Fertilizer-drawn forward osmosis for irrigation of tomatoes

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Abstract— Fertilizer drawn forward osmosis (FDFO) is a low energy desalination concept, designed particularly for fertigation. This study was aimed to evaluate associated operational issues related to FDFO real application targeting tomato crop fertilizer requirements to prepare draw solution (DS) to desalinate seawater feed solution (FS). Commercially available fertilizers as NH_4NO_3, NH_4Cl, KNO_3, KCl, $NH_4H_2PO_4$ and urea were used to prepare mixed fertilizer DS (MFDS) in varying nitrogen:phosphorous:potassium (N:P:K) ratios. FO performance in terms of flux and reverse solute flux (RSF) was evaluated using MFDS in different ratios and concentrations. MFDS prepared from different fertilizers resulted in significant variations in FO performances in terms of water flux and RSF. Flux outcome varied from 2.50 LMH to 12.49 LMH depending on fertilizer component present in DS and its concentrations used. MFDS carrying high osmotic pressure components delivered high flux outcome than others. J_w (LMH)/$\Delta\pi$(bar) fluctuation within 0.062 to 0.19 for these MFDS used indicated that the osmotic pressure may not be taken as the only dictating factor for FO outcome. Effects of changing nitrogen fertilizers in a particular NPK MFDS were evaluated to find best performing mixed fertilizer. DS prepared from different nitrogen fertilizers as urea, NH_4NO_3 and NH_4Cl having same NPK concentrations were evaluated and found that NH_4Cl based DS mixtures performed well over others whereas urea and NH_4NO_3 based DS mixtures exhibited same flux. RSF results for these DS indicated that all nitrogen and potassium based MFDS exhibited higher N and K RSF. However, DS using $NH_4H_2PO_4$ delivered extremely low P-RSF of 12.35 g/m^2/h. For seawater quality FS, higher nutrients concentration in the final DS at the end of long run tests suggested using dilution or any other technique to reduce excessive nutrients before putting it for any direct end use.

Keywords: Forward osmosis desalination, Fertigation for Tomato, NPK crop nutrients, Fertilizer draw solution, Seawater feed

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Introduction

Desalination is a widely used water treatment process for treating brackish and/or sea water source feed to obtain fresh water. Beside considerable technological advancements, existing desalination technologies such as thermal distillation and reverse osmosis (RO) are still believed highly energy intensive (Semiat 2008; Shon et al. 2008) and the rising energy prices resulting high cost of desalination. For this reason, desalination is not considered as an ideal solution for every water user especially agriculture. Apart from the high operating cost of desalination process, other serious issues such as greenhouse gases (GHG) and carbon emissions are also being linked with desalination to evaluate its effectiveness.

In the last few decades, draughts and climate changes are continuously affecting the agricultural water availability and these results in reduced crop area harvested and lower agricultural yield. Agricultural water scarcity is considered as one of the main reasons for rising prices of agriculture food commodities across the globe (de Fraiture 2007) and current trends show that in the coming future, it may seriously affect world food security. Water quality and water scarcity, both are assumed as the most important challenges for food production for our world's growing population needs as they directly influence the crop yield and quality of food (Shalhevet and Yaron 1973; Shalhevet 1994). However, even better water management policies and appropriate water management strategies may help us control major concerns of these water shortage issues for at least next 50 years (de Fraiture and Wichelns 2010).

In this context, forward osmosis (FO) is considered as an emerging green desalination technology using the simple concept of natural osmosis. In FO, 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 towards DS side until concentration of both sides become equal. This movement of water molecules in FO is different from RO process in which water permeates through membrane under high hydraulic pressure. FO utilizes natural osmotic pressure difference between the available DS and the brackish/saline feed water. FO therefore does not require additional energy to pressurize feed water streams as RO needed and hence considered as an environment friendly desalination technology having low carbon footprint.

Looking into this important aspect, in a narrow time span, FO technology has been rapidly evaluated for a wide range of applications such as sea / brackish water desalination (Kessler and Moody 1976; Cath et al. 2006; McCutcheon et al. 2006; McGinnis and Elimelech 2008), wastewater treatment (Cath et al. 2005), power generation (Garcia-Castello et al. 2009), osmotic membrane biological reactor (MBR) (Cath, Gormly et al. 2005; Holloway et al. 2007; Warczok et al. 2007; Achilli et al. 2009), food processing, concentration & recovery of active organic components (Achilli et al. 2009) and direct fertigation (Phuntsho et al. 2011).

Several promising draw solutes such as NH_3-CO_2 mixture (McCutcheon et al. 2005; McCutcheon, McGinnis et al. 2006) and super magnetic nano-particles (Ling and Chung 2011) 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 draw solutions is required to produce the useable product water. Thus FO desalination application for potable water use still remains a challenge (McCutcheon, McGinnis et al. 2006) because the separation and recovery of draw solute from FO product water are not easy and require additional energy too. In all above FO techniques, water recovery and draw solute separation are an energy consuming step that diminishes the true advantage of low energy FO operation.

Considering the increasing water requirements and current water shortages, a new approach was developed for use of FO technology for non-potable use i.e., agriculture. Fertilizer drawn forward osmosis (FDFO) concept was first introduced in 2011 (Phuntsho, Shon et al. 2011). Various types of fertilizers were evaluated as DS against deionized water feed solution (FS) to extract water from it. Unlike many other FO processes, in FDFO, the resultant low concentration fertilizer DS does not require regeneration and thus can easily be used with some concentration adjustments to irrigate any suitable agricultural crops (Phuntsho, Shon et al. 2011; Phuntsho et al. 2012). In this FO process, as the final step of draw solute recovery is eliminated, FDFO really seems to be an effective low cost desalination technology to fulfill irrigation water requirements.

Due to low operating costs, it is being considered that FDFO can be economically used for the brackish/sea water desalination to provide useable water to the largest water consuming agricultural sector. We have an access to abundant reservoirs of sea water along its long coastal areas and inland underground brackish water as well. These water resources can be employed using FO to get beneficial agricultural water to help reduce the current water deficit, a barrier to the increasing food demand in domestic and international markets.

Transforming lab scale FDFO results to practical application, this study focuses on real tomato crop's water and fertilizer requirements. Tomato (*Lycopersiconesculentum)* is one of the most popular and widely grown vegetable crops in the world. As of many other crops, tomato is also sensitive to salinity. In most of the cases, tomato yield is reduced when irrigated with water having EC is above 2–3 dS m^{-1}(mmhos/cm) (Cuartero and Fernández-Muñoz 1998). This yield may even reduce to 50% with irrigation water conductivity of 8 mmhos/cm (Shalhevet and Yaron 1973). Sodium cations compete with the potassium cations for the roots uptake sites, and chloride competes for the uptake of nitrate-nitrogen and will impede plant development (Hebbar et al. 2004).

Water and fertilizer requirements vary for different types of tomato grown and these vary for its various plant growth stages as well. Our current study is tailored to water and fertilizer requirements of field grown tomatoes. Based on various climate conditions, soil quality and soil moisture, field grown tomato crop requires 400 - 800 kL/ha water for its whole growth period (Shalhevet and Yaron 1973; Brouwer and Heibloem 1986; Mitchell et al. 1991). Tomatoes grown on light soils require about 6,000 kL/ha of water for the average crop period of about 120 days (Warner et al. 2004). Table 1 shows NPK nutrients requirements of tomato crop during its various growth stages. These values are later used to prepare mixed fertilizer draw solutions (MFDS) 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 (Claude J. Phene 2004; Hartz and Bottoms 2009). We see enough potential for this large quantity of fertilizer as it can be potentially used to prepare DS for FDFO process.

