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Impact of reverse nutrient diffusion on membrane biofouling in fertilizer-drawn forward osmosis

Sheng Li[a], Youngjin Kim[b,c], Laura Chekli[b], Sherub Phuntsho[b], Ho Kyong Shon[b], TorOve Leiknes[a], Noreddine Ghaffour[a,*]

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

[b] School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Post Box 129, Broadway, NSW 2007, Australia

[c] School of Civil, Environmental and Architectural Engineering, Korea University, 1-5 Ga, Anam-Dong, Seongbuk-Gu, Seoul, 136-713, Republic of Korea

noreddine.ghaffour@kaust.edu.sa

Abstract

Biofouling in fertilizer-drawn forward osmosis (FDFO) for water reuse was investigated by spiking pure bacteria species *Pseudomonas aeruginosa PAO1+GFP* and using three different fertilizers KNO_3, KCl and KH_2PO_4 as draw solutions. The performance of FO process for treating synthetic wastewater was assessed and their influence on the membrane fouling and in particular biofouling was evaluated relative to the type of different fertilizers used and their rates of reverse diffusion. FO performances using KNO_3 as draw solute exhibited severer flux decline (63%) than when using KCl (45%) and KH_2PO_4 (30%). Membrane autopsy indicated that the mass of organic foulants and biomass on fouled membrane surface using KNO_3 as draw solute (947.5 mg/m^2 biopolymers, 72 μm biofilm thickness and 53.3 mg/m^2 adenosine triphosphate) were significantly higher than that using KCl (450 mg/m^2 biopolymers, 33 μm biofilm thickness and 28.2 mg/m^2 ATP) and KH_2PO_4 (440 mg/m^2 biopolymers, 35 μm biofilm thickness and 33.5 mg/m^2 ATP). This higher flux decline is likely related to the higher reverse diffusion of KNO_3 (19.8 $g/m^2/h$) than KCl (5.1 $g/m^2/h$) and KH_2PO_4 (3.7 $g/m^2/h$). The reverse diffused potassium could promote the organics and bacterial adhesion on FO membrane via charge screening effect and compression of electrical double layer. Moreover, reverse diffused nitrate provided increased N:P nutrient ratio was favorable for the bacteria to grow on the feed side of the FO membrane.

1. Introduction

With the current world's economic growth, a 53% increase in the global water demand is expected by 2030, up to 6.9 trillion m^3/year as a total demand [1]. The agricultural sector currently consumes about 70% (global average) of accessible freshwater, however, 15–35% of this water is used unsustainably [2]. To alleviate this water stress around the world, wastewater reuse has been intensively investigated in the past two decades. However, it is essential to sufficiently treat wastewater before reuse for irrigation, not only to protect human health but also the quality and quantity of the crops grown using treated wastewater effluent. A variety of wastewater treatment methods have been investigated for irrigation reuse [3, 4]. Some studies compared various technologies treating secondary wastewater effluent, including microfiltration (MF), soil-aquifer infiltration, and aerobic membrane bioreactor (MBR) [5-9]. However, these technologies are not effective in removing micro pollutants (i.e. constituents of emerging concern) and trace metals from wastewater, limiting the potential application of the reclaimed wastewaters [10] including for irrigation. Anaerobic membrane bioreactors (AnMBR) have been studied to treat wastewater because of its several advantages, including complete rejection of suspended solids, high organic rejection and biogas production and low sludge production [11]. However, high membrane fouling issues are still obstacles for both AnMBR and membrane filtration post-treatment (e.g., RO and NF), ultimately increasing the energy consumptions [12]. Osmotic membrane bioreactor (OMBR) has been proposed as a suitable alternative by integrating AnMBR with forward osmosis (FO) to overcome these issues [13-15]. A study has reported that trace organic compounds could be removed up to 80-90% by the FO process depending on the type of commercial membranes. With the increase of pressure on the feed side, the rejection of trace organic compounds decreased probably due to membrane deformation, increased external concentration polarization (ECP) and lower reverse salt flux (RSF) [16]. Bell et al. [17] has also demonstrated that the FO process using cellulose triacetate (CTA) membranes could achieve a steady-state water flux over 100 days. Because the rejection of ions by the FO membranes, the salinity of OMBR system might increase over time, but the incorporation of MF or UF units can substantially control the salinity build-up in OMBR and achieve a stable operation [18, 19].

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The FO process has been investigated for various applications in wastewater treatment, for example, activated sludge [20], drilling mud and fracturing wastewater from oil and gas industry [21], digester centrate [22], primary effluent [23], and secondary and tertiary treated effluents [24]. Although OMBR can provide high rejection of contaminants, it also exhibits some limitations, such as efforts to recover pure water from diluted draw solution (DS) and the inhibited biological process due to the reversely transported draw solute [13]. Recently, fertilizer-drawn forward osmosis (FDFO) has been investigated because the diluted DS can be used directly for irrigation purposes without the need for a draw solute separation and recovery process [25, 26]. In FDFO, the FO process is driven by a concentrated fertilizer solution and thus the clean or 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 and a highly concentrated fertilizer solution will be utilized as feed solution (FS) and DS in the FDFO process, respectively. Consequently, a diluted DS (fertilizer solution) can be obtained and supplied for greenhouse irrigation or fertigation [27]. Moreover, when the FDFO is used as a pretreatment of AnMBR, the concentrated wastewater can improve the digestion efficiency of downstream AnMBR and lead to a higher bio-methane production [28]. Three critical criteria affecting the success of the FDFO system are: i) maximization of water flux; ii) minimization of reverse solute flux and iii) control of membrane fouling (especially biofouling).

It has been reported that commercial solid fertilizers can be used as draw solutes for extracting reusable water from wastewater [29, 30]. Although an effective fouling control by using chemical cleaning has been reported in the same study, the impact of RSF on fouling was not addressed.

