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Fertilizer-drawn forward osmosis for irrigation of tomatoes

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ABSTRACT

Fertilizer-drawn forward osmosis is a low-energy desalination concept particularly developed for the irrigation use of desalinated water. It has an advantage of not requiring regeneration of the draw solution (DS), thus, it can be used directly for the purpose of irrigation without any additional treatment. The current study was aimed to evaluate the real application of forward osmosis (FO) targeting irrigation of tomato crops based from their fertilizer requirements. Fertilizer-DSs were prepared to drive seawater desalination using commercially available fertilizers such as NH_4NO_3, NH_4Cl, KNO_3, KCl, $NH_4H_2PO_4$, and urea. DSs were prepared to represent varying nitrogen:phosphorous:potassium (N:P:K) ratios used in assorted tomato growth stages. The FO performance evaluated in terms of the flux and reverse solute flux (RSF) showed significant variations in outcome. The resultant flux for different DSs was influenced by the particular fertilizer present in DS mixture and its concentration. This flux varied from 2.50 to 12.49 LMH. Comparatively, DS carrying high osmotic pressure components showed high-flux outcome. The fraction $J_w/\Delta\pi$ of these fertilizer-DSs varied from 0.062 to 0.19 LMH/bar, which indicates a changing flux outcome against the same osmotic pressure. To select the best performing fertilizer-DS, nitrogen source fertilizers like urea, NH_4NO_3, and NH_4Cl were further evaluated for 10-0-10 NPK value. It was found that NH_4Cl-based DS mixtures performed better than urea- and NH_4NO_3-based DS. The RSF results indicated that all nitrogen- and potassium-based DS exhibited higher N- and K-RSF. However, the DS using $NH_4H_2PO_4$ delivered extremely low P-RSF of 12.35 $g/m^2/h$. Long-term run tests with seawater quality feed solution resulted in FO producing a final DS enriched in nutrients greater than the tomato plant's requirement. This implies that the use of dilution or any other technique to reduce excessive nutrients is essential before using the final DS for tomato irrigation.

Keywords: Forward osmosis desalination; Fertigation of tomato; NPK crop nutrients; Fertilizer-draw solution; Seawater feed

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1. Introduction

Desalination is a widely used process to remove dissolved salts from brackish or seawater to obtain fresh water. Besides the considerable technological advancements in the existing desalination technologies, such as thermal distillation and reverse osmosis (RO), desalination is still believed to be a highly energy-intensive process [1,2]. Additionally, the continuous rise in energy prices further results to high cost of desalination. For this reason, desalination was never considered as an ideal solution for every water user especially in agriculture.

In the last few decades, draughts and climate changes are continuously affecting the agricultural water availability, which result in reduced crop harvested area and lower agricultural yield. Agricultural water scarcity is one of the main reasons for rising prices of agriculture food commodities across the globe [3] and the current trends show that in the coming future, it may affect the world food security even more severely. Both water quality and water scarcity are considered as the most important challenges for food production of our world's growing population needs as they directly influence the crop yield and quality of food [4,5].

Forward osmosis (FO) is considered as an emerging green desalination technology using the simple concept of natural osmotic pressure to drive desalination. When a self-constructed draw solution (DS) possessing high osmotic pressure is placed against any feed water across a semi-permeable membrane, naturally, the water starts flowing toward the DS side until the salt concentration on both sides of the membrane becomes equal. Water molecules in FO moves differently compared with the RO process where water permeates through the membrane under a high hydraulic pressure. The FO process utilizes naturally available osmotic pressure difference between the available DS and the feed water. FO, therefore, does not require additional energy to pressurize feed water streams as that needed in RO, and hence, it is considered as an economical, low-energy desalination technology having a low-carbon footprint.

Looking into this important aspect, in a narrow time span, the FO technology has been rapidly evaluated for a wide range of applications such as sea/brackish water desalination [6–9], wastewater treatment [10], power generation [11], osmotic membrane biological reactor [10,12–14], food processing, concentration and recovery of active organic components [15], and direct fertigation [16].

Several promising draw solutes such as NH_3-CO_2 mixture [8,17] and super magnetic nanoparticles [18] have been suggested for application in drinking water, yet they are still required to be tested commercially for process economy. In most of FO operations for drinking water production, further treatment of diluted DS is required to produce useable product water. Thus, FO desalination application for potable water use still remains a challenge [8] because the separation and recovery of draw solute from FO product water are not easy and require additional energy too. In all of the above FO techniques, water recovery and draw solute separation are energy-consuming steps that diminish the true advantage of low-energy FO operation.

Considering the current shortages and rising demands of irrigation water, fertilizer-drawn forward osmosis (FDFO) was developed in 2011 for use as an FO technology for non-potable application i.e. agriculture [16]. Various types of fertilizers were evaluated as DS against various qualities of feed solution (FS), and a diluted fertilizer solution is collected at the end of each test. This FO process carry an edge over other FO processes as the resultant low-concentration fertilizer DS does not require regeneration, and thus, can be used directly with some concentration adjustments to irrigate any suitable agricultural crops [16,20]. As the final energy intensive step of draw solute recovery is eliminated in FO, this process really become an effective low-cost desalination technology to fulfill irrigation water requirements.

Due to a low-energy process facet, it is believed that FDFO can be economically used for brackish/seawater desalination to provide useable water to the largest water-consuming agricultural sector. FO can easily be used to abundant reservoirs of seawater along long coastal areas and inland underground brackish water to get low-cost beneficial agricultural water.

Tomato (*Lycopersiconesculentum*) is one of the most popular and widely grown vegetable crops in the world. This study focuses on the real water and fertilizer demands of tomato using the tomato fertilizer requirements as the basis for the preparation of DS. Water and fertilizer requirements vary for different varieties of tomato grown and these two requirements change for the various plant growth stages as well. Based on different climate conditions, soil quality, and moisture, a field-grown tomato crop requires 400–800 kL/ha of water for its whole growth period [5,21,22]. Tomatoes grown on light soils require about 6,000 kL/ha of water for the average crop period of about 120 d [23]. Like many other crops, tomato is also sensitive to salinity. In most of the cases, tomato yield is reduced when irrigated with water having an

Table 1
Nutrient requirements of open-field tomato according to its physical stages [19]

Days after planting	Physiological tomato crop growth stages	Days	kg/ha/d N	kg/ha/d P_2O_5	kg/ha/d K_2O
0–25	Planting—first flowering	25	2.3	3.8	2.3
26–45	Rapid growth—flowering	20	3.0	1.3	4.4
46–70	Fruit set—fruit ripening	25	4.0	0.0	8.0
71–105	Fruit ripening—harvest	35	5.1	0.0	10.3
Total nutrients (kg)		105	397.1	120.0	705.7

electrical conductivity above 2–3 dS m^{-1} (mmhos/cm) [24]. This yield may even be reduced to 50% with irrigation water conductivity of 8 mmhos/cm [5]. Sodium cations compete with the potassium cations for the root uptake sites, and chloride competes for the uptake of nitrate nitrogen and will impede plant development [25]. Table 1 shows the NPK nutrient requirements of tomato crop during its various growth stages. These values were later used to prepare the mixed fertilizer (DS) for FO experiments. It is estimated that about 2,300–2,450 kg/ha of various fertilizers are required for the whole tomato crop growth period [19,26].

