Membrane Scaling and flux decline during fertiliser drawn forward osmosis desalination of brackish ground water

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Abstract

Fertiliser drawn forward osmosis desalination has been recently studied as one of the feasible applications of forward osmosis (FO) process for irrigation. In this study, the potential of membrane scaling and fouling in the fertiliser-drawn forward osmosis (FDFO) process has been investigated during the desalination of brackish groundwater (BGW). While most fertilisers containing monovalent ions did not result in any scaling issues however, di-ammonium phosphate (DAP) or $(NH_4)_2HPO_4$ as draw solution resulted in significant scaling formation contributing to severe flux decline. Membrane autopsy using scanning electron microscope (SEM), energy-dispersive X-ray (EDS) and x-ray diffraction (XRD) analysis indicated that, the reverse diffusion of DAP towards the feed were mainly responsible for scale formation during the FDFO process. Physical cleaning with crossflow rates similar to normal FDFO process was adopted to evaluate the effectiveness of restoring the membrane flux after inorganic scaling. For the membrane scaled using DAP as draw solution (DS), the flux recovery was about 80-90% depending on the DS concentration used. However, when crossflow rate was increased, the water flux restored almost in full irrespective of the DS concentration used. This study underscores the importance of selecting a suitable fertiliser for FDFO desalination of brackish groundwater to avoid scaling and severe flux decline.

Keywords: forward osmosis, membrane scaling, inorganic fouling, desalination, brackish groundwater

1. Introduction

Recently, the growing water scarcity issues have been driving interest the use of membrane processes such as reverse osmosis (RO) and nanofiltration (NF) for desalination or water reclamation to produce alternative water sources [1] (1-4). However, inorganic scaling and organic fouling pose a significant challenge for the efficient operation of these pressure based membrane processes. Scaling not only increases energy consumption but also increases the operation and maintenance costs and significantly shortens membrane life. Scaling starts to occur when the concentrations of some of the sparingly soluble salts reach super saturation due to high product water recovery and the salts starts precipitating on the membrane surface [1, 2]. Scaling in the salt rejecting membrane processes occurs by either by surface crystallisation or bulk crystallisation or both depending on the operating conditions [3-5].

The most common scaling salts are calcium sulfate, barium sulfate and calcium carbonate during desalination of seawater or brackish water by RO/NF process however, phosphate scaling is a major issue when RO process is applied for wastewater treatment [2, 6, 7]. In fact the presence of phosphate ions can cause a serious scaling problems for the RO membrane process and even anti-scaling agents are not quite effective as in preventing scaling [6].

For some time now, forward osmosis (FO) has been an emerging osmotic membrane process that can potentially be used as an energy-saving alternative to conventional membrane processes [8, 9]. FO utilizes natural osmotic pressure generated by a concentrated draw solution (DS) as driving force to pull water molecules from the feed solution (FS) through a semi-permeable membrane [10]. The diluted DS is then further processed to separate potable water and the draw solutes. However, one of the practical applications of FO technology is for irrigation in which the diluted fertiliser DS containing desalinated water can be used directly for fertigation instead of further subjecting to a separation process. Termed as fertiliser drawn forward osmosis (FDFO) desalination process [11-13], recent studies on this particular process indicated that most commercially available soluble fertilisers can generate very high osmotic pressure and therefore can be used as DS. FDFO process has been recently investigated for desalination of both seawater quality [12, 13] and brackish groundwater [14].

Although, FO process too experiences membrane scaling and fouling however, the absence of hydraulic pressure in the FO operation has been found advantageous in terms of fouling rate and cleaning efficiency. In fact, several studies have demonstrated that inorganic scaling and organic fouling are almost fully reversible by adopting simple physical cleaning/rinsing without the need of chemical cleaning reagents [1, 15, 16]. In some cases, FO process is observed to have low fouling potential or slower fouling rate than the RO process [17-20]. Fouling in FO process is influenced by the feed water quality like in the pressure based membrane process such as RO and NF. In addition, scaling and fouling in FO process could be influenced by additional factor that is not present in the RO process. Reverse diffusion of draw solutes has been cited as one of the major challenges of FO process because it not only results in the economic loss from replenishment cost, but also could complicate feed concentrate management and enhance membrane fouling potential. Reverse diffusion of draw solution salt towards the feed has been observed to play a significant role in influencing colloidal and organic fouling [16, 21]. It also exacerbates the cake enhanced osmotic pressure on the membrane surface in contact with the feed water there by reducing the effective driving force and consequent flux decline [16]. When a DS containing divalent ions such as Mg or Ca is used, the reverse diffusion of Mg or Cg or both could interact with some of the dissolved organic matter present in the feed to form bridging effect significantly affecting the cake formation and flux decline [22, 23].