Table 1 Nutrients requirements of open field tomato according to its physical stages (Claude J. Phene 2004)

The objective of this study was to evaluate the FDFO process performance with special emphasis to better understand issues related to FDFO actual applications such as tomato crop fertilizer requirements, sea water quality feed solution (FS) and use of commercially available fertilizers to prepare DS. The effect of changing nitrogen source fertilizers in a particular MFDS were evaluated to find best performing mixed fertilizer with respect to high water flux and lower RSF. Long terms tests were also aimed to evaluate process effectiveness and to assess the expected final nutrient concentration in the diluted draw solutions.

1. Materials and Methods

1.1 Forward osmosis performance measurements

Lab FO apparatus as shown in Fig. 1 was used to evaluate water permeation through FO membrane. The FO membrane supplied by HTI, USA is made up of cellulose triacetate (CTA) embedded on a polyester woven mesh (Cath, Childress et al. 2006; Tang et al. 2010) was used in this study. All tests were carried out using membrane in normal FO orientation, i.e., the active layer 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 dimensions of 7.7 cm (L), 2.6 cm (W), and 0.3 cm (H) on both sides of the membrane.

Fig. 1. Lab scale FO set-up used in the study.

Flow through each channel was controlled by a variable speed peristaltic pump drive (Cole-Palmer, U.S.A.) monitored by variable area flow meters (Blue-white Industries Ltd., U.S.A.). For the whole study the flow rates were kept constant at 400 ml/min for both FS and DS. Tests were carried out in co-current flow configuration for FS and DS streams and temperature of both DS and FS streams were kept constant at 25°C ± 0.5°C using temperature water bath controlled by heater/chiller. A weighing scale (CUW 4200H by CAS, Korea) connected with a computer was used to monitor the weight loss of the FS which was later used to calculate water flux in FO operation.

1.2 Chemicals and reagents

From the field aspect of FDFO concept, commercially available fertilizers were used in this study to get useful application data. These fertilizers were analyzed in the lab to get information about their NPK ingredients and level of impurities present in it.

MFDS were prepared using the following 6 different fertilizers, NH_4NO_3, NH_4Cl, KNO_3, KCl, $NH_4H_2PO_4$ (MAP), and urea. Prepared MFDS exhibited specific NPK grade (in % for N, P_2O_5 and K_2O) as 11.5-19-11.5, 15-7-22, 10-0-20, 15-0-30 to directly match nutrients requirement for tomato crop at any particular growth stage as shown in Table 1.

FDFO was evaluated against sea water (SW) quality FS which is the largest source of water available on earth. All FS were prepared using 35 g/L NaCl (representing sea water osmotic pressure) dissolved in tap water. NaCl supplied by Chem-Supply Australia was used to prepare FS. Actual sea water quality FS was not evaluated in this study as Ca^{2+} and Mg^{2+} present common sea water posed risk of insoluble suspension formation with phosphate fertilizers. FS prepared with 35 g/L NaCl in tap water exerts osmotic pressure of 27.38 bar (OLI software).

Unlike all previous studies where MQ water was used to prepare FS and DS for FO tests, both DS and FS were prepared in tap 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. Tap water was used to explore any operational issues associated with the use of commercial fertilizer and poor quality water.

1.3 Performance and measurements

Water flux was evaluated with MFDS prepared for various tomato crop growth stage fertilizer requirements. FS samples were also collected at the end of each test and analyzed for RSF. These samples were analyzed for K, P, N concentration in FS using APHA method 3125 protocols

2. Results and discussion

2.1 Screening of fertilizers to prepare MFDS

8 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 evaluated with respect to their suitability to provide NPK nutrients for tomato growth. Among these fertilizers 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 source fertilizer for N and K. These fertilizers were screened and shortlisted for issues such as their availability, price, common use and acceptance by tomato growing community, higher active nutrients (NPK) composition, osmotic pressure, solubility limits, presence of unwanted impurities, ease in DS preparations and previous FDFO studies (Phuntsho, Shon et al. 2011).

$(NH_4)_2SO_4$ was rejected due to difficulties shown in preparing DS at higher concentration. Commercial $(NH_4)_2SO_4$ showed acute difficulties in preparing DS. It took long time to dissolve completely despite using mixing aids and left black insoluble matter even at 2M concentration which was difficult to filter out as it quickly blocked filter paper pores. Removal of suspension was necessary to reduce the chances of pump or membrane damage.

$Ca(NO_3)_2$ was an ideal choice as DS for FDFO process as comparatively it exhibits high osmotic pressure. OLI data showed that 1M $Ca(NO_3)_2$ DS indicates osmotic pressure of 52.32 atm which was highest among all nitrogen fertilizers being evaluated followed by NH_4Cl, NH_4NO_3 and urea. However, $Ca(NO_3)_2$ was eliminated from MFDS component's list as calcium carried high probability of forming insoluble suspensions with phosphates fertilizers (Haynes 1985; Marais 2004) in mixed fertilizers. Although $Ca(NO_3)_2$ beside carrying high osmotic pressure among these fertilizers, was suitable for preparing DS for the last two tomato growth stages not using any phosphate fertilizers, still there was risk that it might leave excessive calcium in the final diluted DS (FDDS) which may harm tomato yield. Ca^{2+} also reduces potassium intake by the plant and tomato yield drops drastically due to plant's K^+ deficiency (Hartz et al. 1999; Hebbar, Ramachandrappa et al. 2004).

NH_4NO_3 was considered partly 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 FDFO process as it is considered as the most popular N-source agricultural fertilizer in the world even for tomato crop too. It is cheap, very soluble even at high concentration, easily available, enriched highly with N (up to 46%). However, OLI software data showed that urea has the lowest osmotic pressure among all available fertilizers.

Commercial NH_4Cl and MAP fertilizers also left insoluble residue during preparation of high concentration MFDS but solutions were filtered out easily. Due to impurities presents in the commercial fertilizers and their solubility issues, all prepared DS were filtered to reduce chances of membrane fouling. Considering evaluated physical and chemical characteristics of these fertilizers, 6 fertilizers were shortlisted for their use as MFDS for FDFO process (Table 2). Out of these, 4 fertilizers were categorized as common fertilizers.

Table 2 Shortlisted fertilizers used to prepare mixed fertilizer DS, showing their NPK nutrient composition and osmotic pressure these fertilizers exerts at 1M concentrations

Preparation of mixed fertilizer DS suitable for tomato application

Looking into average tomato plant life cycle of 120 days and fertilizer requirements, whole tomato crop span is divided into 4 stages, i.e., Planting - First flowering, Rapid growth – Flowering, Fruit set- Fruit ripening and Fruit Ripening-Harvest (Claude J. Phene 2004) hereafter described as S1, S2, S3 and S4 respectively. Shortlisted fertilizers were used to prepare MFDS matching nutrients requirements of tomato plant for these stages. These MFDS were used as DS in the FO experiments and evaluated with respect to pH, flux, RSF and ultimate essential nutrient concentrations in the final DS.

NH_4Cl was preferably selected as the main N-source fertilizer for preparing MFDS carrying N-fertilizer nutrients. Influence of two other N-source fertilizers such as NH_4NO_3 and urea was also studied for preparing these MFDS to evaluate suitability of these two commonly used fertilizers for FDFO process. For that, while preparing N-based MFDS for some of the tests, NH_4Cl was replaced and evaluated for other replacement N-source fertilizers as NH_4NO_3 and urea. This was while replacing N-source from NH_4Cl to urea or NH_4NO_3, the desired NPK value of the new MFDS blend was not changed. However, while replacing NH_4Cl nitrogen source fertilizer in MFDS with NH_4NO_3 or urea, the theoretical osmotic pressure of the MFDS was also changed. For P-nutrient source fertilizer, only MAP was used and for K-nutrient source fertilizer, KCl was used with KNO_3 in the entire study.