This study explores the potential use of a large quantity of fertilizers required for tomato plant to prepare DS of an FO process. The objective of this study was to evaluate the FO flux and the reverse solute flux (RSF) performances using fertilizer DS prepared for various tomato plant growth stages, and also using a seawater-quality FS. Commercially available fertilizers were used to prepare the DS. The effects of changing nitrogen-source fertilizers in a particular DS were evaluated to find how one fertilizer affects the performance in a DS mixture. RSF loss was evaluated for DS adjustment to get the required nutrient level in the final DS, cost control, and waste discharge management. Long-terms tests were also aimed to evaluate the process effectiveness and to assess the expected final nutrient concentration in the diluted DS.

2. Materials and methods

2.1. FO performance measurements

Laboratory-made FO apparatus as shown in Fig. 1 was used to evaluate the water permeation through the FO membrane. The FO membrane made up of cellulose triacetate embedded on a polyester woven mesh [6,27] was supplied by HTI, USA. All tests were carried out using membranes in normal FO orientation i.e. the active layer is facing FS (AL-FS). The specially designed cross-flow membrane cell had a channel on each side of the membrane, which allowed the FS and DS to flow through separately. Each channel had identical dimensions of 7.7 cm (L), 2.6 cm (W), and 0.3 cm (H) on both sides of the membrane.

The flow through each channel was controlled by a variable speed peristaltic pump drive (Cole–Parmer, USA) and monitored by variable area flow meters (Blue-White Industries Ltd. USA). The flow rates were kept constant at 400 mL/min for both FS and DS. Tests were carried out in a co-current flow configuration for FS and DS streams and the temperatures of both DS and FS streams were kept constant at 25℃ ± 0.5℃ using a water bath controlled by a heater/chiller. A weighing scale (CUW 4200H by CAS, Korea) connected to a computer was used to monitor the weight loss of the FS which was later used to calculate the water flux in the FO operation.

2.2. Chemicals and reagents

Commercially available fertilizers, namely: NH_4NO_3, NH_4Cl, KNO_3, KCl, $NH_4H_2PO_4$ (MAP), and urea were used in this study to prepare the DS, so as to get a real application data. These fertilizers were initially analyzed to evaluate their NPK ingredients and the level of other impurities. DS were prepared for specific NPK grade (in % for N, P_2O_5, and K_2O) as 11.5-19-11.5, 15-7-22, 10-0-20, and 15-0-30 to exhibit the nutrient requirement for tomato crop at any particular growth stage as shown in Table 1. DS was filtered through a Whatman filter paper to avoid blocking or fouling of the membrane surface.

FO was evaluated against seawater (SW) quality, FS which represents the largest source of water available on earth. All FS were prepared using 35 g/L NaCl (representing seawater osmotic pressure) dissolved in tap water. NaCl supplied by Chem-Supply Australia was used to prepare FS. Actual seawater quality FS was not evaluated in this study as Ca^{2+} and Mg^{2+} commonly present in seawater posed a risk of insoluble suspension formation with phosphate fertilizers.

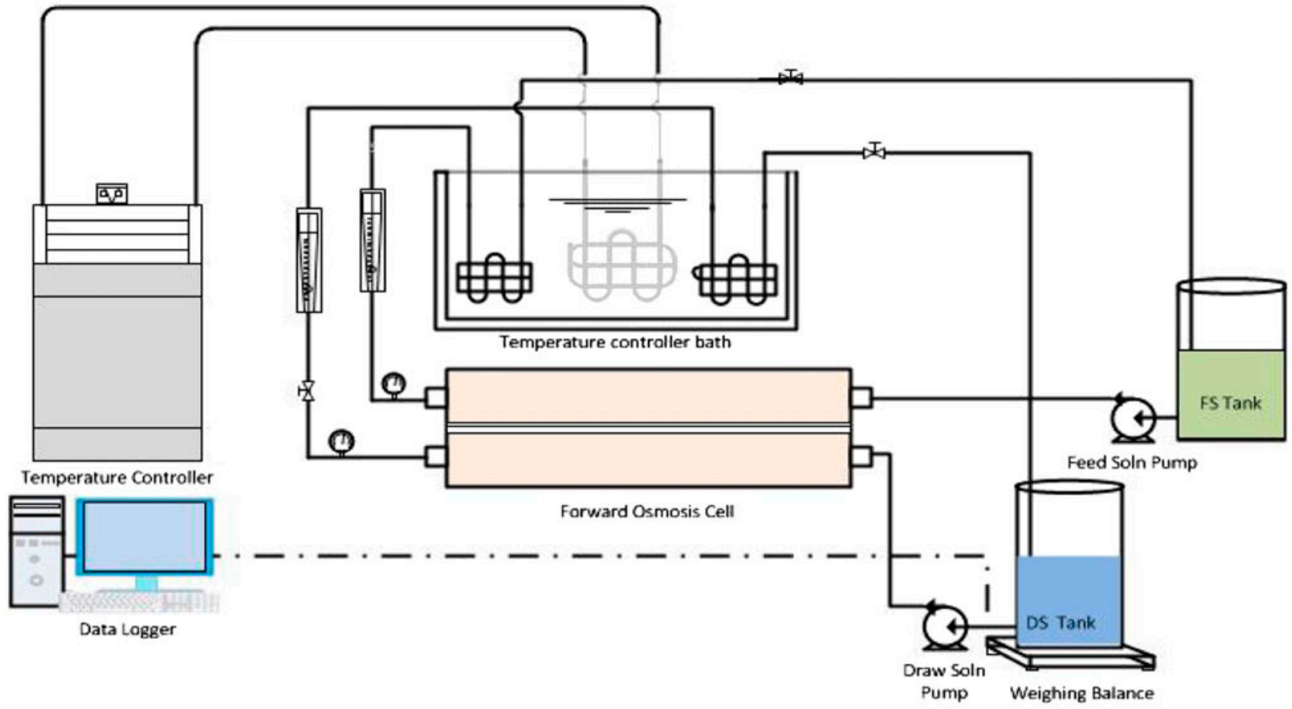

Fig. 1. Lab-scale FO setup used in the study.