This study is part of a project targeting wastewater reclamation through a sequential FDFO and AnMBR process. The FDFO process in this study aims to pre-concentrate the wastewater to be delivered to the AnMBR to improve its performance. When a raw municipal wastewater is utilized as feed, severe membrane fouling can be expected during the wastewater treatment by the FDFO process. There are numerous bacteria already present in raw wastewater and therefore represent a high biofouling potential. Besides, the FDFO process uses fertilizers as DS, which are mostly made up of nitrogen and phosphorous, nutrients necessary for bacteria growth. When fertilizers are used as draw solutes in a FO process, a reverse diffusion of nitrogen and phosphorus into the FO feed channel is inevitable. It has already been reported that reverse

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diffusion of certain fertilizer solutes can significantly enhance membrane scaling [31]. Bell et al. [29] demonstrated that FO is not a low fouling membrane process and proper pretreatments are required to protect the FO membranes from fouling. Moreover, the thin film composite (TFC) membranes exhibited a higher fouling propensity than CTA membranes despite their smoother, more hydrophilic, and more neutrally charged surfaces. Xie et al. [32] reported that reverse calcium diffusion could lead to a significant membrane fouling which was mainly due to the biofouling enhanced by calcium complexation. However, these studies did not address the impact of fertilizers which might have a stronger impact on biofilm formation depending on their corresponding diffusion capability through FO membranes.

The reverse diffused nutrients may also enhance the growth of bacteria in the presence of a carbon source on the FO membrane surface, ultimately leading to an increase of the development of biomass thereby enhancing biofouling. Phosphate nutrient limitation has been demonstrated as a measure to control membrane biofouling [33]. Besides the types of nutrients, the extent of biofilm formation and biofouling on FO membrane could also depend on other factors such as higher reverse diffusion rate of the nutrient and the N:P nutrient ratio. However, at present, it is not clear whether or not the reverse diffusion of fertilizer from the DS will influence the biofouling. To our knowledge, no studies have been reported demonstrating the potential effect of fertilizer reverse diffusion on biofouling in the FDFO process, and which type of fertilizers is preferable to be utilized to minimize membrane biofouling. To render the FDFO process economically feasible, the potential for biofouling of FO membranes should be fully understood and addressed.

Therefore, the main objective of the present study is to investigate biofouling in the FDFO process by spiking *Pseudomonas aeruginosa PAO1+ GFP* in a synthetic wastewater feed, using three different fertilizers potassium nitrate (KNO_3), potassium chloride (KCl) and potassium dihydrogen phosphate (KH_2PO_4) as draw solutes. The reverse diffusion of these three different fertilizer draw solutes was determined and compared. The impact of reverse diffusion of the different fertilizers on flux decline, foulants composition and biomass accumulation on the FO membranes were also investigated. The study provides insights to the impact of different fertilizers on biofouling of FDFO membranes and corresponding fouling mechanisms. This may assist researchers to identify an appropriate fertilizer for the FDFO process from the perspective of limiting biofouling.

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2. Materials and methods

2.1. Draw solution

KNO_3 and KH_2PO_4 fertilizers were used in this study to investigate the impact of reverse diffusion of N and P nutrients on biofouling in the FDFO process. All fertilizers were reagent grade (Sigma Aldrich). The DS was prepared by dissolving 1 M chemical fertilizer in deionized water. The osmotic pressure of these three fertilizers was calculated by using the Morse equation (extension of van't Hoff Equation) (Eq.1). The details of DS are provided in Table 1.

$$\pi = i\phi CRT \qquad\qquad (1)$$

where, i is the number of ions produced during dissociation of solute, ϕ is the unitless osmotic coefficient, C is the molar concentration of all solutes (moles/L), R is the universal gas constant (0.083145 L·bar/moles·K), and T is the temperature on Kelvin scale (K).

Table 1. Details of draw solutions used in this study.

Draw Solution	Mole concentration (M)	Osmotic pressure at 20℃ (bar)
KCl	1	44.8
KNO_3	1	32.6
KH_2PO_4	1	32.3

2.2. Feed solution

Synthetic wastewater was prepared in this study to mimic municipal wastewater effluent and used as FS of the FO process. The composition of synthetic wastewater is shown in Table 2. This synthetic wastewater recipe was also used in a reported FO-AnMBR process for wastewater treatment [34], so that the results of this study can be compared with other studies. FO membrane fouling consists of inorganic scaling, organic and biological fouling [35-37]. Inorganic scaling due to nucleation and crystallization of calcium carbonate and magnesium carbonate on the membrane surface could happen when these species exceed saturation concentration. In this study, however, Ca and Mg scaling is less likely because their concentrations in the feed were only 1.45 ppm and 1.18 ppm, respectively, which is much lower than the saturation concentration. Even at an elevated concentrations (i.e. feed volume reduced from 1 L initially to 760 mL during batch process) due to rejection of Ca and Mg by the FO membrane, Ca and Mg

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concentrations at the end of each FO run were 1.92 and 1.56 ppm, respectively, and not adequate to cause significant scaling issues.

Two bottles of 100 times concentrated stock solution were prepared by dissolving chemicals in deionized water. One was composed of $MgCl_2$ and $CaCl_2$, and the other one was composed of the other components. These two stock solutions were diluted and then mixed properly before experiments. To stimulate the biofouling, pure wastewater bacteria species, *Pseudomonas aeruginosa PAO1+GFP* (Center for Marine Bio-Innovation of UNSW, Australia), were added to the synthetic wastewater. The *Pseudomonas aeruginosa PAO1* was tagged with green fluorescence protein (GFP), so that any biofilm formed on FO membranes could be observed under confocal laser scanning microscopy (CLSM, Zeiss LSM 710) after the fouling experiments. The *Pseudomonas aeruginosa PAO1+GFP* was daily sub-cultured to maintain the bacteria activity. Since around 1×10^5 CFU/100 mL bacteria concentration is widely detected in wastewater [38], bacteria concentration was determined after sub-culturing using a flow cytometer and then corresponding amount of cells were added in each freshly prepared synthetic wastewater to reach the targeted bacteria concentration.

Table 2. Composition of synthetic wastewater.