However, to date, the effect on the use of fertiliser solutions as DS on the inorganic scaling and organic fouling during the FO process has not been studied. FO has the potential to achieve higher feed recovery rate when a high fertiliser DS concentrations are used and hence scaling may become a significant issue both due to supersaturation and reverse diffusion of fertiliser salts. The objective of this study is to investigate the flux decline due to the influence of inorganic scaling of membranes during the desalination of brackish groundwater by the FDFO process. The major factors affecting membrane fouling during the FDFO process were evaluated that includes FS and DS properties. The study also included the investigation on the effects of physical or hydraulic cleaning and their effectiveness on the membrane flux recovery.

2. Materials and Methods

2.1 Draw solution and feed solution

Six different fertilisers were used as DS and they include potassium chloride (KCl), monoammonium phosphate (MAP), diammonium phosphate (DAP), potassium nitrate (KNO_3), ammonium sulphate (SOA) and calcium nitrate ($Ca(NO_3)_2.2H_2O$). All the chemicals were of reagent grade and were supplied by Sigma Aldrich, Australia. The DS were prepared by dissolving the fertiliser salts in deionised or DI water with the aid of a magnetic stirrer mixer.

The feed solution consisted of a synthetic brackish groundwater and its composition is shown in Table 1. This composition simulates the BGW usually found at the Buronga salt interception scheme (SIS) in the Murray-Darling Basin (MDB) [11, 14]. All the compounds in Table 1 were of reagent grade supplied by Sigma Aldrich. Feed with different total dissolved solids (TDS) were prepared and they were designated as BGW10, BGW20 and

BGW35 containing TDS of 7.824, 15.647 and 27.382 g/L respectively. More background for the BGW composition can be found in our earlier publications [11, 14].

Table 1: Composition of the synthetic BGW feed with various TDS concentrations. This composition simulates the BGW usually found at the Buronga SIS in the MDB [11, 14]. Osmotic pressure was calculated using an OLI Stream Analyser 3.2.

2.2 Forward osmosis membranes

A commercial flat sheet cellulose triacetate (CTA) FO membrane (Hydration Technology Innovations or HTI, Albany, USA) was used in this study. This CTA membrane is made from cellulose acetate embedded in a polyester woven mesh and basic characteristics of the this membranes are presented in Table 2. More information on the properties and characteristics of the CTA FO membrane can be found in many other publications [10, 24, 25]. The pure water permeability coefficient of the FO membrane determined in the RO mode was observed ($A = 0.28194 \pm 0.008$ µm/s/atm).

Table 2: Physical and chemical properties of membranes as provided by the manufacturer for TFC FO membranes and from various literatures for CTA membrane.

2.3 FO performance tests for membrane scaling/fouling and physical cleaning

The performance tests for FDFO process was conducted using a lab-scale FO unit consisting of an acrylic FO cell with internal dimensions of 7.7 cm length x 4.6 cm width and 0.3 cm depth (effective membrane area of 2.002×10^{-3} m^2) on both sides of the membrane. The schematic layout of the FDFO process is presented in Figure 2, similar to the unit used in our earlier studies [12, 26, 27]. Both the feed and DS were supplied at crossflow velocities of 8.5 m/s all under counter-current mode and in FO mode (active layer facing FS). The temperature of the feed and DS in all cases was maintained at 25°C with the help of automated heater/chiller control system connected to a temperature water bath. The DS consisted of fertiliser solution while feed water consisted of a model brackish groundwater with characteristics shown in Table 1. Water flux was measured online by keeping DS tank on a digital mass scale and the scale was connected to a computer. Each experiment was carried for longer durations such as at least 20 hours or more.

