and illustration of 8040 spiral wound thin film composite (TFC) FO modules manufactured by Toray Inc.

Figure 2: (a) Average water flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ or LMH), (b) Final TOC concentration in the feed solution, (c) Reverse nutrient fluxes of commercial liquid fertilizer and (d) Reverse salt flux of 1.4 M NaCl and 1.4 M NaCl with 500 mgC/L humic acid draw solutions. Experimental conditions were: feed solution: DI water; draw solutions: commercial fertilizer Part B, 1.4 M NaCl and 1.4 M NaCl with 500 mgC/L humic acid; crossflow velocity: 8.5 cm/s; temperature: 25°C; Operating time: up to 25% water recovery. Error bars are standard deviation of duplicate measurements.

Figure 3: (a) Average water flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ or LMH) at the initial stage (i.e., up to 25% water recovery), final stage (after 75% water recovery), after hydraulic flushing and after osmotic backwashing and water flux recovery after hydraulic flushing and osmotic backwashing (b) Reverse nutrient fluxes of commercial liquid fertilizer. Experimental conditions were: feed solution - synthetic wastewater; draw solutions - commercial fertilizer Part B; crossflow velocity - 8.5 cm/s; temperature - 25°C; Operating time - up to 75% water recovery. Error bars are standard deviation of duplicate measurements.

Figure 4: (a) Water flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ or LMH), (b) Osmotic pressure of commercial fertilizer and accumulated permeate volume, (c) Reverse nutrient fluxes and (d) Relative contribution of osmotic pressure (i.e. calculated bulk osmotic pressure) and hydraulic pressure (i.e. 2 bar applied pressure) to the driving force during pilot-scale operation. Experimental conditions

were: feed solution: synthetic wastewater; draw solutions: commercial fertilizer Part B; Initial DS and FS volumes were 75 L and 1000 L respectively; Operating time: Up to 250 times dilution (based on EC value). The osmotic pressure of diluted draw solution was calculated using the ROSA software (Version 9.1, Filmtec DOWTM Chemicals, USA) based on continuously measured EC values.

Figure 5: (a) CAPEX and (b) OPEX costs per unit volume of product water for FDFO, PAO and different FDFO-PAO configuration processes. N.B. DF = Dilution Factor; Others = Civil engineering, intakes, working capital and contingencies.

Figure 6: Fresh and dry biomass of hydroponic lettuce grown in three different treatments: T1 feeds with FDFO nutrient solution, T2 feeds with commercial fertilizer diluted with distilled water and T3 feeds with half-strength Hoagland's solution.

List of Tables

Table 1: Characteristics of the commercial liquid fertilizer used in this study.

Parameters	Part A*	Part B*
EC (mS/cm)	119.6	107.2
pH	2.63	4.26
TDS (mg/L)	95100	67300
TOC (mg/L)	1136	519.5
Osmotic pressure (bar)**	95.2	66.3
TN (mg/L)	41000	12000
N-NO ₃ ⁻ (mg/L)	33600	8700
N-NH ₄ ⁺ (mg/L)	3800	1400
N-NO ₂ ⁻ (mg/L)	n.d.	n.d.
P-PO ₄ ²⁻ (mg/L)	0	9000
K ⁺ (mg/L)	25400	36800
Ca ²⁺ (mg/L)	36600	0
Mg ²⁺ (mg/L)	0	10340
SO ₄ ²⁻ (mg/L)	0	12900

*Part A also contains Fe and Part B contains essential micronutrients (i.e., Mn, B, Zn and Mo). **The osmotic pressure was calculated using ROSA software (Version 9.1, Filmtech Dow Chemicals, USA).

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

Parameters	Value
Glucose (mg/L)	275
Peptone (mg/L)	100
Beef extract (mg/L)	100
Urea (mg/L)	10
NaHCO ₃ (mg/L)	100
KH ₂ PO ₄ (mg/L)	20
NH ₄ Cl (mg/L)	25
MgCl ₂ ·6H ₂ O (mg/L)	10
CaCl ₂ ·2H ₂ O (mg/L)	5
pH	6.58
EC (mS/cm)	0.226
TOC (mg/L)	175.6
Osmotic Pressure (bar)*	0.14

*The osmotic pressure was calculated using ROSA software (Version 9.1, Filmtech Dow Chemicals, USA).