Blended mixtures showed various changes in physical and chemical properties of the blended mixtures when compared with their individual ingredients solutions. Issues were noticed in preparing higher concentration MFDS as MAP and NH_4Cl fertilizers produced suspensions and left residue at higher concentrations. Similarly, fertilizers containing the same salt i.e., KCl and KNO_3 were mixed carefully as they decreased solubility in the mixture. Hence MFDS for various tomato crop nutrients requirements were prepared to concentrations limits that did not produce any excessive residue or suspensions in solutions.

2.2 Water Flux in FDFO process using mixed fertilizer draw solutes

The performance of MFDS in term of water flux (J_w) for FDFO process is presented in Fig. 2. MFDS were prepared for 4 tomato growth stages namely S1, S2, S3 and S4 representing NPK nutrients values of 11.5-19-11.5, 15-7-22, 10-0-20, 15-0-30 respectively. Based on each stage's fertilizer requirements, MFDS were prepared in various concentration using different quantities of fertilizers but keeping the NPK value same for that particular stage evaluation. MFDS were prepared from 0.25%, 0.33% and 0.5% selected quantities of tomato growth stages requirements showing minimum issues and are represented by suffix -1, -2 and -3 in the bracket of the x-axis label in Fig. 2-7. For stage 4, MFDS were prepared for only 0.15% S4 stage quantity. Different stage MFDS showed flux from 2.51 LMH to 12.54 LMH with seawater FS.

For a solution carrying more than one solute, the expression of total osmotic pressure for a mixture of different solutes can be written as

$$\pi_{Total} = \sum_{\pi=0}^{n} \pi_n \qquad (1)$$

or

$$\pi_{Total} = \pi_1 + \pi_2 + \pi_3 + \pi_4 + \cdots \qquad (2)$$

Subscripts 1, 2, 3, 4... represent various components of the draw solute.

Osmotic pressure differential ($\Delta\pi$) across the membrane, net driving force available for forward osmosis using sea water quality is expressed by

$$\Delta\pi = \pi_{total} - \pi_{sw} \tag{3}$$

MFDS prepared in various concentrations were separately evaluated with these nutrients ratio. OLI software results showed that resultant osmotic pressure of the MFDS was the sum of the osmotic pressure of individual components share present in the mixture and follow Eq. (1) and (2). Eq. (3) was used to obtain net osmotic pressure driving force for FO process. It was observed that the flux changes with rising MFDS concentration but not linearly in all cases (Fig. 2). Flux results did not respond proportionally to changing respective osmotic pressure. Results showed either positive or negative deviation for linear trends. The main reason for these variations in slope for different MFDS seems to be due to type and concentration of individual components present in MFDS. Each MFDS behaved differently depending on the concentration of various components present in the mixture.

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 are fixed for these tests but the slope varies for all MFDS in Fig. 2(a-f). The above flux equation suits ideal or very weak solutions and however, it still accounts for the main driving force (osmotic pressure gradient) for osmosis. From the nonlinear flux results in Fig. 2 results, it is realized that for non-ideal solutions and high DS concentration, other chemical properties of the solutes additionally contribute to these resultant flux variations. Membrane permeability coefficient (A) decreases at high DS osmotic pressures (Mehta and Loeb 1978). High concentrated MFDS results further show high deviation of the theoretical flux to actual flux means that the other relevant forces also increase with DS concentration.

Further, dissimilar slope of the flux and osmotic pressure curves for these MFDS shown in Fig. 2 (a-f) seems to follow earlier research evaluations and confirm that the rising DS concentration does not change water flux linearly in FO (Sutzkover et al. 2000; Suh and Lee 2013) as concentration polarization (both external concentration (ECP) and internal concentraton (ICP)) varies with DS/FS changing concentrations (Mehta and Loeb 1978; McCutcheon, McGinnis et al. 2006; Gao et al. 2013; Suh and Lee 2013). High FS concentration also contributed to increase ECP which directly caused high reduction of the resultant water flux (Suh and Lee 2013). The main reason for the variation in slope for different MFDS seems due to the type and concentration of individual components present in

MFDS. Each MFDS behaved differently depending on the concentration of various components present in the mixture. The effect of membrane properties, DS diffusion coefficients, inter-molecular interactions, ionization energy have been evaluated by many researchers for FO flux but these lack clear reasoning for the changes of flux with osmotic pressure (Paul 1974; Mehta and Loeb 1978; Schaep et al. 1998; McCutcheon, McGinnis et al. 2006; Chung et al. 2012).

Fig. 2. Osmotic pressure and resultant flux changing trends for different MFDS prepared for varying tomato crop NPK nutrients need. 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 MFDS, d) and e) S3 stage with NH_4Cl and when urea replaced NH_4Cl N-fertilizer source in MFDS and f) S4 stage MFDS using urea and NH_4Cl as N-source fertilizers. (AN: Ammonium nitrate, AC: Ammonium chloride and U: Urea represents main N-source fertilizer in respective DS)

Fig. 3 summarizes MFDS flux trends when plotted against the main driving forces as DS osmotic pressure (π) and net osmotic pressure difference available ($\Delta\pi$). The presented data is unable to authenticate 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 FDFO process.

To get further insights of these, FO flux is plotted against ratios $\Delta\pi/J_w$ (bars/LMH), a ratio showing net osmotic pressure required to get unit value of flux (Fig, 4(a)). It shows that several MFDS require different net osmotic pressure ($\Delta\pi$) to provide one LMH flux output. This further indicates that the same osmotic pressure value of a mixed DS may not give us uniform flux output. Most of MFDS mixtures showed $\Delta\pi/J_w$ values around 10 except S2 (AC-1), S2 (AC-2), 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).

Fig. 3. Osmotic pressure, net osmotic pressure and flux outcome trends for various MFDS of varying NPK ratios.

OLI software results of these MFDS show that S2 (AC-1) DS containing NH_4Cl as N-source fertilizer forms large number of ionic species than S3 (U-1) DS using urea as N-source fertilizer. This can be concluded that DS forming more ionic speciation may deliver more flux. The osmotic pressure should not be taken as the only criteria to select DS for FO operation. For the same osmotic pressure, DS with higher diffusion coefficient results in higher water flux (Holloway, Childress et al. 2007). One main reason in these deviations is the presence of DS components carrying high osmotic pressure but additional study is required to explore issues behind the hidden part of DS behavior. Similarly, Fig. 4 (b) also showed similar variation when the ratio of J_w(LMH)/$\Delta\pi$ (bars) was plotted for these MFDS.

These results indicate that there are some other important and effective FO driving forces (other than osmotic pressure) which act during FO process and dictate any resultant flux outcome especially with the mixture of DS. Thermodynamically, transport of a given species must be in the direction to decrease chemical potential for the species (Paul 1974). So for FO process, which reduces this chemical potential between the two solutions across the membrane, it is hypothesized that in a mixture of DS, beside osmotic pressure of DS and FS, 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 their vital roles in dictating FO flux outcome.

2.3 Comparison of flux for changing N-source fertilizer during various plant growth stages

Three N-source fertilizers NH_4Cl, NH_4NO_3, and urea were used to prepare MFDS to meet nutrients requirements for S1 tomato crop growth stage and then evaluated for FDFO process.