Before starting experiments, a fresh new FO membrane was used and the whole membrane system was stabilized for 20 mins with DI water on both sides of the membrane. The initial baseline flux of the virgin membrane was then obtained using 1.0 M NaCl as DS and DI as FS. All the FO experiments were conducted in the batch mode of operation. The DS and FS were recycled back to their respective tanks after passing through the FO membrane. The initial volumes of both DS and FS were fixed at 2.0 L each. As the volume of DS increases so was its concentration that decreased with time. Correspondingly, the volume of the FS decreased with time thereby becoming more concentrated with time.

After FDFO experiment using fresh membrane, the membrane-cleaning regime was performed to evaluate the flux recovery after the FO membrane was subjected to inorganic scaling. The DS and FS tanks were replaced with DI water and the membrane was subjected to similar operation as FO process (crossflow of 8.5 cm/s) for 20 mins. Following this physical cleaning, the second baseline flux for flux recovery was obtained using 1.0 M NaCl as DS and DI as FS. The percentage ratio of the recovery baseline flux to initial virgin baseline flux (normalised) was assessed as a flux recovery rate.

Figure 1: A schematic diagram of the laboratory-scale forward osmosis (FO) system set up used in this study

3 Results and discussion

3.1 Influence of draw solution (DS) properties on inorganic scaling

Fertilisers are made up of compounds that contain major essential elements for the plants such N, P, K, Ca, Mg and S. However, when such compounds are used as DS during the FO process especially for the desalination of BGW containing several scaling precursor ions could adversely affect the membrane process. Ca^{2+}, Mg^{2+} and PO_4^{3+}/HPO_4^{2-} ions are all scaling precursors that accelerates membrane scaling and fouling undermining the efficiency of the RO desalination plants [22, 23, 28]. These ions could interact with the feed ions and promote membrane scaling and membrane fouling resulting in flux decline and ultimately undermining the process efficiency.

Six different fertilisers were randomly selected from our earlier studies to observe if they have any adverse influences on the process efficiency during the long-term operation of the FDFO process. Although these fertilisers were earlier used as DS for the desalination of BGW, the experiments were mostly short-term and did not observe any significant issues of flux decline due to scaling [14]. Other studies on FDFO process did not consider BGW but was rather focussed on evaluating the suitability of fertilisers as draw solutes where performance experiments were conducted using either pure water or NaCl solution [11-13].

The water fluxes as a function of operation time for the six fertiliser DS tested at 1 M concentration are presented in Figure 2 using BGW10 as FS. Most fertilisers showed a gradual decrease in the water flux with time except for DAP. This gradual decrease in the water flux is because of the decrease in the driving force (osmotic pressure difference) with time. Since the FO process was operated under batch mode, in which both the DS and FS were recirculated, the DS becomes diluted and FS tank becomes concentrated with time. However, a rapid decline in water flux observed for DAP as DS is quite in contrast to other DS used. In fact, after about 4 hours of operation, the water flux rapidly declined almost reaching zero. These results indicate that, long-term observation of the performances of the fertiliser DS is important as some of the DS could promote membrane scaling and fouling of the membrane. Such significant flux decline was not observed during the short-term experiments in the laboratory experiments using BGW in our earlier studies [14].

Figure 2: Variation of water flux with time for the six different fertiliser solutions during the FDFO process for the desalination of BGW. Operating conditions are DS: 1.0 M, FS: BGW10.

Autopsy of the fouled membrane with DAP as DS was conducted to study the composition of the scales formed during FO process using DAP as DS. Membrane autopsy involved both destructive and non-destructive observation of fouled membrane which can provide an understanding of the scaling and fouling phenomenon at microscopic level [29, 30]. Figure 3 presents the SEM images showing the formation of significant scales on the membrane surface using DAP as DS. Scales were observed on both the surfaces of active layer and the support layer as shown in Figure 3(a) and (b) however, the scales formed on the active layer surface (facing the FS) was more significant. The scales were also observed on the walls of the acrylic membrane cell facing the FS (Figure 3(c)). A closer observation of scaling layer revels a flaky crystals layer formed on the membrane surface which was mainly responsible for the sharp flux decline when DAP was used as DS.