Table 3: Chemicals composition of Half-Strength Hoagland's solution ^a

Compounds	Amounts per volume of water		
	<i>Stock concentrate #1</i>		
	500 mL	1 L	
KNO ₃	25.26 g	50.52 g	
KH ₂ PO ₄	14.42 g	28.84 g	
MgSO ₄ ·6H ₂ O	11.48 g	22.96 g	
Micronutrient concentrate	50 mL	100 mL	
	<i>Stock concentrate #2</i>		
	Ca(NO ₃) ₂ ^b	45.69 g	91.38 g
	Fe-EDTA 13%	2.41 g	4.82 g
	<i>Micronutrient concentrate</i>		
	200 mL	1L	
	H ₃ BO ₃ ^c	0.57 g	2.85 g
MnSO ₄ ·H ₂ O	0.30 g	1.5 g	
ZnSO ₄ ·7H ₂ O	0.04 g	0.2 g	
CuSO ₄ ·5H ₂ O	0.01 g	0.05 g	
MoO ₃ ·2H ₂ O	0.004 g	0.02 g	

^a All chemicals were analytical or reagent grade.

^b The iron chelate was thoroughly mixed before adding the dissolved Ca(NO₃)₂

^c H₃BO₃ was dissolved in boiling water. Other salts were added and mixed in 100 mL of water. The dissolved H₃BO₃ was added to the rest and the final volume adjusted.

Table 4: Water quality of diluted draw solution at different stages of pilot-scale operation and final nutrient solution for hydroponic application

	After FO	After PAO 1	After PAO 2	Final Product (Part A + Part B)
pH	5.91	6.84	7.12	6.15

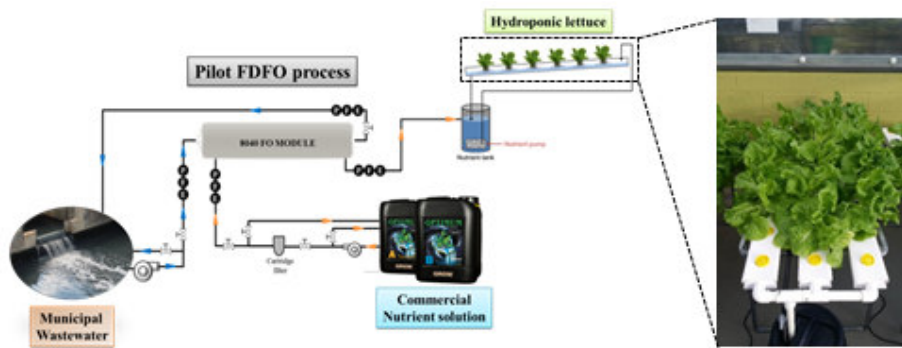
EC (mS/cm)	8.53	1.22	0.47	1.65
TDS (mg/L)	5500	751	262	696
TOC (mg/L)	21.12	9.74	0.65	5.54
TN (mg/L)	800	100	45	204 (212)*
NO ₃ ⁻ (mg/L)	610	82	33.5	159 (169)*
NH ₄ ⁺ (mg/L)	93	9.5	3.5	17.5 (20.5)*
P-PO ₄ ³⁻ (mg/L)	660	90	30	29.5 (36)*
K ⁺ (mg/L)	2180	270	100	201 (249)*
Ca ²⁺ (mg/L)	0**	0**	0**	137 (146)*
Mg ²⁺ (mg/L)	750	100	38	31.5 (41.5)*
SO ₄ ²⁻ (mg/L)	940	120	45	42 (51.5)*

* Values in brackets are the ones obtained when diluted the fertilizer with distilled water.