Fig. 4. Flux J_w (LMH) and net osmotic pressure gradient for MFDS $\Delta\pi$ (bars) behavior with various ratios $\Delta\pi/J_w$ (bars/LMH) and J_w(LMH)/$\Delta\pi$(bars).

NH_4NO_3 and urea are the most popular fertilizers used as the nitrogen source for the tomato crop. Earlier it was reported that these two fertilizers (NH_4NO_3, and urea) give low flux and high RSF and may not be favored for FDFO process (Phuntsho, Shon et al. 2011). However, these two fertilizers were evaluated for their synergic effects with other fertilizer blends as DS and compared with NH_4Cl based mixtures.

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

Evaluation of different MFDS prepared for S1 tomato growth stage requiring NPK fertilizer ratio of 11.5-19-11.5 was done for FDFO process. Each N-source fertilizer was evaluated for three different concentrations (0.25%, 0.33% and 0.5% of fertilizer quantities required for S1 stage). Results in Fig. 5 indicate that the mixtures carrying MFDS components having less osmotic pressure (π) such as urea and NH_4NO_3 showed lower flux output. However, MFDS containing NH_4Cl for the same NPK values showed higher resultant flux than other N-source fertilizer blends. Using OLI software, it is revealed that at 1M concentration, NH_4Cl showed π of 43.5 atm which is 83% and 29% higher than π of 1M urea and NH_4NO_3 respectively. This shows that in a mixture of DS solutes, the higher osmotic pressure value component mainly quantifies π and flux of the mixed DS which in this case is NH_4Cl. Thus NH_4Cl based MFDS showed higher resultant flux than other N-source fertilizer blends. However, the differences shown vary with their concentration and presence of other components in a particular MFDS.

In contrast, at 1M concentration, urea shows π of 23.7 atm whereas NH_4NO_3 shows π of 33.7 atm at 1M concentration which is 42% higher than urea. Despite these differences in π, both NH_4NO_3 and urea showed nearly the same flux for MFDS having the same NPK ratios. From these results, we may also conclude that in these MFDS, π exerted by these two fertilizer fractions (urea and NH_4NO_3) in MFDS does not contribute significantly to the overall π of the MFDS carrying other major components as KCl, MAP, and KNO_3 in mixed DS. Thus, due to the lower π of these two fertilizers, the resultant flux is dictated not by the π of urea and NH_4NO_3 but by other components of MFDS. These results again may be considered due to influence of intermolecular associations between the different components of the DS.

2.4 Reverse solute flux using MFDS blend

FS samples were collected at the end of each MFDS experiment and analyzed in the lab to evaluate any draw solute reverse diffusion across the membrane to the feed side. Since RSF is considered as loss of valuable DS inputs, it was regularly monitored for all MFDS to prepare guidelines for cost control and waste discharge management. Moreover, in FDFO process, as RSF involves diffusion of nutrients towards the FS side which is normally discarded or dumped back to other receiving bodies, excessive nutrient present may too create algal bloom and eutrophication problems in the receiving water.

Fig. 6 and 7 compare flux and net osmotic pressure (Δπ) of MFDS to NPK RSF (in $g/m^2/h$). Similar to FO flux, RSF outcome also showed varying behavior with MFDS. Apparently, all nitrates based MFDS blends indicated high RSF values. Moreover, MFDS 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 (Paugam et al. 2003; Paugam et al. 2004; Wang et al. 2005). For most of the RSF results for S1 and S2, it is observed that N-RSF is higher than K- and P- RSF which is perhaps due to small size of N – hydrated radii. RSF for the K and P always remained on the lower side for nearly all MFDS. However S3 and S4 results further indicates that the K- RSF is higher than N-RSF for these two stages. These results are due to high potassium concentration (Table 1) in MFDS for stage S3 and S4.

Some of the MFDS prepared from KNO_3 also showed high RSF values. Phosphates loss was observed at minimum while using MAP as phosphate /nitrogen nutrient’s source component. MAP based MFDS showed low RSF not only for phosphorus but for nitrogen as well. This suggests that while preparing MFDS for FDFO, higher MAP concentration may help keep this nutrients loss at minimum and improve the overall efficiency of the process.

Tang, She et al. (Tang, She et al. 2010) and and She et al. (She et al. 2012) have presented the following equation to predict reverse draw solute flux across the membrane for single solute

$$\mathrm{J_s} = \mathrm{J_w} \frac{B}{A\beta \mathrm{R_g} T} \qquad (4)$$

Where J_s is the solute flux, J_w the water flux, B the solute permeability coefficient of the membrane, A the water permeability coefficient of the membrane, β the van't Hoff coefficient, R_g universal gas constant and T the absolute temperature. Being other values remain constant for any particular solution, Eq. (4) mainly relies on solute permeability coefficient (B) to determine RSF. Membrane structure and DS composition play an important role in bidirectional diffusion of solutes across the membrane (Hancock and Cath 2009). Solute permeability constant vary inversely with the thickness of the membrane (Wijmans and Baker 1995). Membrane permeability coefficient (A) and solute coefficient (B) are also affected with membrane thickness. By this equation, we may deduce that RSF (J_s) is proportional to pure water flux (J_w) and as J_w increases, RSF should also increase. In contrast, later She, Jin et al. (She, Jin et al. 2012) have found that for many membrane processes, as J_w increases, RSF is reduced. High flux help push solute molecules back to the draw solution (She, Jin et al. 2012) which seems more reasonable and logical. Hence, no other equation is still available that may help us understand RSF potential for a particular DS.

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

Fig. 6 and 7 indicates that all nutrient's RSF i.e., NPK increases with the rise in MFDS concentrations. Additionally, it is also interested to note that in all these case, RSF rises with flux for MFDS increasing concentrations. The resultant high values of flux and RSF are due to high concentrations of MFDS in these particular DS. N and K responded quickly to the DS concentration changes for RSF whereas P RSF did not change much, rather it nearly remained unchanged. Donnan (Donnan 1924) shows that ionic equilibrium on both sides of the membrane dictates the diffusion of ions from one side to other. Osmotic pressures, ionic equilibria and potential differences effect the movement of ions across the membrane (Donnan 1924). For systems containing two electrolytes with a common ion, one part of the electrolyte move faster than the other and changes the potential difference of the electrolytes. The process of diffusion then slowed and the system attained ionic equilibrium back. For FDFO using MFDS against SW quality FS, Cl^- is the common ion in both DS and FS. Other parts of the DS such as NH_4^+/NO_3^- and K^+ having smaller hydrated radii moves faster than Na^+ ions indicates high N- and K- RSF. Kirkwood-Buff theory also helps to some extent to investigate the changes in associations and interactions on addition of some common co-solvents (Chitra and Smith 2002). So identification of exact phenomenon for the diffusion of ions from a solution of various solutes is quite complex and still needs answers to many related issues. It can be predicted that the main reason for the uniform P-RSF outcome with these MFDS are owing to the size of the PO_4 ions and lower favorable ionic attractions from the ion present on other side of the membrane.

Fig. 7. N, P and K RSF for various MFDS 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 brackets indicates which nitrogen source used to prepare MFDS in that particular stage. Similarly numbers 1, 2 and 3 indicates specific concentration of particular MFDS.

RSF results indicate that due to these fertilizer salt losses through RSF, final diluted draw solution (FDDS) may not end up with the same NPK nutrients ratio in the FDDS as of start of the test. RSF outcome indicates the loss of valuable nutrients and possible deviation from the start-up values. In order to achieve the desired NPK ratio suitable for tomato crop for any of its particular crop period, one needs to take into account RSF results while preparing MFDS. For practical use, to account for RSF loss in FDFO process, starting MFDS therefore will have somewhat higher NPK ratios than Table-1 so that at the end of the process, FDDS may achieve the nearly same NPK nutrients ratio required for any particular growth stage for tomato or other plants. This may help eliminate further NPK balance/ adjustment of the FDDS to make it suitable for direct use.