Unlike all other previous studies where MQ water was used to prepare FS and DS for FO tests, here both DS and FS were prepared in tap water. Tap water was used to explore any scaling and fouling issues associated with the use of a commercial fertilizer and poor quality water. Tap water having conductivity, total hardness, and alkalinity of 22 mS/m, 65 mg $CaCO_3$/L, and 46 mg $CaCO_3$/L, respectively, was used in this study.

2.3. *Performance and measurements*

The water flux performance was evaluated using DS prepared based on the fertilizer requirements of tomatoes in their different growth stages. FS samples were collected at the end of each test and analyzed for RSF particularly the K, P, and N concentration using APHA method 3125 protocols.

OLI Stream Analyzer 3.1 software (launched by OLI Systems, Inc., Morris Plains, NJ) was used to access osmotic pressure and other physical and chemical properties of DS and FS. OLI software indicated that 35 g/L NaCl dissolved in tap water showed an osmotic pressure of 27.38 atm.

3. Results and discussion

3.1. *Screening of fertilizers to prepare DS*

Eight selected commercially available fertilizers i.e. NH_4Cl, $(NH_4)_2SO_4$, $Ca(NO_3)_2$, NH_4NO_3, KNO_3, KCl, urea, and $NH_4H_2PO_4$ (MAP) were initially evaluated for their suitability to provide NPK nutrients for tomato growth. NH_4NO_3, NH_4Cl, and urea were taken as purely N-nutrient source fertilizers, MAP as P and N-source, KCl purely as K-source, and KNO_3 as a source fertilizer for N and K. These fertilizers were evaluated and screened for issues such as farmers' choice and preference for fertilizers, availability, price, NPK nutrients, osmotic pressure, solubility limits, presence of unwanted impurities, and previous FO studies [16].

Two fertilizers were rejected in the initial screening process. $(NH_4)_2SO_4$ was dropped for issues in preparing DS at higher concentration. $(NH_4)_2SO_4$ showed acute hassle in preparing DS. It took a long time to dissolve it completely despite using mixing aids, and even left black insoluble matter at 2 M concentration which quickly blocked filter paper pores.

Fertilizer carrying higher osmotic pressure such as $Ca(NO_3)_2$ was an ideal choice as DS for FO. However, it was abandoned as calcium carried high probability of forming insoluble suspensions with phosphate fertilizers [28,29]. Furthermore, excessive calcium in the final diluted DS also affect the tomato yield as Ca^{2+} reduces potassium intake by the plant and tomato yield drops drastically due to plant's K^+ deficiency [25,30].

NH_4NO_3 was considered partially for comparison due to its non-availability in granular form. All necessary NH_4NO_3-based DS were prepared from the available liquid NH_4NO_3 fertilizer. Urea was evaluated for FO process as it is considered as the most popular N-source fertilizer for tomato crop. It is cheap, easily available, highly enriched with N (up to 46%), and immensely soluble even at high concentrations. OLI software showed that urea carries the lowest osmotic pressure among all the present fertilizers.

NH_4Cl and MAP also left some residue in preparing concentrated DS but these solutions were filtered easily. Considering their physical and chemical characteristics NH_4Cl, $(NH_4)_2SO_4$, KNO_3, KCl, MAP, urea, and NH_4NO_3 were shortlisted to prepare DS and evaluated for FO DS process (Table 2). Initial four fertilizers were categorized as common fertilizers for DS.

3.2. Preparation of mixed fertilizer DS suitable for tomato application

Looking into the average life cycle of processing a tomato plant of 120 d and its watering and fertilizer requirements, a tomato crop span is divided into four stages i.e. planting—first flowering, rapid growth—flowering, fruit set—fruit ripening, and fruit ripening—harvest [19] hereinafter described as S1, S2, S3, and S4, respectively. Stage S1 indicates the time from planting or seeding during vegetative growth until the first flower appears. Stages S2, S3, and S4 cover the period from flowering to first fruit set, from fruit ripening to first harvest, and from first harvest to the end of the last harvest, respectively. Fertilizer requirement for various growth stages of tomato was used to prepare the fertilizer DS. These four growth stages, respectively, require fertilizers of 11.5-19-11.5, 15-7-22, 10-0-20, and 15-0-30 NPK values. The shortlisted fertilizers were used to prepare fertilizer DS matching, the nutrient requirements of tomato plant for the different stages.

NH_4Cl was preferably selected as the primary N-source fertilizer for preparing the fertilizer DS carrying nutrients. The influence of the other two N-source fertilizers such as NH_4NO_3 and urea was also studied by preparing the DS of the same NPK value and the FO performances were evaluated. NH_4Cl was separately replaced by NH_4NO_3 and urea in the DS mixture without affecting the DS NPK ratio. However, OLI software indicated that all these DS showed varying osmotic pressure. For P-nutrient source, only MAP was used and for K-nutrient source, KCl was used with KNO_3 in the entire study. KNO_3 also contributed to N-nutrients.

Compared with the individual fertilizer components, the fertilizer blends showed several changes in physical and chemical properties of the DS. MAP and NH_4Cl fertilizers produced suspensions and left residue at higher concentrations. Similarly, fertilizers containing the same salt component, i.e. KCl and KNO_3, showed difficulties in mixing as their solubility decreases in the mixture. For these reasons, the fertilizer DS for various NPK values was prepared according to their solubility limits in a given mixture.

Table 2
Shortlist of fertilizers used to prepare mixed fertilizer DS, showing NPK nutrient composition and osmotic pressure at 1 M concentration

Commercial/chemical name/chemical formula	N/P/K N/ P_2O_5/K_2O	Osmotic pressure (1 M concentration) atm	Commercial/chemical name/chemical formula	N/P/K N/ P_2O_5/K_2O	Osmotic pressure (1 M concentration) atm
Ammonium chloride; NH_4Cl	25/0/0	43.5	Ammonium nitrate; NH_4NO_3	34/0/0	33.7
Mono ammonium phosphate (MAP); $NH_4H_2PO_4$	18/46/0	43.8	Potassium nitrate; KNO_3	14/0/44	37.2
Urea; $(NH_2)_2CO$	46/0/0	23.7	Potassium chloride; KCl	0/0/60	44
Ammonium sulfate*; $(NH_4)_2SO_4$	21/0/0/(24)	46.14	Calcium nitrate*; $Ca(NO_3)_2$	15.5/0/0/(26.5)	48.8

*Not used to prepare DS for this study.