Compounds	Concentration (ppm)
Glucose	275
Peptone	100
Beef extract	100
Urea	10
$NaHCO_3$	100
KH_2PO_4	20
NH_4Cl	25
$MgCl_2 \cdot 6H_2O$	10
$CaCl_2 \cdot 2H_2O$	5

2.3. FO Membranes

Cellulose triacetate (CTA) membranes provided by Hydration Technology Innovations (HTI Company, USA) were used in this study for the FO experiments. Detailed characteristics of this type of FO membrane can be found elsewhere [36].

2.4. Experimental protocol

FO experiments were conducted using a lab-scale system, similar to the one described elsewhere [39]. The FO cell had two symmetric flow channels on both sides of the FO cell for FS and DS. The effective surface area of FO membranes within the cell is 20 cm^2. Variable speed gear pumps (Cole-Parmer, USA) were used to provide a constant cross-flow velocity of 8.5 cm/s for both FS and DS recirculation at room temperature (20 °C). DS tank was placed on a digital balance for on-line recording of weight changes and used for water flux calculation. Conductivities and temperatures of both FS and DS were also continuously measured and recorded for each experiment to monitor the reverse diffusion of draw solutes to the FS side.

Before each experiment, the FO system was thoroughly cleaned according to the procedure shown in supplementary Table S1 to ensure that the FO system did not contain any trace of organic contaminant and/or bacteria which might influence the initial experimental conditions. After cleaning, the FS and DS of 1 L each were re-circulated in the FO system. When the volume of DS increased by 240 mL, the driving force of the FO process was reduced due to the dilution of DS, at which point experiments were paused and both FS and DS were refreshed to recover the initial driving force of the system. For each experiment, the FS and DS were refreshed 6 times and the total volume of permeate was 1,680 mL. The refreshed FS and DS were prepared according to the procedure described in previous sections. The FS and DS were sampled every day for water quality analyses, which included liquid chromatography with organic carbon detection (LC-OCD) for the determination of different fraction of dissolved organic carbon, ion chromatography system (ICS-1600, DIONEX) for NO_3^- and PO_4^{3-} analyses, inductively coupled plasma − mass spectrometry (ICP-MS, Agilent Technology 7500 series) for K^+ analyses. The principle of the LC-OCD is size exclusion chromatography, and the definition of different organic fractions and their concentration calibration are based on the reported paper by Huber et al. [40]. After the experiment, half of the fouled membranes (10 cm^2) were submerged in deionized water to recover the foulants using 60 minutes sonication at 40 kHz (Branson 1510).

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The biomass concentration of recovered foulants by sonication was determined using adenosine triphosphate (ATP) determination kit (A22066, Molecular Probes). The other half of the fouled membrane was evaluated using CLSM in terms of biofilm visualization and thickness estimation. The ATP and CLSM analyses were immediately conducted after taking out the fouled FO membranes after each experiment to minimize the potential impact of bacteria bioactivity.

Before using the synthetic wastewater in the experiments, MQ water was tested as FS under the same experimental conditions to investigate the background flux decline caused by the dilution of DS and the water flux recovery after refreshing both FS and DS. Although the flux declined during each run for both tested fertilizers with MQ water as feed water, the water flux could be fully recovered after refreshing both the FS and DS. This indicates no fouling of the membranes and the flux decline can be attributed to the driving force reduction due to the dilution of DS. Afterwards, the synthetic wastewater was applied for the biofouling investigation.

2.5. Analytical Methods

LC-OCD was applied to investigate the removal of different fractions of organics by the FO membranes and the foulants on the FO membranes after experiments. Samples were pre-filtered with 0.45 μm filters to prevent the blockage of separation columns. Each sample was run twice in the LC-OCD. Different fractions of organics were isolated according to the time required to be eluded out from the separation column. Consequently, the concentration of different fractions of organics was calculated by chromatograph area integration.

A calibration for anion detection was established using ICS analyzer and NO_3^- and PO_4^{3-} standard solutions with a series of concentration of 0, 5, 10, 25, 50 ppm. DS samples were diluted 100 times to ensure that the concentration of samples was within the range of calibration. Calibration was conducted every round of measurements. A similar calibration procedure was conducted for the cation concentration detection with ICP-MS as well. The RSF was determined to quantify the amount of reversely diffused draw solutes into the FO feed water, calculated based on Eq. 2:

$$RSF = (C_{F\_end} \times V_{F\_end} - C_{F_{ini}} \times V_{F_{ini}})/(A \times T) \quad (2)$$

where C_{F_ini} and C_{F_end} are the draw solute concentration in the feed water at the beginning and the end of the FO process, and V_{F_ini} and V_{F_end} are the volume of feed water at the beginning and

the end of FO process. A is the effective FO membrane area used in this study (20 cm^2), and T is the time of the FO experiment (24 hours).

ATP analyses were conducted following the standard protocol provided by the manufacturer. Low concentration standard ATP solution was prepared by diluting 5 mM ATP solution in deionized water. The following concentrations were prepared for the calibration: 0 nM, 1 nM, 500 nM, and 1 μM. Calibration was conducted for every measurement together with the target samples to ensure the measurement accuracy. Each sample was duplicated to ensure its reproducibility.

CLSM analyses were conducted on an up-right CLSM platform (LSM 710, Zeiss), applying 488 nm argon laser for laser line excitation. Since the PAO1 bacteria was tagged with GFP, dye staining of samples were not required. As the top morphology of the FO membrane could change when it dries, and thus influences the biofilm observation, membrane samples in a wet state were directly placed on a glass slide for analyses after experiments. For each membrane sample, the biofilm was visualized at three different locations (top, center, and bottom of the 1×10 cm membrane sample) to ensure the representativeness of results. After visualization of the biofilm, the corresponding thicknesses at three locations of each sample were estimated via the "Z-stack" function within the ZEN software of the Zeiss LSM 710.

3. Results and discussion

3.1. Performance of the FO system

The different fractions of organics in FS and DS were analyzed by LC-OCD (chromatograph depicted in Figure 1) and their corresponding integration values are shown in Table 3. In the original FS, different fractions of organics were present, including biopolymer (14.1 ppm-C), humic acids (24.3 ppm-C), building blocks (41.4 ppm-C), low molecular weight (LMW) neutrals (7.8 ppm-C), and LMW acids (93.8 ppm-C). However, because of the rejection of FO membranes, most of the large molecular weight substances are removed. In fact, except for some LMW neutrals, all the other organic components in the DS were not detectable by the LC-OCD, indicating an excellent rejection of these organic compounds by FO membranes (i.e. DOC rejection rate of more than 97%).