Figure 3: SEM images of CTA membrane after experiment with DAP as DS and BGW as FS. a) active layer of the membrane surface, (b) both active layer and support layer of the FO membrane, (c) on the wall of the acrylic membrane cell facing FS and (d) magnified image of the scaling layer. Experimental conditions are DS: 3 M DAP, FS: BGW35

There are two possible reasons for severe membrane scaling in the FO process. The first relates to the supersaturation of feed ions and second relates to the reverse diffusion of draw solute ions that may interact with the feed ions. In a pressure based membrane processes such as RO and NF, scaling occurs due to complex phenomenon that involves both crystallisation and transport mechanism [2]. Nucleation and growth of inorganic scales on the membrane surfaces is a common problem for any RO systems [2]. Crystallisation occurs due to permeation of feed water, which leaves salts or ions behind on the membrane surface resulting in the supersaturation of ions that promotes nucleation, which then induces growth of crystals and then scale formation on membrane surfaces [3-5]. Scaling in RO process therefore increases with the increase in the feed recovery rates as the super saturation point is reached earlier. Similar scaling mechanism may be involved during the FDFO process because the BGW feed contains several scaling precursors ions such as Mg^{2+}, Ca^{2+} and HCO_3^- and SO_4^{2+} which could precipitate to form scales such as $CaCO_3$, $MgCO_3$ $CaSO_4$. However, if this mechanism was responsible for the scale formation, the flux decline could have been observed for almost all the fertiliser DS once the supersaturation has reached. Given that the flux decline was observed only for DAP the scale formation in the FDFO process in this case is mainly due to the influence of DS properties.

In any FO processes, the draw solute diffuses towards the feed in opposite direction to the water flux and this phenomenon is commonly described by reverse solute flux. The reverse diffusion of draw solutes or ions towards the FS from the DS could interact with feed ions forming insoluble scaling compounds. Reverse diffusion of certain draw solute ions such as Ca^{2+} and Mg^{2+} has also been found responsible for accelerating organic fouling by interacting with the colloids and organic matter [16, 21].

In order to identify the composition of the scaling layer, EDS analysis was carried out on the active layer of the scaled membrane to determine the composition and the scaling layer and the results are presented in Figure 4. The results show that the scaling layer is composed of large proportion of Na, Ca, Mg and P. Other than P however, all other elements shown in Figure 4 are already present in the FS and are hence related to the feed properties. The presence of P in the scaling layer on the active layer side of the FO membrane confirms that the reverse diffusion of $(NH_4)_2PO_4$ from the DS might have played a role in the formation of scales. Our earlier study with 1 M DAP as DS and 5,000 mg/L NaCl as FS has shown that, for every litre of water extracted by FO process, 0.26 g/L of P reverse diffuse towards the FS [13]. The reverse diffusion of $(NH_4)_2PO_4$ across the membrane could react with the ions present in the FS such as Mg and Ca. Their combination particularly with Ca, and Mg could result in the formation of scales resulting in severe flux decline during the FO process.

Calcium phosphate and magnesium phosphate scaling is usually a major issue when RO process is applied for wastewater treatment because of the presence of phosphate nutrients [2, 6, 7]. The combined effects of increased phosphate levels with high calcium and bicarbonate level increase the likelihood of phosphate scale formation on the membrane [31]. Therefore, these results indicate that, despite the absence of phosphate in the BGW FS, phosphate scaling could become a significant issue when a DS containing phosphate ions are used for the desalination of BGW by the FO process although not all phosphorous compounds could form severe scaling. For example, MAP did not indicate any scaling issue from the results presented in Figure 2. In addition, this study also shows that, the inorganic scaling in the FO process is promoted by additional factor: reverse diffusion of draw solutes.

Figure 4: The EDS spectrum for the active layer of the membrane surface. Experimental conditions are DS: 3 M DAP, FS: BGW35.