3.3. Water flux in FO process using mixed fertilizer-draw solutes

The performance of fertilizer DS in terms of water flux (J_w) for FO process is shown in Fig. 2. DS were prepared for four tomato growth stages namely S1, S2, S3, and S4 representing NPK nutrient values of 11.5-19-11.5, 15-7-22, 10-0-20, and 15-0-30, respectively. To prepare the specific NPK value DS, various fertilizers were mixed in pre-determined quantities. Fertilizer DS was prepared for 25, 33, and 50% NPK fertilizer quantity per hectare for various stages and is represented by suffix −1, −2, and −3, respectively, in the bracket of the *x*-axis label in Fig. 2. Due to solubility issues, for stage four, the fertilizer DS was prepared for only 15% NPK quantity per hectare. This fertilizer DS was separately evaluated with FO flux, RSF, and ultimate essential nutrient concentrations in the final DS. Flux ranges from 2.51 to 12.54 LMH with seawater FS for these fertilizer DS.

For a solution carrying more than one solute, the expression of total osmotic pressure for a mixture of different solutes can be written as $\pi_{\text{Total}} = \pi_1 + \pi_2 + \pi_3 + \pi_4 + \ldots$ where the subscripts 1, 2, 3, 4 … represent the various components of the draw solute. The OLI software showed that the resultant osmotic pressure of DS was the sum of the osmotic pressure of the individual components present in the mixture. It was observed that the flux changed with rising DS concentration but not linearly in all cases (Fig. 2). Flux results did not respond proportionally to changing of the respective osmotic pressure. Results showed either positive or negative deviation for linear trends. The main reason for these variations in slope for different DS seems to be due to the type and concentration of individual components present in DS. Each DS behaved differently depending on the concentration of various components present in the mixture.

The basic flux equation ($J_w = A\sigma\Delta\pi$) reveals that the flux should change linearly with osmotic pressure gradient available across the semi-permeable membrane as other parameters were fixed for these tests. However, the slope of the flux varies for all the DS in Fig. 2(a)–(f). The above flux equation suits ideal or very weak solutions however, it still accounts for the main driving force (osmotic pressure gradient) for osmosis. From the non-linear flux results in Fig. 2, it is realized that for non-ideal solutions and high-concentration DS, other physical and chemical properties of the solute components additionally supported these resultant flux variations. The membrane permeability coefficient (A) decreases at high DS osmotic pressures [31]. High-concentration DS results further showed notable deviation of the theoretical flux to actual flux which reflects that the other relevant forces increase with the DS concentration.

Furthermore, the dissimilar slope of the flux and osmotic pressure curves for the DS shown in Fig. 2(a)–(f) follow earlier research evaluations and confirm that the rising DS concentration does not change the water flux linearly in FO [32–34]. Both external concentration polarization (ECP) and internal concentration polarization (ICP) also vary with the changing DS/FS concentrations [8,33,35,36]. High FS concentration also contributed to the increase in ECP which directly caused high reduction of the resultant water flux [33]. The main reason for the variation in slope for different DS seems to be due to the type and concentration of individual components present in DS. Each DS behaved differently depending on the concentration of various components present in the mixture. The effect of membrane properties, DS diffusion coefficients, inter-molecular interactions, and ionization energy has been evaluated by many researchers for FO flux but they lack clear reasoning for the changes of flux with osmotic pressure [8,36–39].

Fig. 3 summarizes the FO flux performance of the various DS in conjunction with the main FO driving forces such as DS osmotic pressure (π) and net osmotic pressure difference available ($\Delta\pi$). The presented data are unable to authenticate the presence of any fixed correlation between the osmotic pressure and the resultant flux for varying DS especially when the DS and FS concentrations are high for FO process.

To get further insights the FO flux is plotted against the ratio $\Delta\pi/J_w$ (bar/LMH), which depicts the net osmotic pressure required to get a unit value of flux (Fig. 4(a)). It shows that several DS require different net osmotic pressure ($\Delta\pi$) to provide a unit flux (LMH) output. This further indicates that the same osmotic pressure of two DS mixtures may not give a uniform flux. Most of DS mixtures show $\Delta\pi/J_w$ values around 10 except S2 (AC-1), S2 (AC-2), and S2 (AC-3), which showed lower value for this fraction (more effective DS) and S3 (U-1) and S1 (AN-3) showing higher value for this fraction (less effective DS).

Using OLI software, it is revealed that S2 (AC-1) DS containing NH_4Cl as N-source fertilizer forms a large number of ionic species than S2 (U-1) DS using urea as N-source fertilizer. This can be concluded that the DS forming more ionic speciation delivers more flux. The osmotic pressure should not be taken as the only criterion to select DS for FO operation. For the same osmotic pressure, DS with higher diffusion coefficient results in higher water flux [13]. This further reflects that DS carrying more ionic species also present higher diffusion coefficient. The role of DS