However, in terms of the rejection of LMW neutrals, around 4 ppm-C was detected in all draw solutions. Considering the 1.24 dilution factor of DS after experiments, the real increment

of LMW neutral in DS could be about 5 ppm-C. The presence of LMW neutrals in the DS indicates its penetration through the FO membranes. Although the rejection of LMW neutrals was significantly lower than the other compounds, the total organics removal rates were higher than 97% for al fertilizers tested. The low removal rate of LMW neutrals was probably contributed by the urea or uncharged organic matter contained in the synthetic wastewater. The poor removal of urea by FO membranes has also been reported by another study [39]. Moreover, LMW neutral compounds have been demonstrated to be difficult to remove by FO membranes. That is probably due to two hypotheses: i) the increase in membrane surface charge might potentially result in an increase in the molecular weight cut-off (MWCO) property of the membrane due to membrane swelling, as described for NF and RO membranes [41], reducing the rejection of the LMW neutral compounds, and ii) higher hydrophilicity generated by the fouling layer on the membrane may allow a higher amount of LMW neutral compounds to partition through the membrane, and eventually, decrease the rejection [42].

Table 3. Different fractions of organic matter in the initial FS and DS after experiments. The data reported are average of duplicate tests.

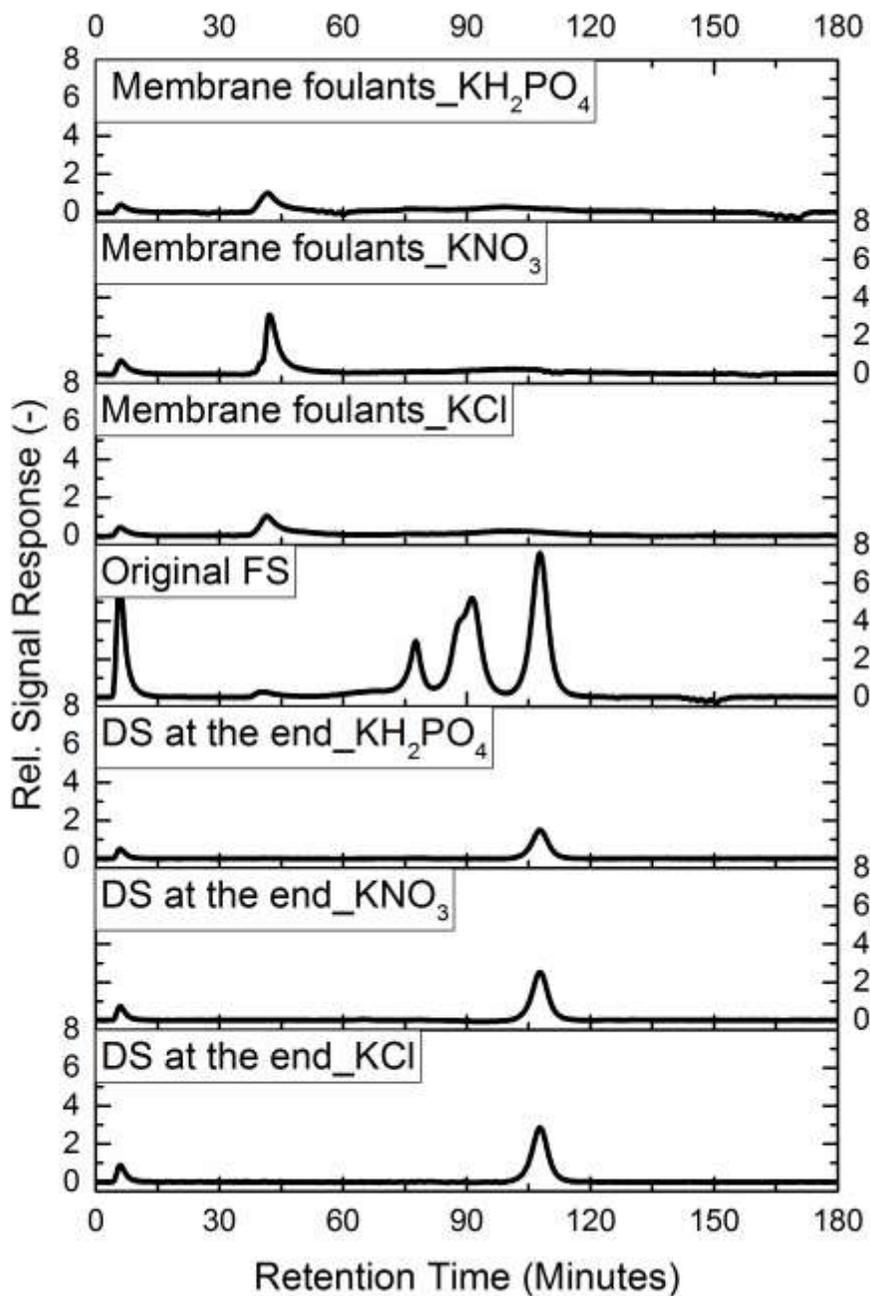|	Biopolymer	Humic acids	Building Blocks	LMW neutrals	LMW acids	DOC	DOC Rejection rate
	ppm-C	ppm-C	ppm-C	ppm-C	ppm-C	ppm-C	
FS	14.1	24.3	41.4	7.8	93.8	181.4	
DS_KCl	N.D	N.D	N.D	4.2	N.D	4.2	97.1%
DS_KNO$_3$	N.D	N.D	N.D	4	N.D	4	97.2%
DS_KH$_2$PO$_4$	N.D	N.D	N.D	3.9	N.D	3.9	97.3%

Note: N.D (not detectable)

Figure 1. LC-OCD chromatographs of original feed solution, draw solution at the end of experiment when using KCl, KH_2PO_4 and KNO_3 as DS, and membrane foulants on FO membranes using KCl, KH_2PO_4 and KNO_3 as DS.