There are several types of phosphate salts because phosphate can form different polymeric ions and the most thermodynamically stable form is calcium hydroxyapatite (HAP) and calcium fluoroapatite [31]. In order to identify the scaling compounds on the membrane, XRD analysis was carried out for the fouled membrane samples. Immediately after the FO experiment, the scaled membrane was removed from the FO cell and then rinsed thoroughly with the DI water to remove any residual solution from the scales. The membrane was then dried overnight in the desiccator before the thick and loose top layer of the scale was brushed off before XRD analysis and the results are presented in Figure 5. The XRD results indicate that the scales formed on the membrane surface are mainly composed of magnesium phosphate ($MgHPO_4$) (Figure 5(a)) and magnesium ammonium phosphate ($MgNH_4PO_4.6H_2O$) or struvite (Figure 5(b)). These insoluble compounds are formed because of the reverse diffusion of $(NH_4)_2HPO_4$ towards the feed during the osmotic process which then reacts with the magnesium ions present in the FS. Struvite precipitation is one of the major operational problems during the wastewater treatment works [32] including for RO treatment process [6]. A slight increase in FS pH (8.0) was observed after the FO process was started which might also made ideal condition for the formation of struvite as alkaline pH is condusive environment for struvite formation [33].

Although, calcium phosphate and calcium sulphate could also be responsible for scale formation however, the XRD analysis could not clearly confirm the presence of calcium phosphate in the scaling layer. Calcium phosphate mainly hydroxyapatite or $Ca_5(PO_4)_3(OH)$ has been found to seriously cause inorganic scaling during the RO process [2]. However, the absence of calcium scaling in this case is likely because the Ca (52 mg/L) concentration in the BGW5 FS was significantly lower than the Mg (779 mg/L) in the BGW10 FS making the Mg ions more available for interaction with the phosphate ions.

Other potential scaling compound is $CaSO_4$ or gypsum since the FS contains both Ca^{2+} and SO_4^{2-} in the BGW FS. Gypsum is one of the significant scaling compounds often experienced during the RO membrane process [6, 34, 35] and also the FO process [1, 36]. However, neither the EDS analysis nor the XRD analysis could detect the presence of sulphur or sulphate and hence the gypsum scaling was not formed in this study. This is also reasonable given that this lab-scale FO experiments were conducted at very low feed recovery rates (less than 5%) and hence super saturation of $CaSO_4$ at this recovery rate is not expected in this study.

As discussed earlier, scaling in the pressure-based membrane processes such as RO and NF starts with the nucleation that induces growth of crystals on the membrane surface [3-5]. However, given that the low recovery rate at which the lab-scale FDFO process is operated, the potential of nucleation and surface crystallisation is not very significant. Bulk crystallisation could have been mainly responsible FDFO process using DAP as DS because a significant amount of scales were also observed on the walls of the acrylic membrane cell, not expected if surface crystallisation is the dominating factor for scale formation. The presence of small amount of Na^+ and Cl^- in Figure 4 might be because of the salt remains after the membrane has been dried and not necessarily, the scales formed during the FO process, as most sodium and chloride compounds are highly soluble.

Figure 5: XRD analyses of the scales deposited on the membranes surface showing the presence of (a) magnesium phosphate and (b) struvite. Operation conditions are DS: 3M DAP, FS: BGW35.

The results in Figure 2 show that the severity of the flux decline increases with operation time finally reaching to near zero flux after about 16 hours of operation. This shows that the thickness of the scaling layer keeps increasing with time as result of continuous reverse diffusion of DAP from the DS. This also indicates that, if the reverse diffusion or reverse draw solute flux is increased, the rate of scale formation may also increase and hence could proportionately increase the severity of flux decline. The reverse draw solute flux increases when a higher DS concentration is used. Therefore, FDFO experiments were conducted to see how the DS concentration affects the scaling potential and the flux decline during the FDFO process using BGW as FS. $NH_4H_2PO_4$ or MAP was used as a typical non-scaling fertiliser DS and compared with the DAP as DS at various concentrations.