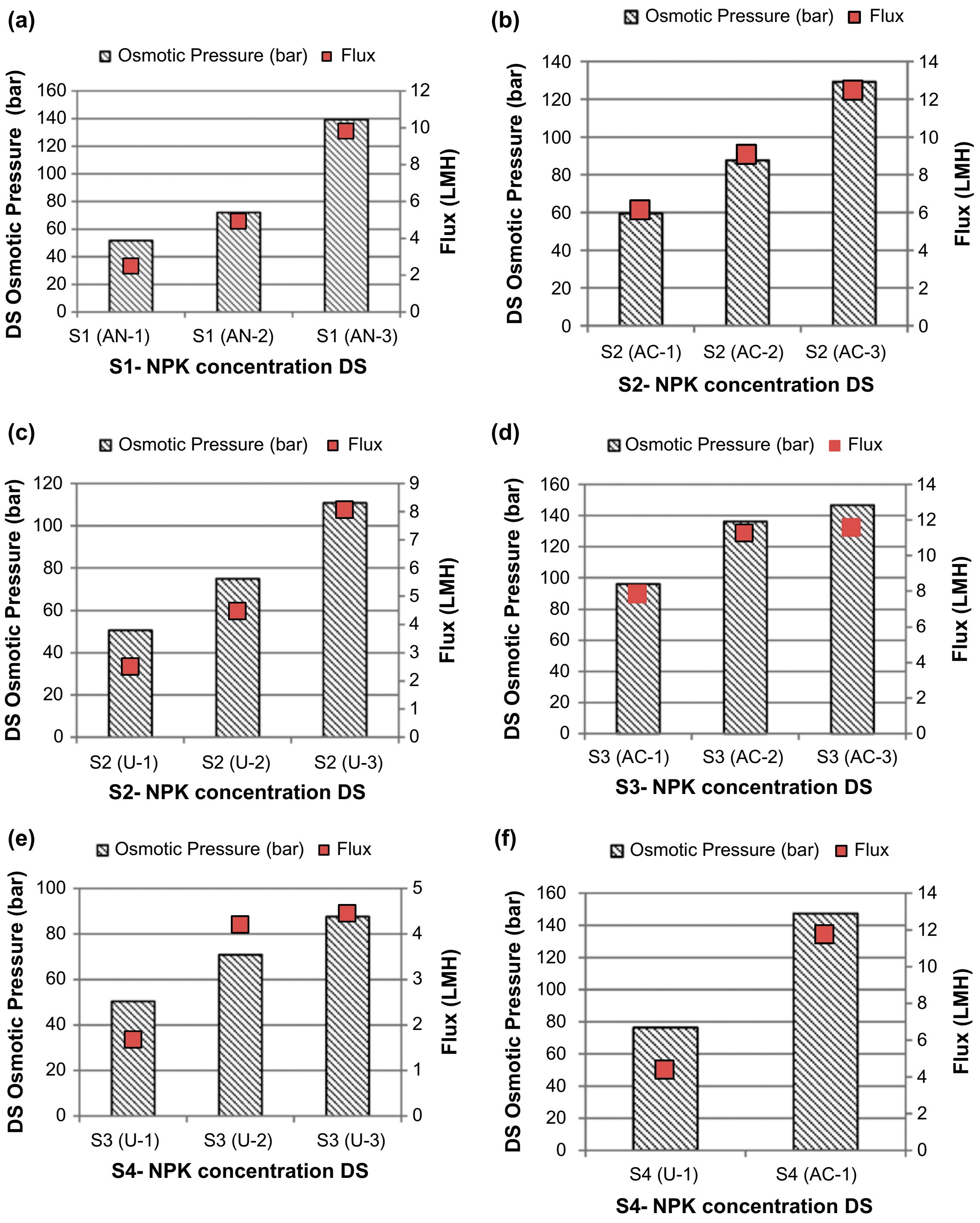

Fig. 2. Osmotic pressure and resultant flux changing trends for different DS prepared for various tomato crop growth stages: (a) S1 stage with NH_4NO_3 as N-source fertilizer, (b) S2 stage using NH_4Cl as N-source, (c) S2, urea replaced NH_4Cl N-source in DS, (d) and (e) S3 stage with NH_4Cl and urea replaced NH_4Cl N-fertilizer source in DS, and (f) S4 stage DS using urea and NH_4Cl as N-source fertilizers. Note: AN: Ammonium nitrate, AC: Ammonium chloride, and U: Urea represents main N-source fertilizer in respective DS.

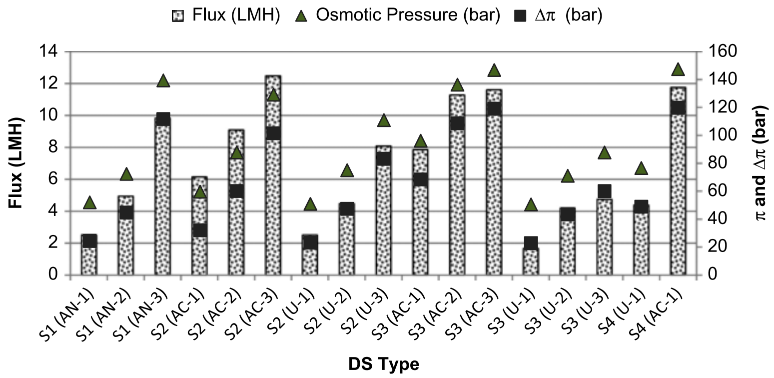

Fig. 3. Effect of osmotic pressure and net osmotic pressure on FO-flux outcome for various DS mixtures.

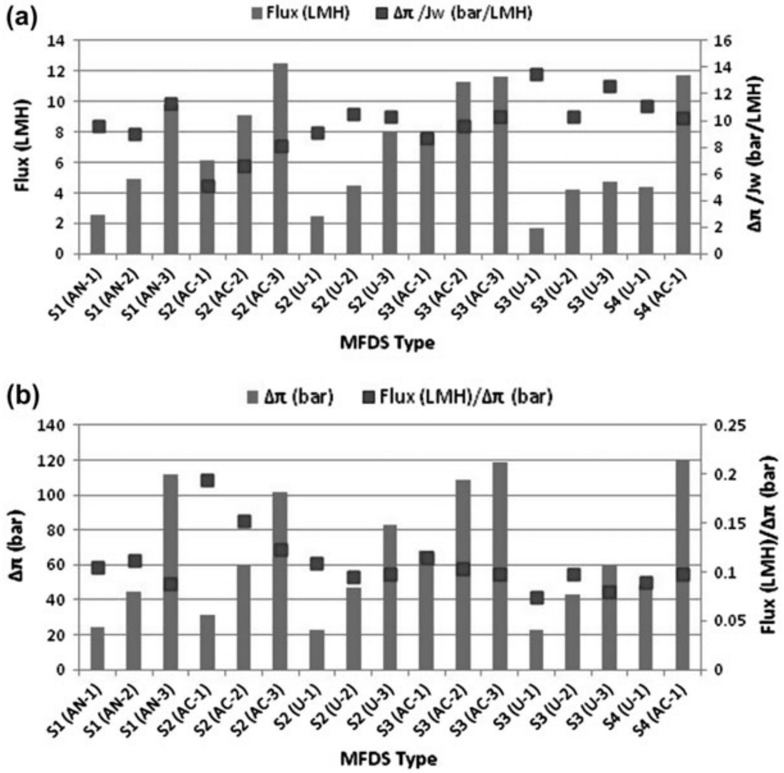

Fig. 4. Comparison of (a) Flux and $\Delta\pi/J_w$ (bars/LMH) and (b) Net osmotic pressure gradient $\Delta\pi$ (bars) and J_w(LMH)/$\Delta\pi$ (bars) for different mixed fertilizer DS.

components carrying high osmotic pressure is important but additional study is required to fully explore the phenomenon of DS behavior.

Fig. 4(b) also showed similar variation when the ratio of $J_w/\Delta\pi$ was plotted for these DS mixtures. Thermodynamically, the transport of a given species must be in the direction to decrease chemical potential for the species [37]. So for an FO process, which reduces this chemical potential between the two solutions across the membrane, it is hypothesized that in a mixture of DS, besides the osmotic pressure of DS and FS, the chemical properties of their individual solutes such as inter-molecular interactions, ionization potential, chemical potential, ionic charge, ionic interactions between DS species and FS components, and others also play vital roles in dictating the FO flux outcome.