3.2. Impact of different fertilizers on membrane flux and reverse diffusion of draw solutes

The normalized flux decline of all fertilizers, as a function of accumulated feed volume, are shown in Figure 2. After extracting 240 mL of water from FS, both FS and DS were refreshed to recover the reduced driving force caused by the dilution of DS after one run. A full recovery of normalized flux should be expected if no fouling occurred during the FO experiments. However, refreshing the FS and DS did not recover the permeability or the water flux of the FO membranes. A sharp decrease of the normalized flux in the first run was observed for all fertilizers, from 100% down to around 80%. After the first refreshing of FS and DS, membrane permeability was partially recovered, but the flux kept decreasing in the following runs for all fertilizers indicating that the FO membranes were fouled. Moreover, refreshing the FS and DS after each run did not show obvious improvements on recovering the initial permeability of FO membranes, except for the first three runs.

Although FO membrane fouling was evident for all fertilizer DS, the flux decline using KH_2PO_4 was significantly lower than KCl and KNO_3 (Fig. 2) at the end of the whole experiment. After seven runs, the normalized flux of KH_2PO_4 decreased to around 70% of the initial flux, while the flux of KCl and KNO_3 was down to 55% and 32%, respectively. Moreover, it is interesting to see that KH_2PO_4 and KCl exhibited a similar initial flux of each cycle after refreshing the FS and DS. Since the FO processes were operated using similar feed properties and under similar flux conditions, the higher flux decline for KCl and KNO_3 is most likely related to the reverse diffusion towards the FS, which could enhance the bioactivity on the FO membrane surface on the feed side and reduce the repulsion force between negatively charged organics/organisms in FS and FO membranes via charge screening effect and compression of electrical double layer [43, 44].

As reported by many other studies, reverse diffusion of draw solutes is inevitable in the FO process [20, 45-47]. The extent of reverse diffusion of draw solutes and their impact on the membrane fouling depends on the types of draw solutes used and its properties [48] and this likely caused the differences in the flux decline using different fertilizer draw solutes. At the beginning of the experiments, almost no NO_3^- and only a small amount of K^+, Cl^- and PO_4^{3-} were detected, because the synthetic wastewater contained only 16.6 ppm Cl^-, 5.74 ppm K^+, 14.26 ppm PO_4^{3-} and no NO_3^- at all (Fig. S1). However, after one FO cycle, the detected reverse draw solute fluxes in FS were 19.8, 5.1 and 3.7 $g/m^2/h$ for KNO_3, KCl and KH_2PO_4, respectively. The

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RSF of K^+ is associated with the diffusion of anions and depends on the specific fertilizers. It demonstrated that nitrate has a much higher reverse diffusion rate than chloride and phosphate in the FO process, consistent with other studies [22, 39] probably because of the smaller molecular size and hydrated radius compared to chloride and phosphate [39].

Since the fertilizers draw solutes used in this study, except for KCl, contain nitrogen and phosphorus, necessary compounds for bacterial growth, their reverse diffusion might promote biofilm growth and formation on the FO membrane surface. The N:P nutrient ratio is an important factor for the bacterial growth and the rapid growth has been reported to occur around 9:1 [49]. The synthetic wastewater used in this study had a N:P ratio of only 2.5:1, which is much lower than the requirement of ideal rapid growth. However, the N:P ratio could be significantly altered during the FO process due to reverse diffusion through the FO membrane from the DS towards the feed side, especially when fertilizer DS containing nitrogen was used. Since KNO_3 contains nitrogen and also has a relatively high RSF, it contributes to a rapid increase in the N:P ratio during the FO process, likely enhancing the bacterial growth and biofilm formation on the membrane surface. This could be one of the reasons why KNO_3 resulted in severerer flux decline compared to KCl and KH_2PO_4 as draw solute although they were operated under identical conditions. A small amount of phosphate also reversely diffused into the feed side when KH_2PO_4 was used as draw solute, however, this may not have much impact on the bacterial growth in the absence of enough nitrogen to affect the N:P ratio. KCl is a fertilizer for plants, but chloride is not a nutrient for bacterial growth. Therefore, the RSF of KCl might not significantly influence the biofilm formation on FO membranes. Moreover, KCl has been reported to have an inhibitory effect on bacterial growth [50]. The impact of the RSF of KCl on flux decline was most likely due to the charge screening effect caused by reverse diffused potassium ions around the FO membrane surface on the FS side. The charge screening effect could also be another mechanism of the severerer fouling of KNO_3.
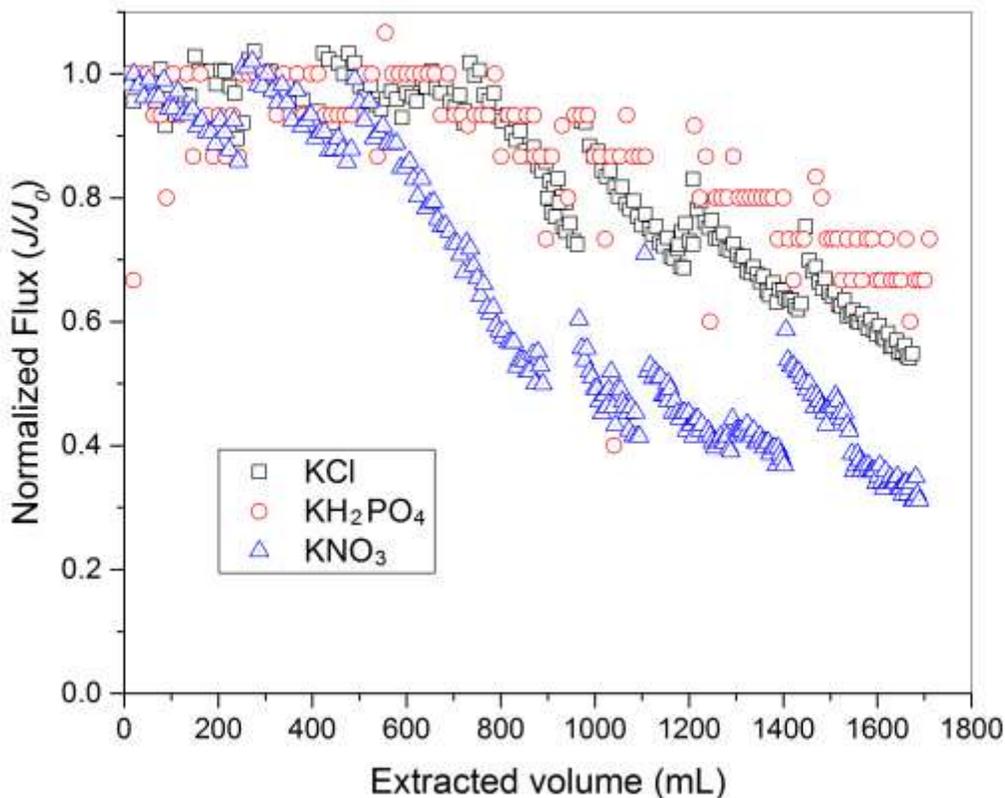
Figure 2. Normalized flux decline as a function of accumulated volume of treated water for three fertilizers: 1) KCl; 2) KNO_3; and 3) KH_2PO_4. Experiments were conducted at room temperature with 8.5 cm/s cross flow velocity. The FS was synthetic wastewater described in the materials and methods section.