References:

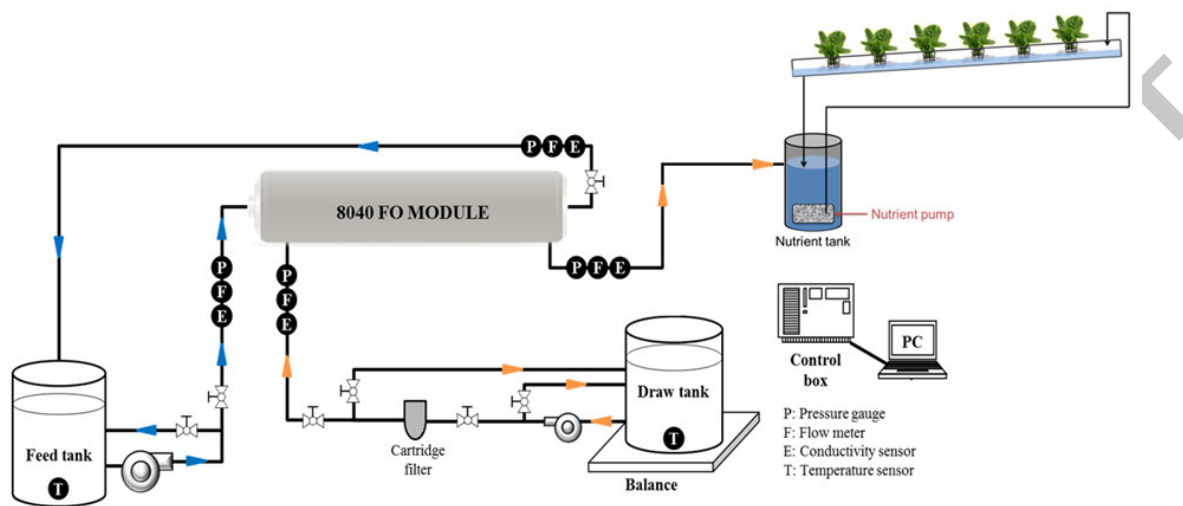
- [1] L. Chen, Y. Gu, C. Cao, J. Zhang, J.-W. Ng, C. Tang, Performance of a submerged anaerobic membrane bioreactor with forward osmosis membrane for low-strength wastewater treatment, *Water Res.*, 50 (2014) 114-123.