2.5 Long run tests for MFDS and expected final diluted draw solution (FDDS) concentration

S2 and S4 based NPK MFDS were evaluated for flux for long run tests using two N-fertilizers (NH_4Cl and urea). These tests were operated for long time to evaluate flux outcome responds to long time test run. NH_4Cl nitrogen source was used to prepare MFDS having NPK (11.5-19-11.5) ratio. Two other MFDS were prepared for S4 stage, one with NH_4Cl as main N-source fertilizer and other urea as N-source fertilizer for the same NPK (10-0-10) blend.

Fig. 8 shows the flux behavior for MFDS prepared to meet S4 stage nutrients requirements. S4-NH_4Cl MFDS was prepared using KCl and NH_4Cl having concentration of 1.2M and 2.02M respectively. Similarly S4-Urea MFDS was prepared using KCl and urea having individual concentration of 1.2M and 0.97M respectively. Starting with the same NPK nutrients value for both MFDS, the results showed that in the beginning of the test, huge difference between the water flux is recorded for NH_4Cl and urea based N-source MFDS blends. But as the tests were continued to proceed for more than 2000 minutes, steadily the gap became narrow. There may be two reasons for this trend. Firstly, NH_4Cl based MF blend showed high initial flux, more water passed towards that side and reduces the concentration of the DS by diluting it quickly. This dilution lowers the available driving force $\Delta\pi$, resulting sharp decline of the flux. On the other hand, as urea based MFDS had lower initial flux, water permeation towards DS was slow, little dilution occurred over the same period of time so urea based DS did not show a sharp flux declining trend. After a certain period of operational run, due to dilution difference attributed to varying flux, NH_4Cl based DS possesses lower $\Delta\pi$ as compared to urea based DS. Thus as the test proceed toward the final stage, the available osmotic pressure of NH_4Cl based MFDS became close to the urea based MFDS and showed nearly equal flux.

Fig. 8. Long run FDFO flux trends for three MFDS prepared to meet S2 and S4 stage NPK nutrients 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 MFDS.

Additionally, in the recirculation mode FO test, as the test proceeded, DS keeps on diluting due to water permeation through FO membrane whereas at the same time the FS gets concentrated in respect to the solutes present in the FS. Continuous water permeation towards DS side reduced the overall concentration of salts in the DS with time that results in reduction of available $\Delta\pi$. Comparably, during the continuous operation run, FS concentration changes just marginally in comparison to 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 overall flux keeps decreasing continuously. 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 resultant flux. On the other hand, concentrating FS along with RSF support also cause increase of solutes concentration on the FS side which too affects $\Delta\pi$ in a longer test run.

Long run flux decline shown in Fig. 8 is not only due to the decrease of overall osmotic pressure difference ($\Delta\pi$) between DS and FS. McCutcheon and Elimelech (McCutcheon and Elimelech 2006) illustrated that due to concentration (CP) effects the concentrations at the membrane surface are quite less than the bulk DS and FS concentrations and this small effective osmotic pressure difference available at the membrane surface gives lower actual flux in FO. In either membrane orientation mode (AL-FS or AL-DS), CP phenomenon is developed on both sides of the membrane which restricted FO achieving the high theoretical flux through FO operations (Cath, Gormly et al. 2005; Achilli, Cath et al. 2009; Phuntsho et al. 2012). Similar CP effects are also noticed in Fig. 8 as the flux decline observed is more than possible DS dilution and FS concentration affects. 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 dilution and concentrations of DS/FS contributed to reduce available osmotic pressure across the membrane’s active layer which resulted lower flux outcome compared to high theoretical flux potential. FO membrane always gives 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, we achieve lower FO flux based on the $\Delta\pi_{effective}$ across the membrane interface instead of flux based on $\Delta\pi_{bulk}$, the difference in osmotic pressure between DS and FS themselves.

3. CONCLUSIONS

FDFO performances were evaluated using suggested MFDS concentrations required for tomato growth and seawater FS with special emphasize to understand practical issues related to FDFO process.

Various MFDS exhibited flux from 2.50 LMH to 12.49 LMH depending on DS components and their concentrations used. DS carrying high osmotic pressure components delivered high flux outcome than others. For the same NPK ratio, MFDS prepared from different nitrogen fertilizers indicated that NH_4Cl based DS mixtures performed well over others whereas urea and NH_4NO_3 DS mixtures exhibited same flux beside having significant osmotic pressure difference between urea and NH_4NO_3. J_w(LMH)/$\Delta\pi$(bars) value fluctuation within 0.062 to 0.19 for these MFDS indicated that the osmotic pressure may not be taken as the only dictating factor for FO outcome.

Nitrogen and potassium based MFDS showed higher N and K RSF. However, DS using $NH_4H_2PO_4$ delivered extremely low P-RSF ranging from 12-18.35 g/m^2/h. Long run tests showed that with seawater FS, FO gave FDDS 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, FDDS either requires substantial dilution using additional fresh water or some other post treatment technique to recycle additional nutrients to bring its nutrient level down to match crop’s acceptable levels. The study also confirms that for direct fertigation, FDFO desalination is more suitable for low salinity feed water.

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

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List of Tables

Table 1 Nutrients requirements of open field tomato according to its physical stages (Claude J. Phene 2004)

Days after Planting	Physiological tomato crop growth stages	Days	kg/ha/day		
			N	P_2O_5	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

Table 2

Shortlisted fertilizers used to prepare mixed fertilizer DS, showing their NPK nutrient composition and osmotic pressure these fertilizers exerts at 1M concentrations

Commercial /Chemical Name /Chemical Formula	N/P/K $N/P_2O_5/K_2O$	Osmotic Pressure (1M Concentration) atm	Commercial /Chemical Name /Chemical Formula	N/P/K $N/P_2O_5/K_2O$	Osmotic Pressure (1M 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 sulphate*; $(NH_4)_2SO_4$	21/0/0/(24)	46.14	Calcium nitrate*; $Ca(NO_3)_2$	15.5/0/0/(26.5)	48.8

*Rejected fertilizers not included in preparing MFDS for study

List of Figure captions

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Fig. 3. Osmotic pressure, net osmotic pressure and flux outcome trends for various MFDS of varying NPK ratios.