3.3. Composition of organic foulants on the FO membrane surface

To get a better understanding on the composition of the foulants on the FO membrane surface, fouled membrane samples were taken after experiments and sonicated to extract and recover the foulants. Organic and biological fouling were considered major contributors to the flux decline, and inorganic scaling did not occur under the conditions tested. A detailed composition of the organic foulant was analyzed using LC-OCD, with chromatograph presented in Figure 1 and the corresponding fractional integration values in Figure 3.

For both the fertilizer DS, three types of organics were detected in the foulant: biopolymers, building blocks and low molecular weight (LMW) acids. Biopolymers are normally composed of polysaccharides and proteins [40]. As shown in Figure 3, biopolymers are the dominant component of the foulants for FO experiments using all fertilizer DS, with their foulant mass measuring 945.2, 450 and 440 mg/m^2 for KNO_3, KCl and KH_2PO_4, respectively. The dominant role of biopolymers in FO membrane fouling layers is also supported by another study on water harvesting from wastewater via FO process [39]. The sources of these biopolymers on the fouled FO membranes are from the synthetic wastewater itself and also those probably produced by the bacteria attached on the FO membrane surface. Because of the hydrophilic and gel-like characteristic of biopolymers [51], they could easily attach on the membrane surface while the other organic compounds play a minor role in forming the fouling layer on the FO membrane as it is operated without hydraulic pressure. TEP, one sub fraction of EPS, has been reported to be an important membrane foulant, originating from both algae and bacteria, and also found in both seawater and wastewater [52]. Our previous study has shown that transparent exopolymer particles (TEP) could also be produced by bacteria in the water, and the biopolymer fraction is the main component of bacterial TEP [53]. Moreover, due to the lectin-like property of TEP substances [53], they could promote biofilm formation by agglutinating the bacteria in the feed water, accommodating them on the initial organic fouling layer, and collecting other necessary components (such as nitrogen and phosphorus in feed water) for the reproduction of agglutinated bacteria.

Besides biopolymers, a substantial amount of building blocks was also detected in the fouling layer of the FO membranes using KNO_3, KCl or KH_2PO_4 as DS. Building blocks are considered to be the breakdown of humic substances in water [40]. The presence of building blocks could be from the deposition of organics present in the synthetic wastewater, or from the biodegradable by-products of deposited macro molecular weight biopolymers. It has been reported that yeast is detected as building blocks in LC-OCD.[39] Bacteria have the potential to release some enzyme to biodegrade the organics with macro molecular weight to a smaller size for their uptake [54]. The amounts of building blocks measured on the membranes were 265, 240 and 230 mg/m^2 for KNO_3, KCl and KH_2PO_4, respectively. In addition, a small amount of LMW acids was found in the membrane foulants, 5, 1 and 15 mg/m^2 for KNO_3, KCl and KH_2PO_4,

respectively. Compared to the amount of biopolymers and building blocks, LMW acids appear negligible.