Figure 6 shows the influence of DS concentration on the water flux during the FO desalination process using BGW10 as FS. The increase in MAP concentration increases the water flux proportionately without any sudden or sharp flux decline as shown in Figure 6(a) unlike DAP in Figure 6(b). Similar observations were made with the other four fertiliser DS and hence only MAP has been presented as a representative experimental result. However, DAP concentration showed a significant influence on the membrane scaling and flux decline as shown in Figure 6(b). When higher DAP concentrations are used, the flux decline observed was not only severer but also occurred much earlier than when lower DAP concentrations were used. This shows that when higher DS concentrations are used, the reverse draw solute flux increases as it is a direct function of concentration gradient (ΔC) [21, 37-39] and hence increases the rate of scale formation at the membrane surface thereby resulting in more severe flux decline.

Figure 6: Variation of FO water flux with time during the FO process at different concentrations using (a) MAP and (b) DAP as DS. Operating conditions are DS: DAP/MAP, FS: BGW10.

3.2 Influence of feed water properties on the water flux decline

Earlier, we have shown in Figure 5 that, Ca, Mg and P were responsible for the formation of scaling layer on the membrane surface. While the P came from the DS due to reverse diffusion, Ca and Mg were already present in the FS and they have been long recognised as the scaling precursors in the salt rejecting membrane processes such as RO and NF [2, 3, 6, 34]. Therefore, it is clear that the feed properties play a significant role in the formation of scales or membrane fouling layer that contributes to scaling or fouling and consequently flux decline.

The influence of feed properties on the flux decline was investigated using 1 M DAP as DS and by varying the feed water quality in terms of TDS and the types of ions present in the feed and the results are presented in Figure 7. When a BGW feed with higher TDS is used as shown Figure 7(a), the initial water flux was not only lower but the flux decline was also more rapid and also occurred much earlier. When a BGW with higher TDS is used, the reverse diffusion of DAP from the DS has more access to the scaling ions such as Ca and Mg resulting in rapid scaling and thicker cake layer formation that is responsible for rapid flux decline.

In order to assess which cation (Ca or Mg) was more responsible for scale formation, experiments were conducted with 3 M DAP as DS and by removing either Ca or Mg or both from the FS and replacing them with NaCl to maintain similar TDS. The results presented in Figure 7(b) show that when both Ca and Mg ions are absent in the FS, the water flux is quite normal with only gradual decline attributed to decrease in the driving force due to batch operation of DS and FS. These results confirm that, Ca and Mg are mainly responsible for the formation of the scales during the FO process using DAP as DS. When one of the ions Mg or Ca was removed from the FS, the water flux decline was still observed although the flux decline was more severe when Mg ion was removed and only Ca was present as a precursor. This indicates that Ca is responsible for more severe fouling than Mg during the FDFO process with DAP. Although the flux decline was still observed even in the absence of Ca ions, the rapid flux decline occurred only after certain time of operation.

XRD analysis in Figure 7(c) indicates that, the scaling layer is composed of hydroxylapatite or $Ca_{10}(PO_4)_5(OH)_3$ when magnesium was removed from the FS. Hydroxylapatite has very low solubility under alkaline pH which therefore promotes rapid scale formation and severe flux decline. Further, the increased presence of spectator ions such as Na^+ after replacing Mg^{2+} also probably leads to decreased solubility of hydroxylapatite and thereby contributing to severer flux decline [40]. XRD analysis for scales formed after removing Ca^{2+} ions from FS indicates the presence of both magnesium phosphate and struvite in the scales. Given that both hydroxylapatite and struvite have minimum solubility at moderately alkaline pH [41], it is difficult to correctly ascertain the actual cause of more severe flux decline with Ca than Mg. It is likely because, under alkaline pH of the FS, calcium phosphate is less soluble than struvite and hence its scale formation is more rapid than magnesium phosphate or struvite scales.

Figure 7: Influence of feed properties on the water flux during FO process presented as a variation of water flux with operation time in the FO process using (a) BGW feed of different TDS using 3 M DAP as DS and (b) FS containing different cation composition in BGW35using 3 M DAP as DS and (c) XRD analysis of the scaling layer formed when Mg^{2+} ion was removed from the BGW35 FS.