Graphical abstract



ACCEPTED MANUSCRIPT

Figure 1



ACCEPTED MANUSCRIPT

Figure 2

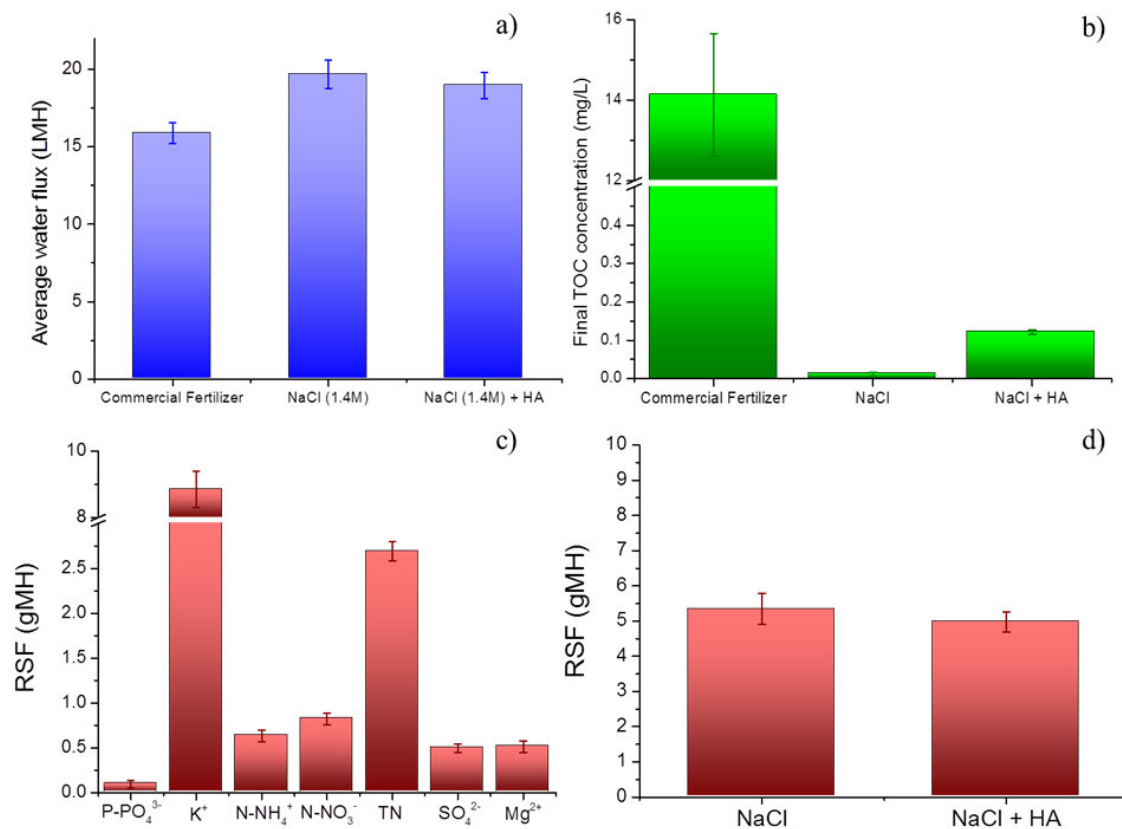


Figure 3

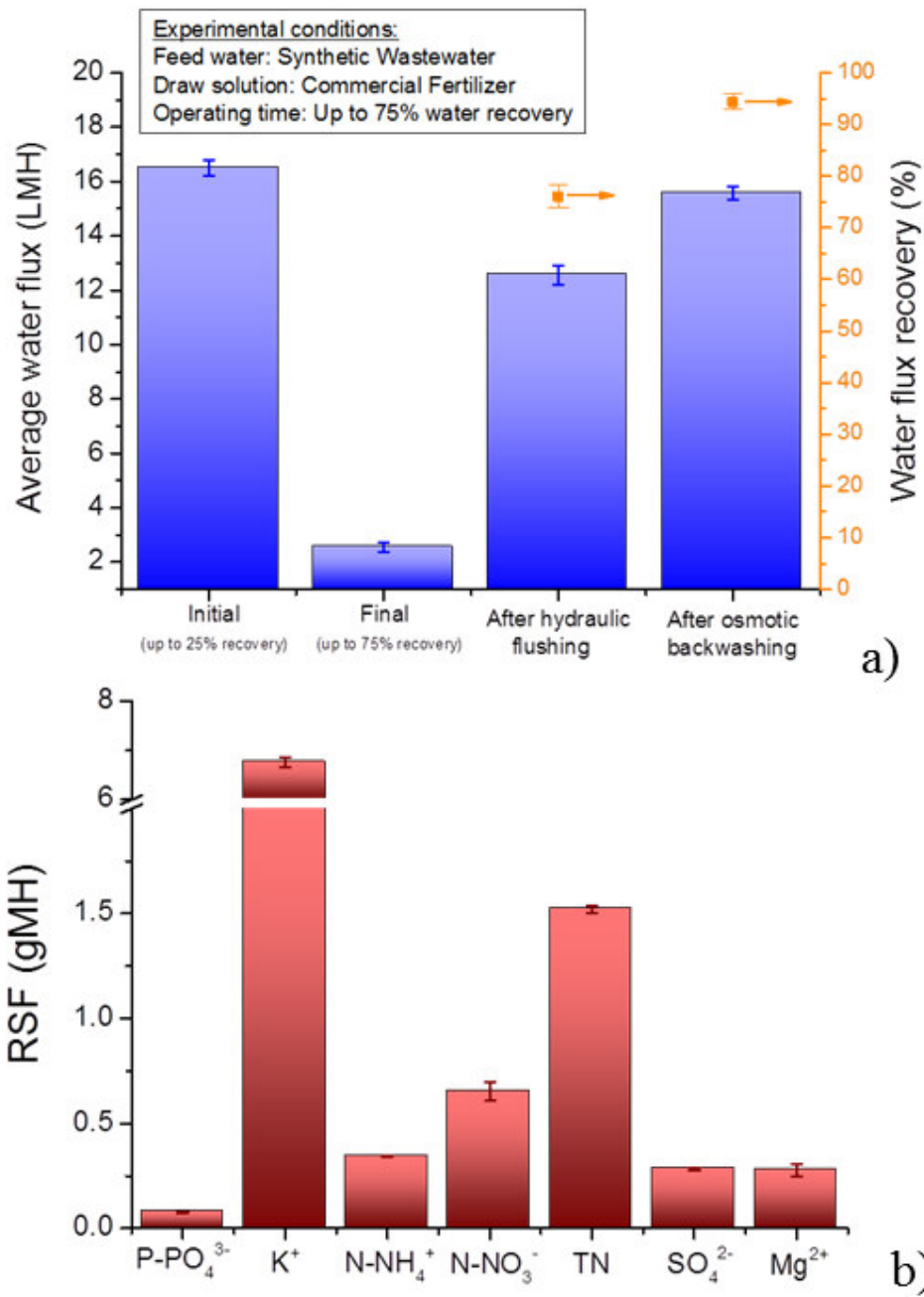


Figure 4

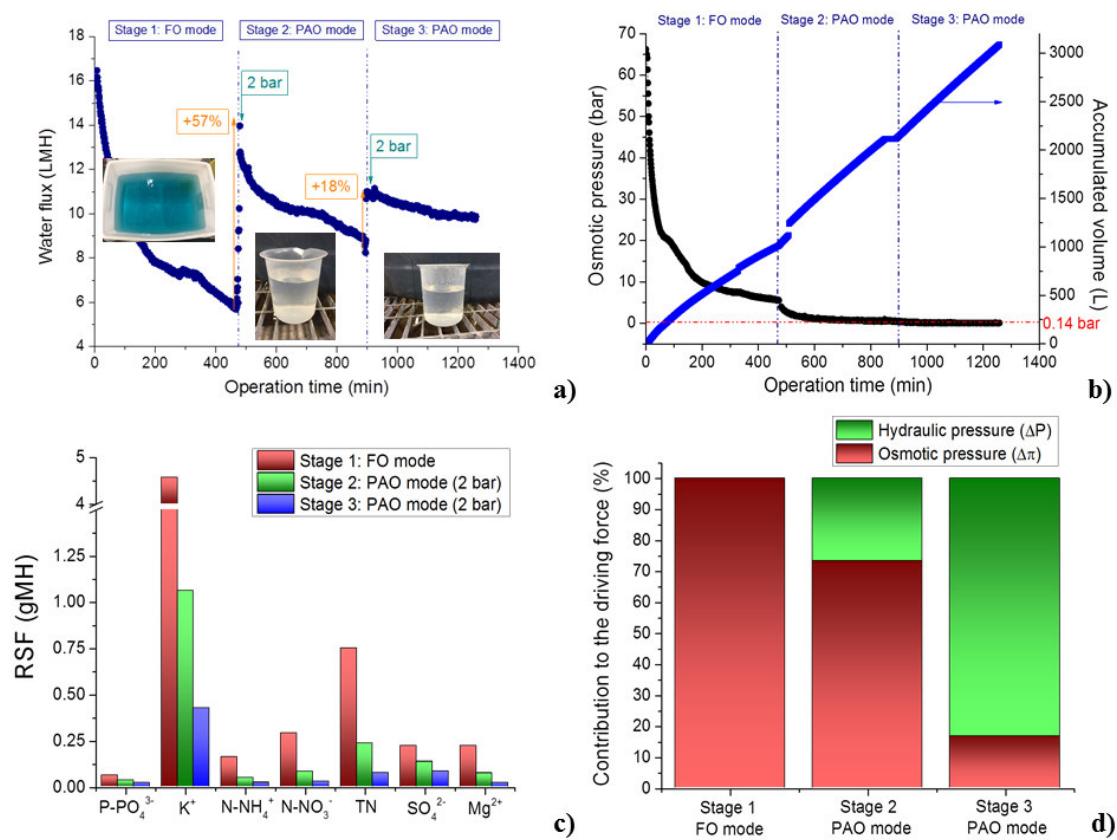
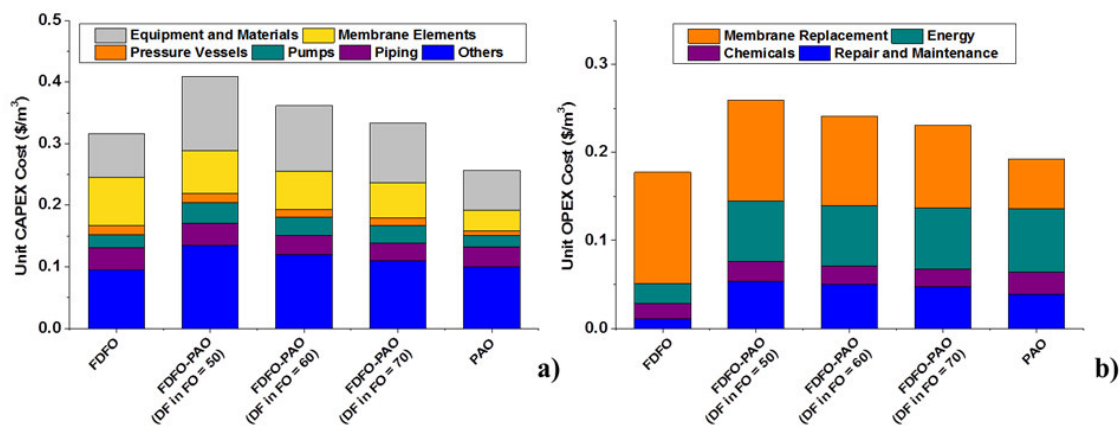