Comparing the foulant mass deposited on the membrane surface, it is clear that the biopolymer is the major fouling component for all fertilizers DS, despite its relatively lower composition in the FS compared to humic substances and building blocks (Table 3). The mass of the biopolymer in the membrane foulant for KNO_3 DS is almost double than that of KCl and KH_2PO_4 as DS while the mass of building blocks was observed comparable for the three fertilizers. Since the original synthetic feed water used for both the fertilizer DS was identical (in organic composition) and the FO membranes were subjected to similar operating conditions (except for types of DS), the biopolymer composition is expected to be similar. However, the higher biopolymer content observed in the membrane fouling layer using KNO_3 as draw solute indicates that this additional membrane fouling was most likely from the biopolymers produced by bacteria agglutinated on the fouling layer. These results suggest that the enhanced biological activity of the membrane using KNO_3 as DS is as a result of the reverse diffusion of nitrate to the feed side that increased the N:P ratio more suitable for bioactivity.
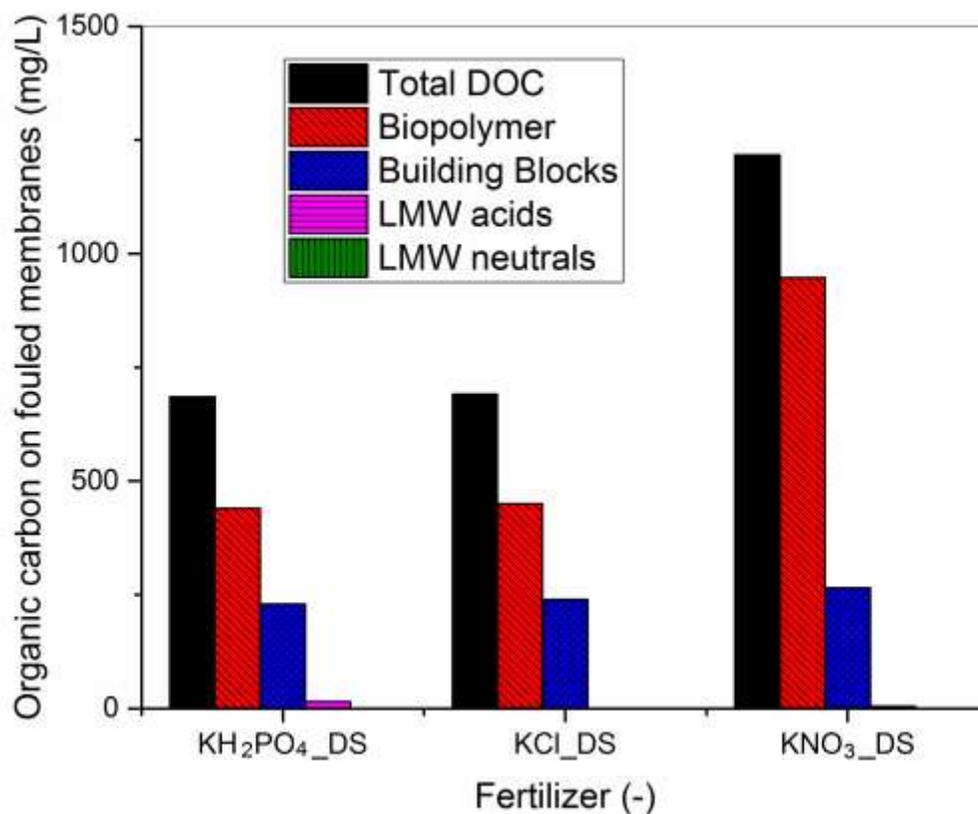
Figure 3. Different fractions of foulants on FO membranes when using KCl, KNO_3 and KH_2PO_4 as draw solutions. The data reported are average of duplicate tests.

3.4. Biomass on FO membranes

To demonstrate the higher bioactivity on the FO membranes using KNO_3 as draw solute, the biofilm thickness and ATP content in foulants were determined. Figure 4 shows 3D CLSM profiles of FO membranes using different fertilizer as DS, and the corresponding biofilm thickness on the membranes (evaluated from the CLSM profiles) and ATP contents within the foulants. It is clear from this figure that the biofilm thickness and coverage on the membrane surface when using KNO_3 (72 µm) was much more pronounced than when using KH_2PO_4 (35 µm) and KCl (33 µm). Biofilm thickness was found to be similar for the KH_2PO_4 and KCl. Regarding the ATP content within the foulants, it is also consistent with the results of biofilm thickness analyses, although a slightly less ATP was detected for KCl than KH_2PO_4 fertilizer.

The ATP concentration for membranes using KNO_3 (53.3 mg/m^2) was also higher than those using KH_2PO_4 (33.5 mg/m^2) and KCl (28.2 mg/m^2). As FO membranes were subjected to similar feed water composition, initial bacteria number and operation conditions, the bioactivity on the FO membrane surface should have been similar irrespective of the types of DS when discarding reverse diffusion.

However, different fertilizer DS exhibited different RSF and biofilm formation. KH_2PO_4 exhibited the lowest RSF (Fig. 3) and also caused a low biofilm formation. KCl showed a relatively higher RSF than KH_2PO_4 but with a similar and even less biofilm formation, while the KNO_3 displayed the highest RSF and most significant biofilm formation as well. This is probably due to two mechanisms: 1) the reverse diffusion of positively charged potassium ions reduced the repulsion force between negatively charged *P. aeruginosa* [55] and negatively charged CTA of membranes via charge screening effect and compression of electrical double layer [56]; 2) the reverse diffusion of N and P enhanced the bacterial growth on the membrane surface as mentioned in section 3.2.

It has been reported that the initial adhesion of *P. aeruginosa* on RO membranes could be better facilitated due to charge screening effect [55]. Since the CTA material of FO membranes are also negatively charged [56], FO membranes could be influenced by the charge screening effect as well. Moreover, *P. aeruginosa* can produce a large amount of EPS which could further promote the biofilm formation via 1) agglutinate bacteria in bulk flow on the biofilm; 2) aggregate nutrients in bulk flow for the metabolism requirements of bacteria on biofilm.