3.3 Influence of physical cleaning of the water flux recovery

The effectiveness of physical cleaning on the recovery of water flux in the FO process after scaling or fouling was studied. Before the membrane was subjected to the FDFO process, the baseline flux was obtained by using 1 M NaCl as DS and DI water as FS. After the FDFO experiments, the membranes were subjected to physical cleaning using DI water on both sides of the membrane at the same crossflow velocity as the fouling experiment 400 ml/min or (8.5 cm/s) for 20 mins. The base line flux was again obtained using 1 M NaCl as DS and

DI water as FS to study the restoration of water flux. The percentage of water flux restored was observed as a percentage ratio of the restored flux to the initial baseline flux (normalised) of the virgin membrane and the results are presented in Figure 8.

Although a noticeable flux decline was not observed with the fertiliser DS other than DAP however, it was thought that nucleation to form surface crystals might start due to long-term operation of the FDFO process. Therefore, in order to evaluate the existence of surface crystals, three different fertilisers were selected: Calcium nitrate (CAN) with the highest water flux, KNO_3 with the lowest water flux and DAP that resulted in severe membrane scaling. The results in Figure 8(a) show that, the physical cleaning is able to restore the water flux almost fully for both CAN and KNO_3. This shows that the surface crystallisation was either absent or even it was formed, the physical cleaning was adequate to fully restore the water flux. However, for DAP as DS, the water flux could be restored only up to about 80% when the normal cleaning regime of 400 ml/min for 15 min is applied. This shows that a higher crossflow velocity or/and longer cleaning duration is/are required to clean the membrane more effectively. Therefore, a higher crossflow velocity (1600 L/min) was adopted for physical cleaning of the membrane scaled during the FDFO process using DAPas DS. The same Figure 8(a) shows that the flux recovery could increase significantly when a higher crossflow velocity was adopted for physical cleaning. The water flux recovered almost fully when a higher crossflow velocity was applied for cleaning for the same duration.

In the next cleaning experiment, the influence of cleaning on the water flux recovery was evaluate for FO membranes fouled to different degrees by operating using different DAP DS concentrations. One of the other observations made from Figure 8(b) is that, when a higher DAP concentration was used, the water flux recovery was slightly lower than when a lower DAP concentration was used. These could be true and in fact consistent with our earlier observation in Figure 6(b) that, when FO is operated at high flux using higher DS concentrations, the cake layer formed could be more rapid, thicker and probably denser due to high convective force created by the water flux. Such cake layer could not be easily removed when a lower crossflow shear cleaning was adopted resulting in lower flux recovery rates. However, irrespective of the DAP concentrations, the flux recovery was almost full when a higher crossflow rate was adopted (data not shown). All the above results indicate that, the reverse diffusion of draw solute causes bulk crystallisation on the feed side which although results in severe flux decline, the flux could be fully recovered by adopting appropriate physical cleaning regime.

Figure 8: Flux recovery of the FO membrane after membrane has been fouled by inorganic foulant (a) using three different types of DS and BGW35 as FS and (b) using different concentrations of DAP as DS and BGW10 as FS. The cleaning regime was conducted at a crossflow rate of 400 ml/min for 20 minutes except for DAP(1600) which was conducted at 1,600 ml/min crossflow cleaning.

4 Conclusions

In this study, the inorganic scaling and flux decline in the FDFO process during the desalination of brackish groundwater have been investigated. The study also evaluated the effectiveness of physical cleaning on the membrane flux recovery. The following inference has been drawn from this study:

- When FDFO is applied for the desalination of brackish groundwater containing multivalent ions, it is important to consider the influence the reverse diffusion of draw solute on the scaling and flux decline potential

- Reverse diffusion of draw solutes plays a significant role on membrane scaling and flux decline during the FDFO desalination of BGW
- Amongst the six fertilisers tested as DS, $(NH_4)_2HPO_4$ or DAP was found to have the worst scaling effect during the FDFO process using brackish groundwater
- Membrane autopsy using SEM , EDS and XRD indicates that magnesium phosphate, magnesium ammonium phosphate or struvite and calcium phosphate (hydroxylapatite) were mainly responsible for membrane scaling when DAP is used as DS
- Physical cleaning was observed to be quite effective in recovering the pure water flux of the membrane after FDFO process.
- Although a rapid flux decline was observed using DAP as DS however, the water flux recovered almost fully. This shows that the reverse diffusion of draw solute causes scaling due to bulk crystallisation however the flux could be fully recovered by adopting appropriate physical cleaning regime.

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