Fig. 4. Flux J_w (LMH) and net osmotic pressure gradient for MFDS $\Delta\pi$ (bars) behavior with various ratios $\Delta\pi/J_w$ (bars/LMH) and J_w(LMH)/$\Delta\pi$(bars)

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

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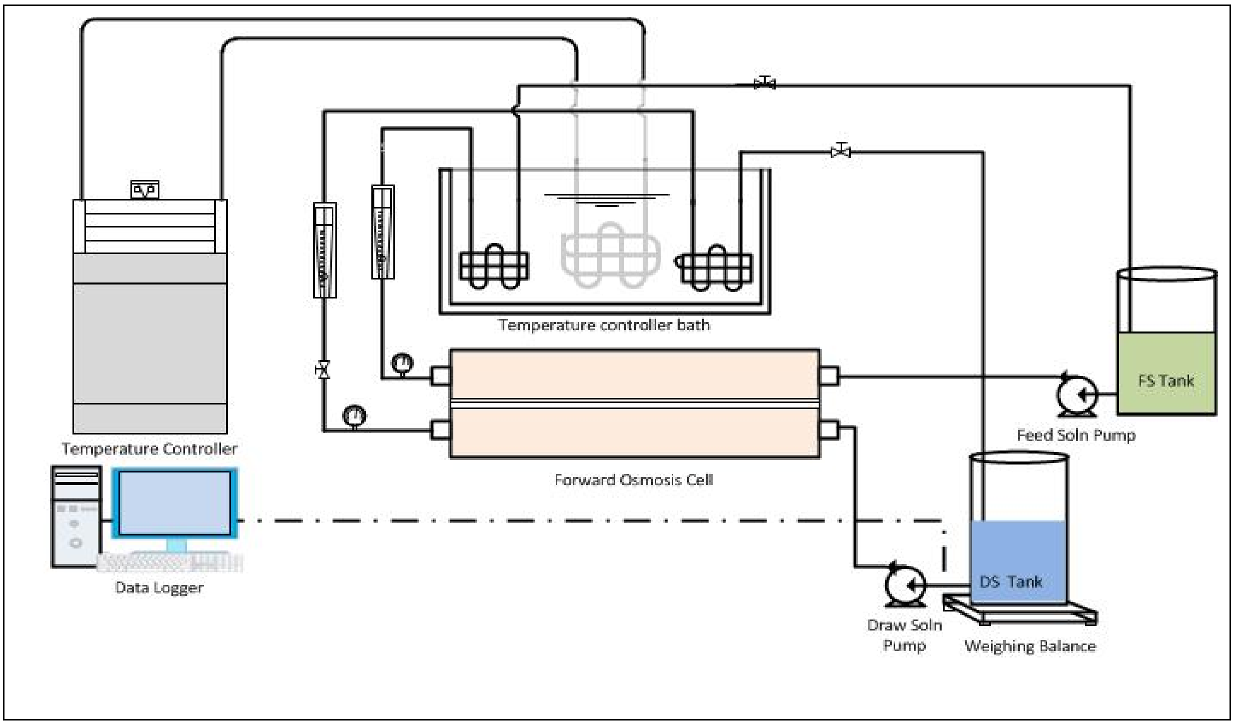

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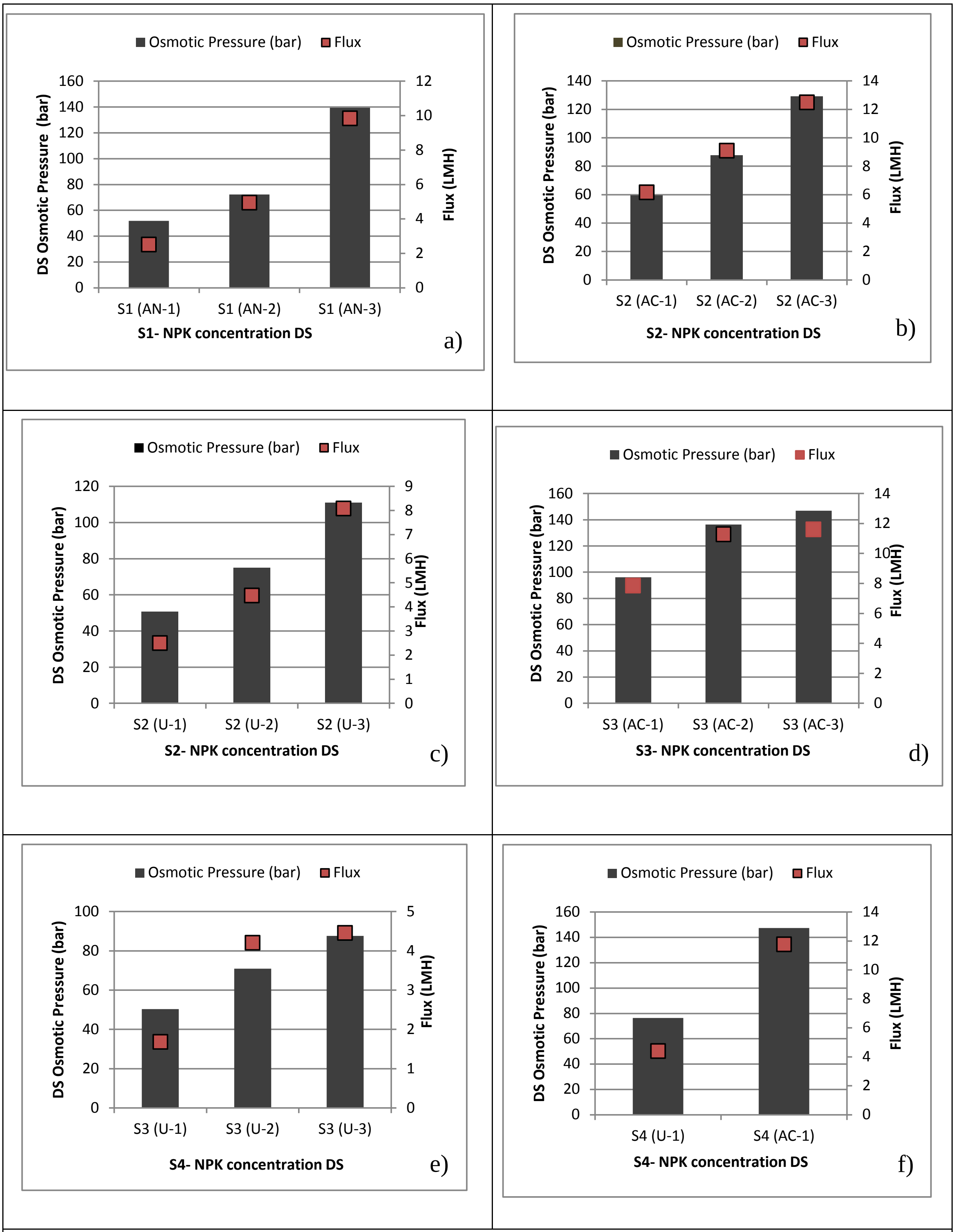

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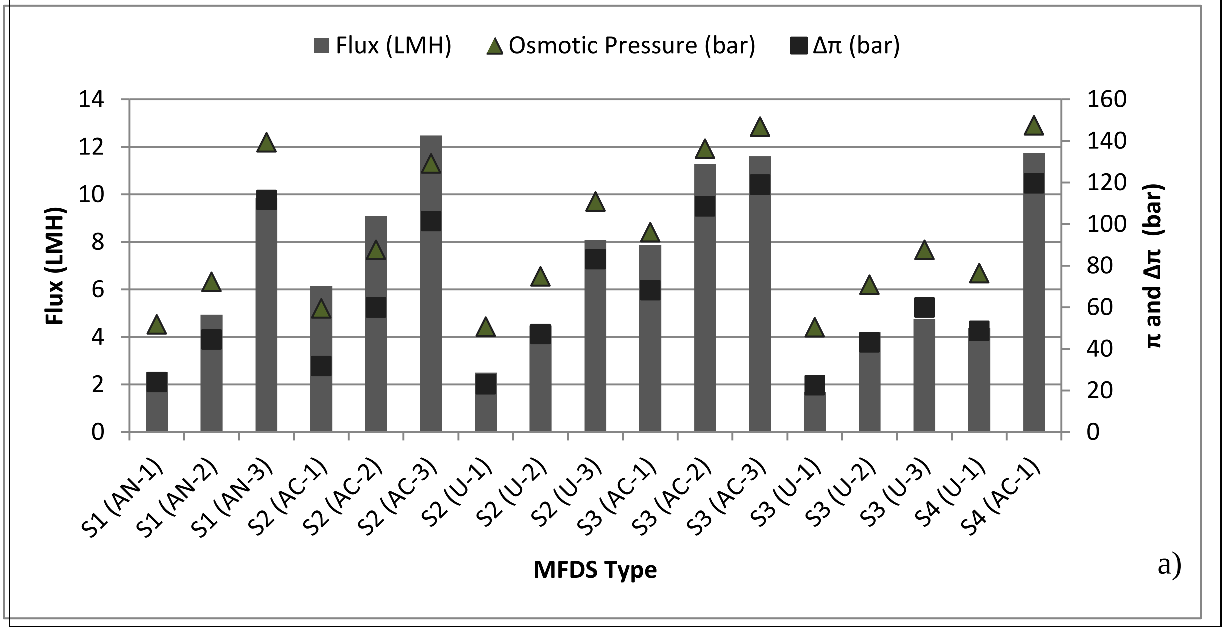