For the experiments conducted with KCl draw solute, the charge screening was most likely the main mechanism of biofilm formation because KCl cannot induce a nutrient promoting bacterial growth even though it is widely used as a plant fertilizer. Furthermore, the increased KCl concentration might even inhibit the bacterial growth [50]. For the experiments conducted with KNO_3 and KH_2PO_4 draw solutes, both the charge screening and promoted bacterial growth via reversed diffused N and P were likely involved due to the requirement of N and P for the bacterial growth. Since the RSF of KCl is higher than KH_2PO_4, a higher charge screening probably better facilitated initial bacteria attachment on the membranes, compensating the lack of nutrient promotion. However, the less ATP (live bacteria number) on the membrane using KCl as DS rather than KH_2PO_4 indicates that the higher RSF of KCl did not promote bacterial growth on membranes.
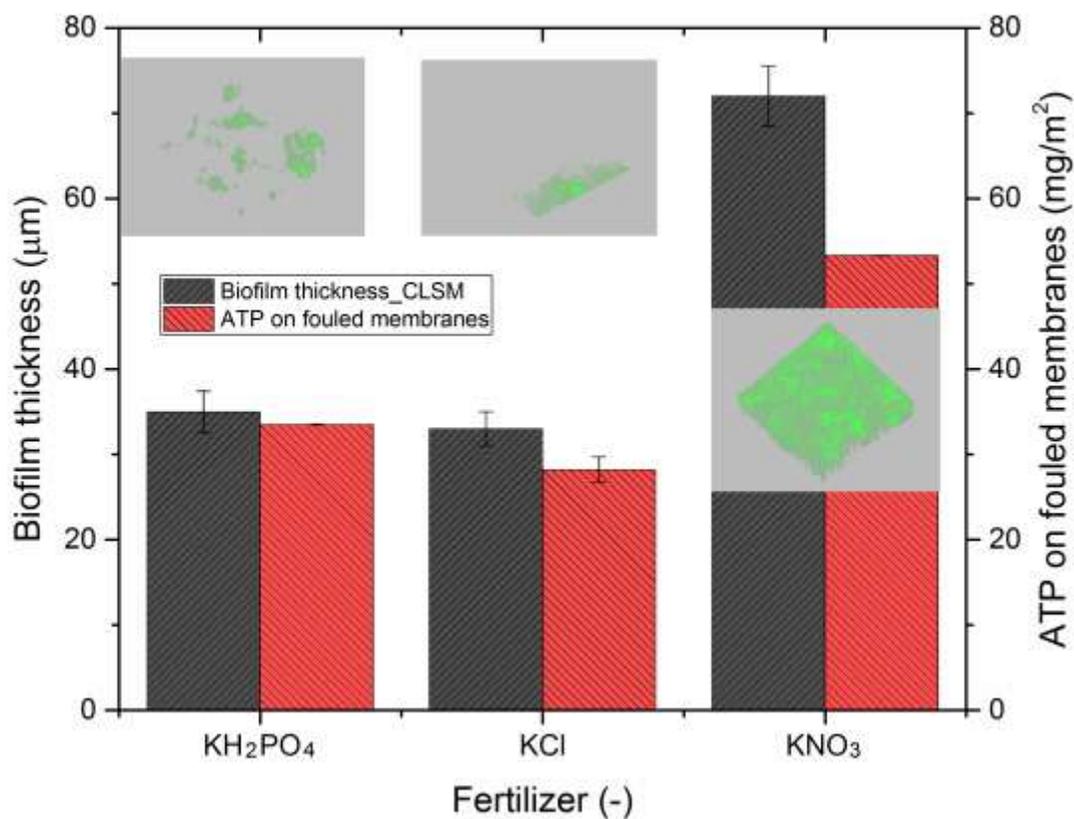
Figure 4. 3D CLSM profiles of draw solutions used in this study, the biofilm thickness of fouled FO membranes evaluated according to the CLSM profile and corresponding ATP contents within isolated foulants for three fertilizer draw solutes: KCl, KNO_3 and KH_2PO_4 (Error bars for ATP and biofilm thickness stand for the deviation of 3 and 5 separate analyses, respectively).

4. Conclusions

This study investigated the impact of RSFs of different fertilizer draw solutes (KCl, KNO_3 and KH_2PO_4) on the membrane biofouling in a FDFO system treating synthetic wastewater. The FDFO process rejected most of the pollutants in wastewater (>97%), except for part of neutral organics with low molecular weights. KNO_3 exhibited a severer biofouling issue than KCl and KH_2PO_4, which was demonstrated by a severer membrane flux decline using KNO_3 as DS (63%) than KCl (45%) and KH_2PO_4 (30%). It corresponded to a significantly higher amount of biofoulants and biomass on the membrane using KNO_3 as DS than KCl (450 mg/m^2

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biopolymers, 33 μm biofilm thickness and 28.2 mg/m^2 ATP) and KH_2PO_4 (440 mg/m^2 biopolymers, 35 μm biofilm thickness and 33.5 mg/m^2 ATP). The severer biofouling caused by KNO_3 was most likely because the reverse diffusion of potassium and nitrate. The presence of potassium could enhance bacterial adhesion via charge screening effect, and nitrate increase the N:P nutrient ratio on the membrane surface up to a suitable level for rapid bacterial growth (9:1).

The long-term low fouling operation is one of the key issues for the success of FDFO application. This study provides a better understanding on how the draw solutes of FDFO process influence the development of membrane biofouling, which is important for the ideal draw solute selection in future and a better fouling control strategy development. This study also suggests that three criteria are critical for the selection of an appropriate draw solute for this novel FDFO process for wastewater reuse in terms of biofouling: i) stable and high water flux; ii) low reverse diffusion of draw solutes; iii) limited usage of nitrate containing fertilizer.

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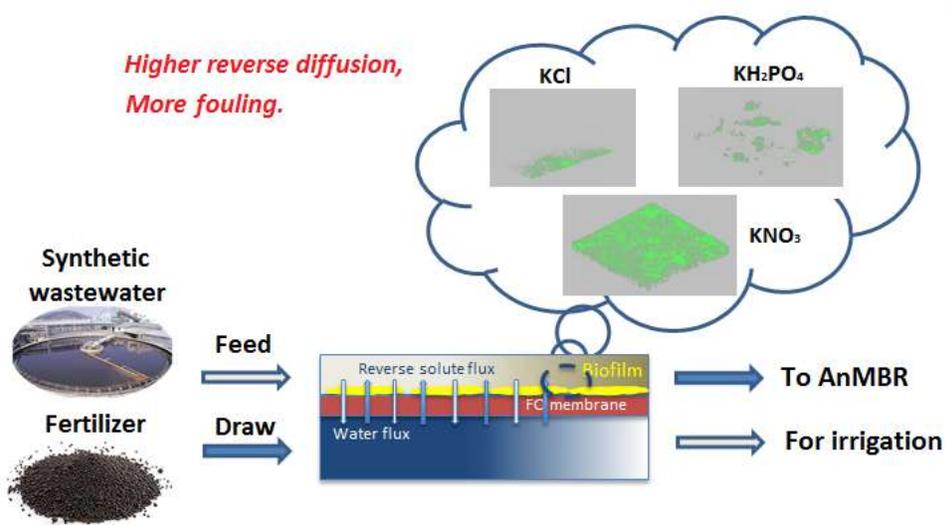
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Highlights

1. Biofouling in FDFO was investigated using KNO_3, KCl and KH_2PO_4 as draw solutions

2. FO performances using KNO_3 as draw solute exhibited most severe fouling

3. Fouling of KCl was related to the charge screening effect via reverse diffusion

4. Fouling of KNO_3 was likely related to both charge screening and promoted biofilm

5. Biopolymer is the main component in the fouling layer for all draw solutes

Graphical abstract