3.4. *Comparison of flux for changing N-source fertilizer during various plant growth stages*

Three N-source fertilizers namely: NH_4Cl, NH_4NO_3, and urea were used to prepare DS to meet

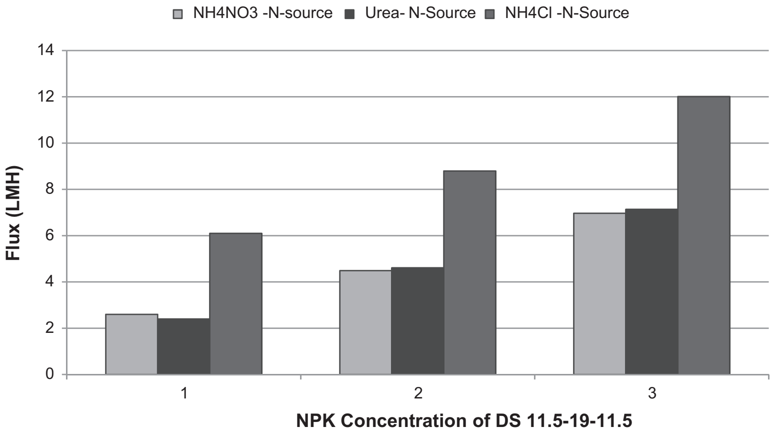

Fig. 5. Water flux with varying N-source component in mixed fertilizer DS: NH_4Cl N-source-based DS shows the highest flux, whereas Urea- and NH_4NO_3-based DS gives lower but nearly the same flux (Stage: S1**)**.

nutrient requirements of S1 tomato growth stage and then evaluated for FO process.

NH_4NO_3 and urea fertilizers give low flux and high RSF and may not be favored for FO process [16]. However, these two fertilizers were evaluated for their synergic effects with other fertilizer blends as DS, and were compared with NH_4Cl-based mixtures.

The tomato crop stage S1 NPK ratio of 11.5-19-11.5 was further evaluated for FO process. DS was prepared for NH_4Cl, NH_4NO_3, and urea N-source fertilizers and evaluated for 25, 33, and 50% fertilizer quantity that is required per hectare of S1 stage. Fig. 5 indicates that the mixtures carrying DS components having less osmotic pressure (π) such as urea and NH_4NO_3 showed a lower flux output. However, DS containing NH_4Cl for the same NPK values showed a higher resultant flux. OLI software further revealed that at 1 M concentration, NH_4Cl showed π of 43.5 atm, which is 83 and 29% higher than the π of 1 M urea and NH_4NO_3, respectively. This confirms that in a mixture of DS solutes, the higher osmotic pressure value component mainly quantifies π and flux of the mixed DS. Thus, NH_4Cl-based DS showed a higher resultant flux than those of other N-source fertilizer blends. However, the differences in flux outcome vary with their concentration and the presence of other components in a particular DS.

In contrast, at 1 M concentration, urea shows π of 23.7 atm whereas NH_4NO_3 shows π of 33.7 atm, which is 42% higher than that of urea. Despite these differences in π, both NH_4NO_3 and urea showed nearly the same flux for two DS prepared for the same NPK ratio. From this, we may also conclude that in these DS mixtures, urea and NH_4NO_3 fertilizer fractions exert inconsiderable π in the overall osmotic pressure of the DS. DS carrying KCl, MAP, and KNO_3 as other main components of the DS contributes to a notable portion of the overall π. Due to the lower π contribution of these two N fertilizers, the resultant flux was not dictated by the π of urea and NH_4NO_3 components but by other components of DS. These results again may be due to the influence of intermolecular associations between the different components of the DS.

3.5. RSF using DS blend

FS samples were collected at the end of each experiment and were analyzed to evaluate any draw solute diffusion across the membrane to the feed side. Figs. 6 and 7 compare the flux and net osmotic pressure ($\Delta\pi$) of DS with NPK RSF (in $g/m^2/h$). Similar to the FO flux results, RSF outcome also showed varying behavior with different fertilizer DS blends. Apparently, all nitrate-based DS blends indicated high RSF values. Moreover, DS having high concentration of urea or NH_4NO_3 showed high RSF in terms of nitrogen. Nitrates due to smaller molecular size penetrate deeply into the membrane [40–42]. Some of the DS prepared from KNO_3 also showed high RSF values.

RSF is considered as a loss of valuable DS inputs which raises the FO operating cost. RSF was regularly monitored for all DS to collect data for cost control and waste discharge management. Moreover, concentrated FS carrying RSF solutes is normally discarded or dumped back to other receiving bodies, wherein the excessive nutrients present in the FS concentrate create algal bloom and eutrophication problems in the receiving water.

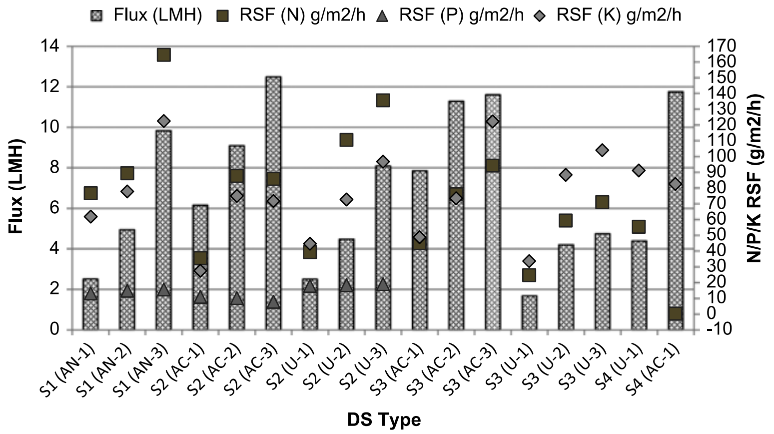

Fig. 6. Nitrogen (N), Phosphorous (P), and Potassium (K) RSF behavior for DS in FO process. All these RSF values are taken as GMH ($g/m^2/h$). P-RSF shows values for the first two stages S1 and S2 as phosphate fertilizer was not used to prepare DS for S3 and S4 stages.