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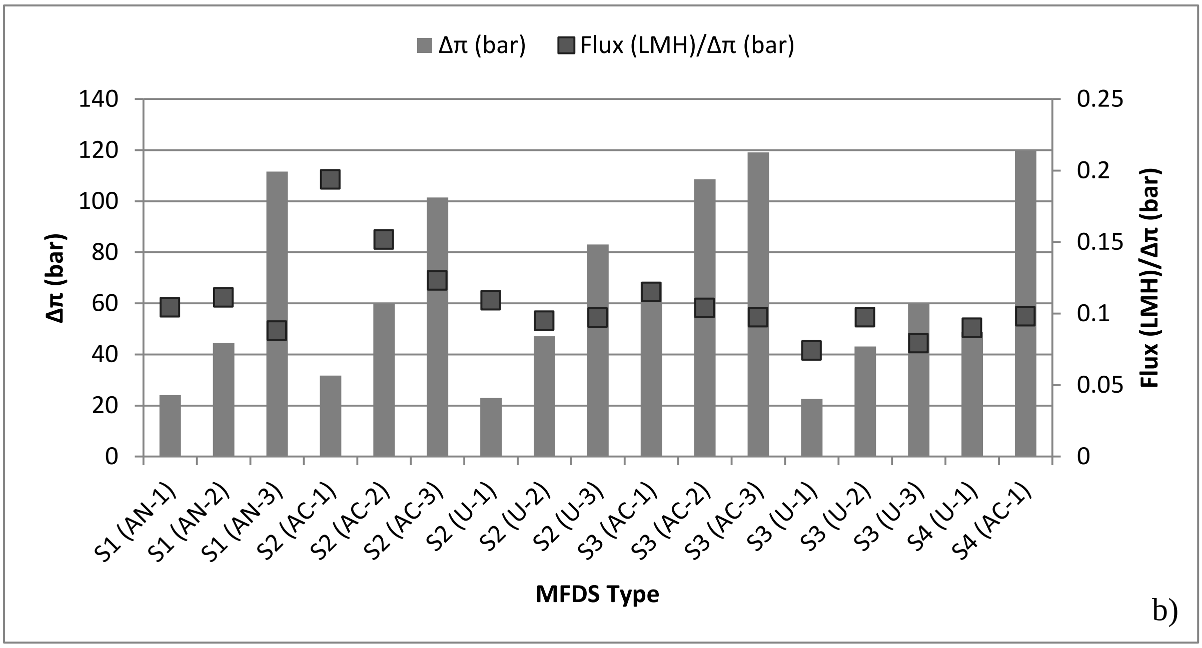

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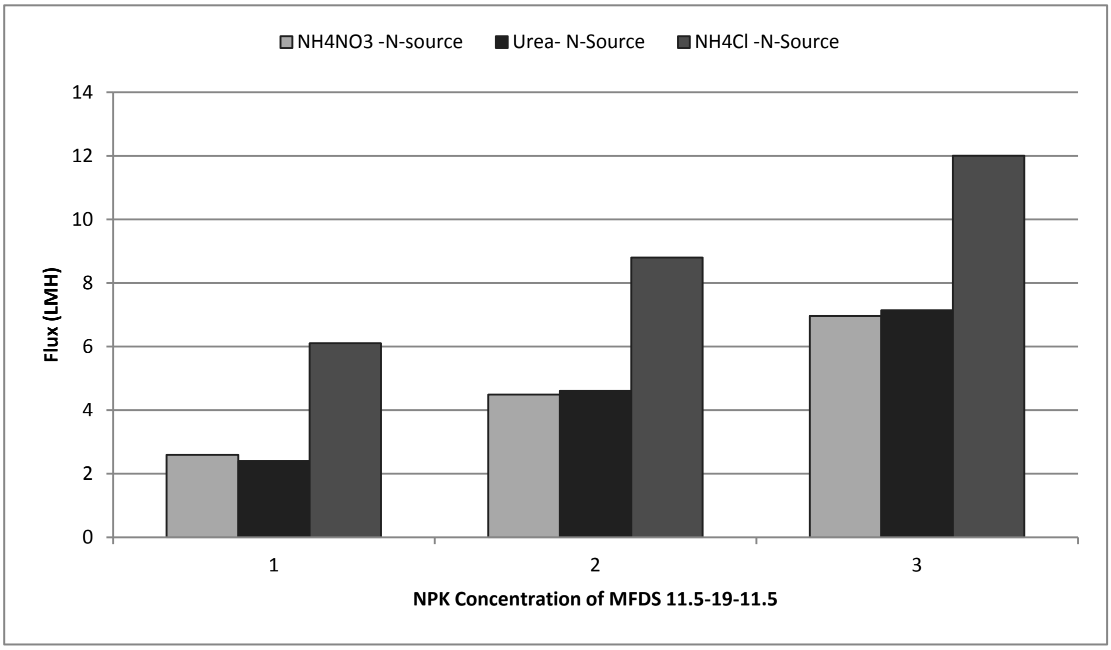

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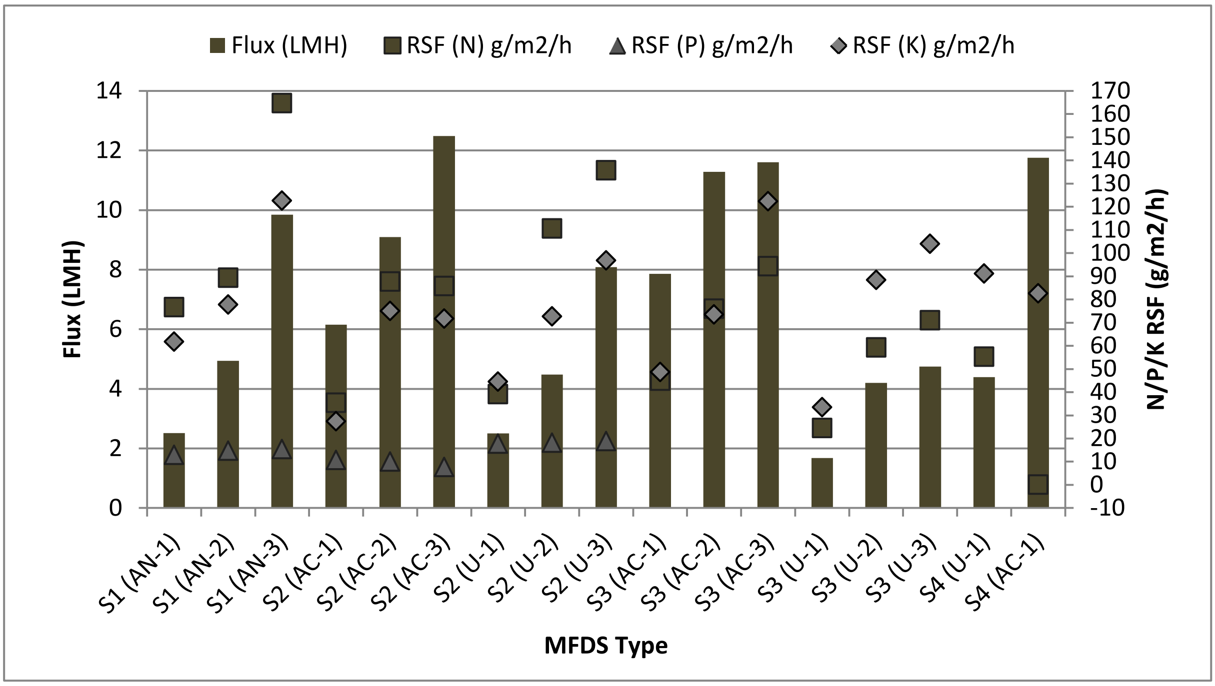