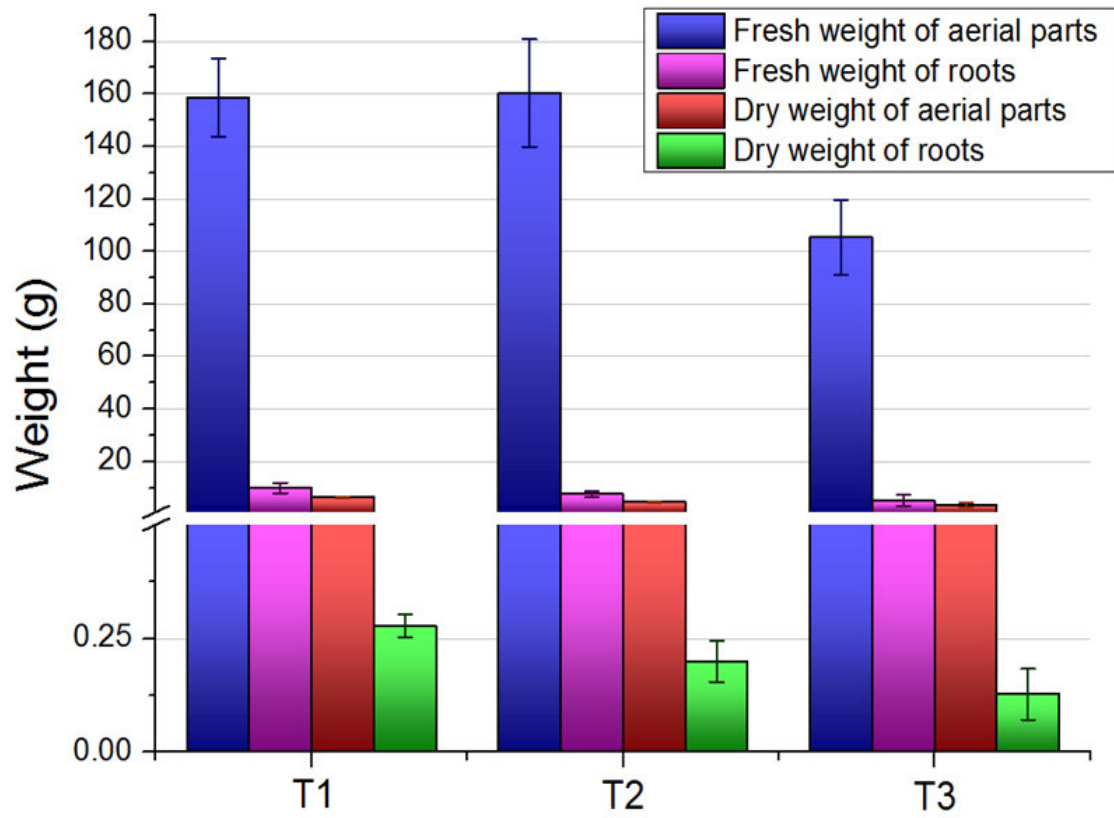


Figure 5



ACCEPTED MANUSCRIPT

Figure 6



ACCEPTED

Research highlights:

- Feasibility of FDFO to produce nutrient solution for hydroponics was evaluated
- Commercial hydroponic solution used as DS provides the required balanced nutrients
- Diluted nutrient solution produced by pilot FDFO was suitable for hydroponic use
- Coupling FDFO with PAO at the latest stages, can help save operational costs
- Lettuce plants fed with FDFO solution showed no signs of nutrient deficiency

ACCEPTED MANUSCRIPT