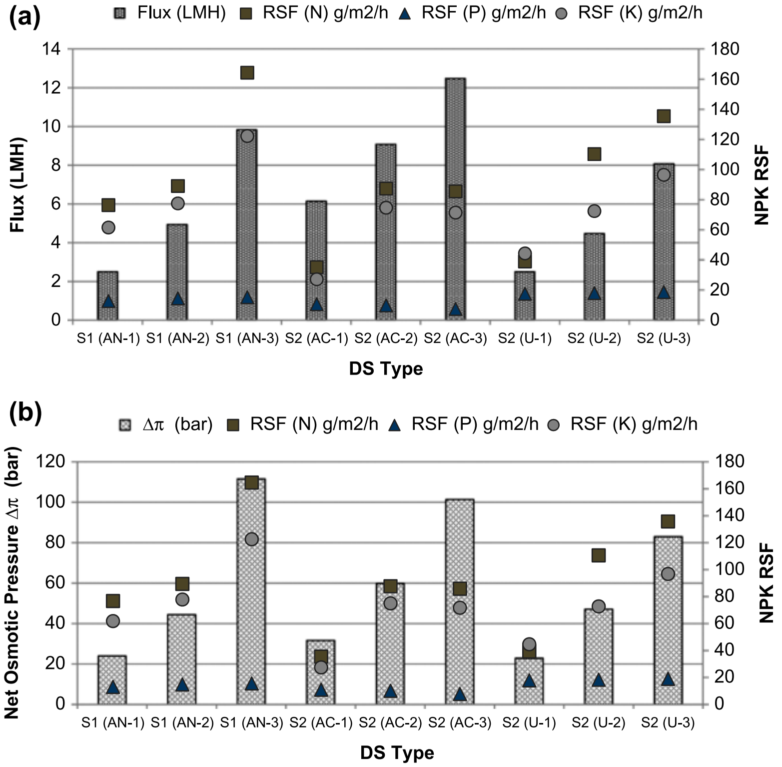

Fig. 7. N, P, and K-RSF for various DS used. (a) Flux (LMH) plotted along with RSF for N, P, and K (b) Net osmotic pressure ($\Delta\pi$) plotted along with RSF for N, P, and K. Along horizontal axis, first two letters in the brackets indicate nitrogen source used to prepare DS for that particular stage. Similarly numbers 1, 2, and 3 indicates specific concentration of particular DS.

For most of the RSF results for S1 and S2 tomato growth stages, it is observed that N-RSF is higher than K-and P-RSF, which is probably due to the small size of N–hydrated radii. RSF for K and P always remained on the lower side for nearly all DS blends.

However, the S3 and S4 stage DS results further indicate that the K-RSF is higher than N-RSF for these two stages. These results are due to the high potassium concentration (Table 1) in the DS mixtures for Stages S3 and S4. Phosphate loss was observed at a minimum while using MAP as phosphate/nitrogen nutrient source component. MAP-based DS showed low RSF not only for phosphorus but for nitrogen as well. This suggests that higher MAP concentration in the DS helps to keep this nutrient loss at a minimum and improve the overall efficiency of the process.

Tang et al. [27] and She et al. [43] have presented the following equation to predict the reverse draw solute flux across the membrane for a single solute:

$$J_s = J_w \frac{B}{A\beta R_g T} \tag{1}$$

where J_s is the solute flux, J_w the water flux, B is the solute permeability coefficient of the membrane, A is the water permeability coefficient of the membrane, is the van't Hoff coefficient, R_g is the universal gas constant, and T is the absolute temperature. Eq. (4) mainly relies on the solute permeability coefficient (B) to determine RSF while maintaining all other parameters constant for any particular solution. The membrane structure and DS composition play an important role in the bi-directional diffusion of solutes across the membrane [44]. The solute permeability constant varies inversely with the thickness of the membrane [45]. The membrane permeability coefficient (A) and solute coefficient (B) are also affected by the membrane thickness. By this equation, we may deduce that RSF (J_s) is proportional to the pure water flux (J_w), and as J_w increases, RSF should also increase. However, a later study by She et al. [43] has found that for many membrane processes, as J_w increases, RSF is reduced. This was attributed to the high flux that helps to push the solute molecules back to the DS [43], which seems more reasonable and logical.

Figs. 6 and 7 indicate that the RSF of N, P, and K nutrient raises with the increase in DS mixture concentrations. The resultant high values of flux and RSF are due to the high concentrations of DS in the particular DS. The RSF of N and K responded quickly to the DS concentration changes, whereas the P-RSF did not change much, rather it nearly remained unchanged. Donnan [46] shows that the ionic equilibrium on both sides of the membrane dictates the diffusion of ions from one side to the other. Osmotic pressures, ionic equilibria, and potential differences affect the movement of ions across the membrane [46]. For systems containing two electrolytes with a common ion, one part of the electrolyte moves faster than the other and changes the potential difference of the electrolytes. The diffusion process then slows down and the system attains back the ionic equilibrium. For FO using fertilizer DS against SW quality FS, Cl^- is the common ion in both DS and FS. The other components of the DS such as NH_4^+/NO_3^- and K^+ having smaller hydrated radii move faster than Na^+ ions, which indicates a high N- and K-RSF. Kirkwood–Buff theory helps to some extent in investigating the changes in associations and interactions by the addition of some common co-solvents [47]. The diffusion of ions from a solution carrying various solutes is quite complex and still needs answers to many related issues. It is predicted that the uniform P-RSF outcome with these fertilizer DS is owed to the size of the PO_4 ions and lower favorable ionic attractions of the ion present on the other side of the membrane.

The RSF results indicate that due to the fertilizer salt losses through RSF, the final diluted DS may not end up with the same NPK nutrient ratio in the final DS at which tests were started. The RSF outcome indicates the loss of valuable nutrients and possible deviation from the start-up values. To achieve the desired NPK ratio suitable for tomato crop for any particular crop period, the RSF loss adjustments would be required to prepare the fertilizer DS. For practical use, to account for RSF loss in an FO process, the starting DS therefore is required to have somewhat higher NPK ratios to what is required theoretically so that the final DS may achieve the same NPK nutrient ratio required for any particular growth stage for tomato or other plants.

3.6. Long-term run tests for fertilizer DS and expected final DS concentration

Using NH_4Cl and urea as N-source fertilizers, one DS was prepared for S2 and two DS were prepared for S4 stage NPK ratio and these DS were evaluated for flux trends for long-term run tests up to 60 h. The NH_4Cl as nitrogen-source fertilizer was used to prepare DS having 11.5-19-11.5 NPK ratio (S2 stage). Two other DS were prepared for S4 stage, one with NH_4Cl as the main N-source fertilizer and the other with urea as the N-source fertilizer for the same 10-0-10 NPK blend (S4 stage).