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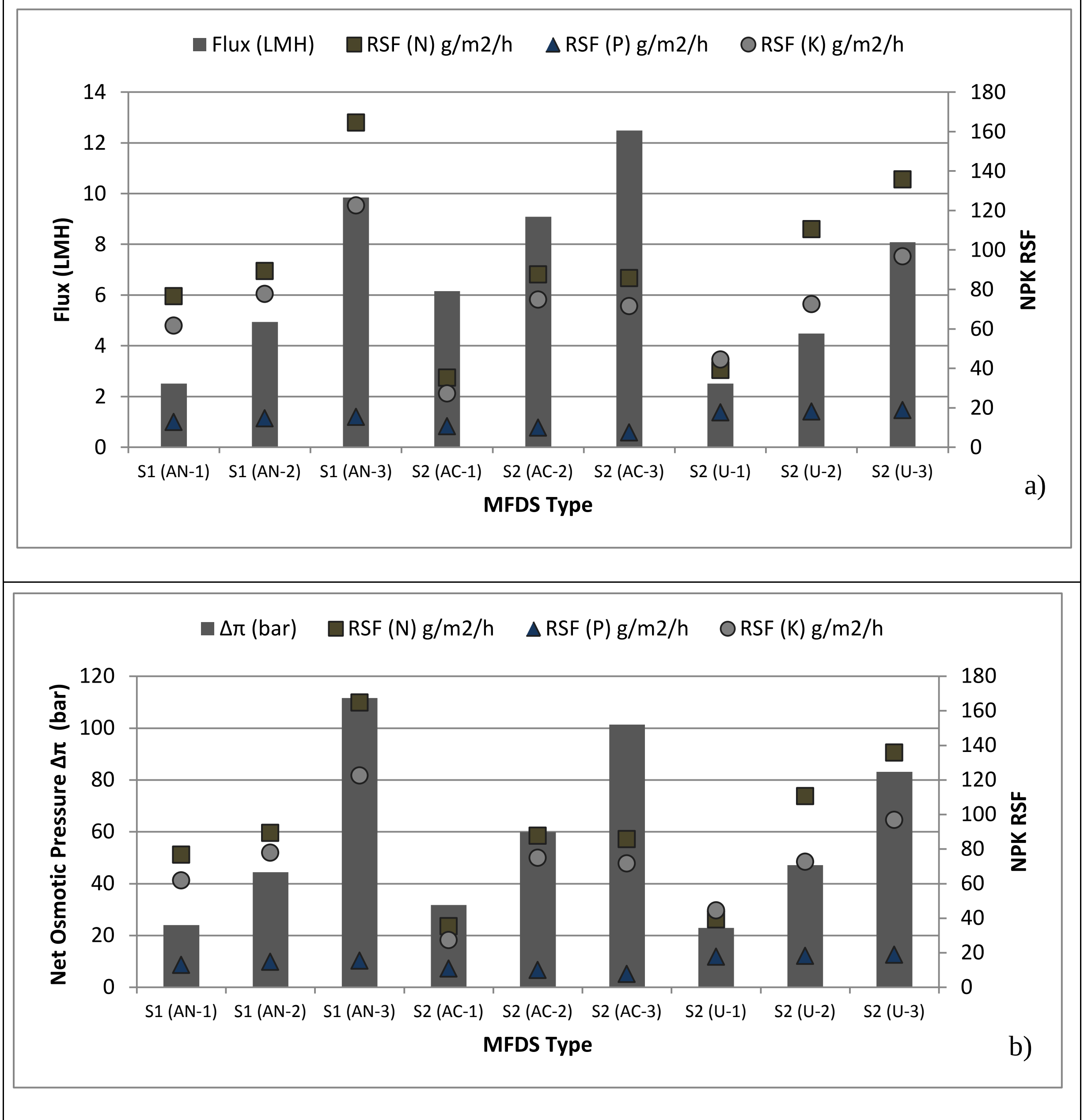

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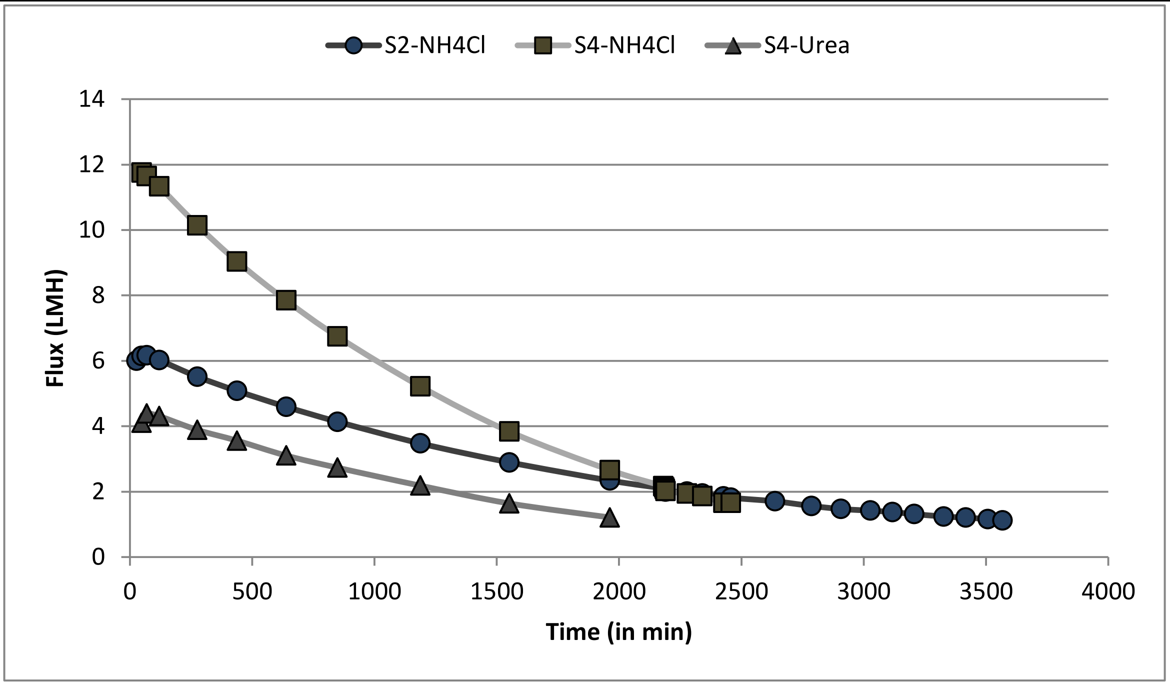

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