Fig. 8 shows the flux behavior of DS prepared to meet the S4 stage nutrient requirements. S4-NH_4Cl DS was prepared using KCl and NH_4Cl having concentrations of 1.2 and 2.02 M, respectively. Similarly, an S4-Urea DS was also prepared using KCl and urea having individual concentrations of 1.2 and 0.97 M, respectively. Starting with the same NPK nutrient value for both DS, at the beginning of the test, these DS showed obvious differences in initial water flux. But as the tests were continued for more than 2000 min, their flux gap was observed to become narrower with time. There may be two reasons for this trend. Firstly, the

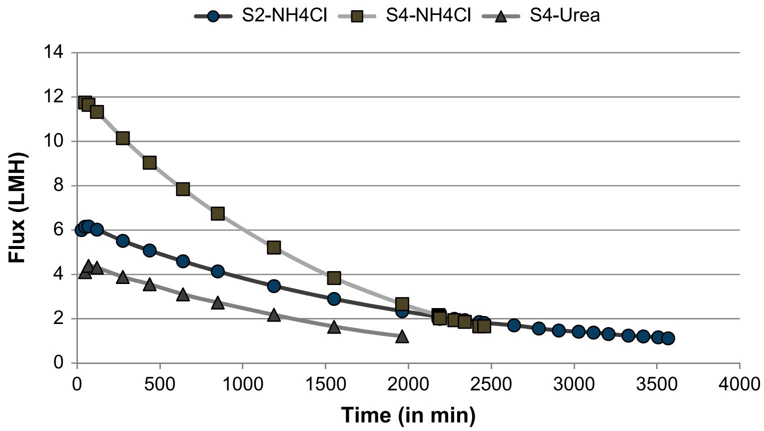

Fig. 8. Long-run FO flux trends for three DS prepared to meet S2 and S4 stage NPK requirement. Stage S2 DS used NH_4Cl N-source. Two S4 DS were used with different N-source fertilizers. One used NH_4Cl and other used urea as a nitrogen-source fertilizer to prepare DS mixtures.

NH_4Cl-based MF blend showed high initial flux, i.e. more water passed toward the concentrated side, quickly diluting the DS. This dilution lowered the available driving force $\Delta\pi$, resulting to a speedy flux decline. On the other hand, as urea-based DS had lower initial flux, water permeation toward DS was slow, so that only a little dilution occurred over the same period of time. Thus, the urea-based DS did not show a sharp flux declining trend. After a certain period of operational run, due to the dilution difference attributed by varying flux, NH_4Cl-based DS possesses lower $\Delta\pi$ as compared with urea-based DS. Thus, as the test proceeded toward the final stage, the available osmotic pressure of NH_4Cl-based DS became close to the urea-based DS and showed nearly equal flux.

Additionally, in the recirculation mode FO test, as the test proceeded, DS keeps on diluting due to water permeation through the FO membrane whereas at the same time the FS gets concentrated with respect to the solutes present in the FS. The continuous water permeation toward the DS side reduced the overall concentration of salts in the DS with time that results to a reduction of the available $\Delta\pi$. Comparably, during the continuous operation run, the FS concentration changes just marginally in comparison with the higher DS concentration, which do not either affect FS osmotic pressure or contribute to lower the available flux driving force i.e. $\Delta\pi$. As these processes continue for long duration, DS dilution brings the driving force down and as a result, the overall flux keeps decreasing continuously. The DS dilution plays a major role in reducing the net available osmotic pressure (based on the bulk osmotic pressures of the DS and FS) to deliver a resultant flux. On the other hand, concentrating the FS along with RSF support also causes an increase of solute concentration on the FS side which too affects the $\Delta\pi$ in a longer test run.

The long-term test flux decline shown in Fig. 8 was not only due to the decrease of overall osmotic pressure difference ($\Delta\pi$) between the DS and the FS. McCutcheon and Elimelech [48] illustrated that the concentration polarization (CP) affects the DS and FS concentrations at the membrane active layer and causes a lower actual flux in FO. In either membrane orientation mode (AL-FS or AL-DS), the CP phenomenon is developed on both sides of the membrane, which restricted FO to achieve a high-theoretical flux through FO operations [10,12,49]. Similar CP effects are also noticed in Fig. 8 as the flux decline is more than possible to be due to the DS dilution and FS concentration effects. Severe CP development is noticed on both sides of the membrane. ECP is severe as high-concentration FS is used in this study.

ICP and ECP, along with the dilution and concentrations of DS/FS contributed to the reduced available osmotic pressure across the membrane's active layer, which resulted to a lower flux outcome compared with the high-theoretical flux potential. The FO membrane always gives a flux driven by the concentrations present at the membrane surfaces and not by the actual concentrations of DS and FS. As a result of DS/FS concentration difference at the membrane interface, the resultant lower FO flux was based on the $\Delta\pi_{\text{effective}}$ across the membrane interface instead of the flux based on the $\Delta\pi_{\text{bulk}}$ i.e. the difference in osmotic pressure between the DS and FS themselves. These also help to reduce the flux in the long-term run operation.

3.7. Dilution of final diluted DS

After a long-term test run of 60 h, the final DS at the end of FO tests was evaluated for nutrient concentrations. The final DS showed high concentrations of TDS compared with that of the final FS. Due to the water flux and solute movement toward the FS side, the FS is concentrated over long-term run operations. For FO operations with a fertilizer DS using an SW quality FS, the final DS ends up highly enriched in NPK nutrients (above the crop's nutrient feed level). Looking into this, it is concluded that the dilution of the final DS will be required for FO using an even lower quality brackish FS (2000 TDS) as the maximum NPK nutrient level allowed in feed water for tomato crop is only 200/50/300 ppm, which is far below than the FS initial concentration [49]. Fertilizer-drawn FO system needs a higher level of dilutions to reduce the nutrient concentration acceptable for direct irrigation of tomato crops.

4. Conclusions

FO performances were evaluated using DS prepared from suggested fertilizer nutrient concentrations required for tomato growth, and also using seawater FS.

Various DS exhibited flux from 2.50 to 12.49 LMH depending on the DS components and their concentrations used. The DS mixtures carrying high-osmotic pressure components delivered high-flux outcome compared with others. For the same NPK ratio, the DS prepared from different nitrogen fertilizers indicated that NH_4Cl-based DS mixtures performed well over others, whereas the urea- and NH_4NO_3-DS mixtures exhibited the same flux besides having a significant osmotic pressure difference between urea and NH_4NO_3. Fluctuation of $J_w/\Delta\pi$ ratio within 0.062–0.19 LMH/bar for these DS indicated that the osmotic pressure may not be taken as the only dictating factor for the FO outcome.

Nitrogen- and potassium-based DS showed higher N- and K-RSF. However, DS using $NH_4H_2PO_4$ delivered extremely low P-RSF ranging from 12 to 18.35 $g/m^2/h$. The long-term run tests showed that with the use of seawater FS, the FO gave diluted DS enriched in nutrients, higher than the plant's requirement. Higher concentrations of nutrients in the final DS suggest that before putting it for direct end use, dilution of the final DS will be required to bring its nutrient level down to match the crop's acceptable levels.

This study confirms that FDFO can be used effectively to desalinate seawater feed source using DS prepared from commercial fertilizers.

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