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## SELECTION OF INORGANIC-BASED FERTILIZERS IN FORWARD OSMOSIS FOR WATER DESALINATION


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**Abstract**

The current study aims at the selection of an appropriate draw solute for forward osmosis process. Separation and recovery of the draw solute are the major criteria for the selection of draw solute for forward osmosis process. Therefore in this investigation six inorganic fertilizers draws solute were selected. The selections of inorganic fertilizers as draw solute eliminate the need of removal and recovery of draw solute from the final product. The final product water of forward osmosis process has direct application in agricultural as nutrient rich water for irrigation. These inorganic fertilizers were tested based on their water extraction (water flux) capacity. This experimental water flux was compared with the observed water flux. It was noted that the observed water flux is much higher than the attained experimental water flux. The difference of these two fluxes was used to calculate the performance ratio of each selected fertilizer. Highest performance ratio was shown by low molecular weight compound ammonium nitrate (22.73) and potassium chloride (21.03) at 1 M concentration, whereas diammonium phosphate (DAP) which has highest molecular weight among all the selected fertilizer show the lowest performance ratio (10.02) at 2 M concentration.



Keywords: Forward osmosis, draw solute, water flux, performance ratio, inorganic fertilizers

## Introduction

With the rise in population the demand of fresh water and energy has become important issue of concern. In fact, water and energy are inextricably linked to each other (Zhao, 2012). Therefore, it is relevant to investigate low-energy consumption process for water purification (Shannon et al., 2008). To solve the fresh water crisis, the problems of inadequate access, excessive use, and pollution of water resources should be solved. Therefore, it is necessary to develop new methods for water treatment and desalination is one solution to solve the inadequate accessibility of fresh water.

Forward osmosis (FO) technology is emerging as a promising technology to address the global demands for clean water. It is an energy efficient technology as its intrinsic energy source is the osmotic pressure difference between two solutions (Ling, 2011). It is considered that due to energy gap of chemical potential, water molecules transfer from a lower-concentration solution to a higher-concentration solution across the semi-permeable but rejects the solutes (salts) in the solution (Ling, 2010).The higher concentration solution possesses lower water chemical potential while the lower-concentration solution has the higher water chemical potential (Jacob, 2006).

## Principle of Forward osmosis

The standard water flux ($j_w$) in FO is calculated by the equation given below

$j_w = A(\pi_{DS} - \pi_{FS})$ (1)

Where A is the pure water permeability coefficient of the membrane, $\pi_D$is the osmotic pressure of the draw solute and $\pi_F$ is that of feed solution used. However it is noted that the experimental water flux is always lower than the calculated water flux this is because of two type of concentration polarization occurring during the FO process (Kim et al., 2012). External concentration polarization (ECP) occurs at the surface of the dense active layer of the membrane and internal concentration polarization (ICP) occurs within the porous support layer of the membrane (S. Zhao et al., 2012). According to McCutcheon and Elimelech (2007) considering the CP effects equation 1 is modified as

$Jw=A[\pi_{DM}\exp(-J_W/K_D)- \pi_{FM}\exp(-J_W/K)$ (2)

Where, $\pi_{DM}$ and $\pi_{FM}$ are the osmotic pressures of the DS and FS at the membrane surfaces respectively. K and $K_D$ are the mass transfer coefficient of the feed and draw solute side of membrane. K was defined by Lee et al. (1981) as

$K = \frac{t\tau}{D\varepsilon}$ (3)

Where, D is the diffusion coefficient of the draw solute, t, τ, and ε are the thickness, toruosity, and porosity of the support layer, respectively. Equation 2 is implicit model for osmotic flux using dense symmetric membrane. However in FO the water flux decrease continuously with the continuous dilution of the draw solute therefore ICP and ECP effect also become negligible with very dilute draw solute. This implies that the net movement of water from feed solution to draw solution will occur until the point osmotic equilibrium is reached. It is also anticipated, for each draw solution water flux increase with the increase in draw solution osmotic pressure (concentration) (Achilli et al., 2010).

## Material and Methods

### Desktop screening process

Successful FO operation requires the draw solution of high solubility and hence high osmotic pressure. Therefore almost all the inorganic fertilizers uses in agriculture were initially considered. This list was first shortened through a desktop screening and eliminating fertilizers that are not soluble or are partially soluble in water and also that are not solid at ambient temperature and pressure. Next, OLI Stream Analyzer (OLI Systems, Inc., USA) a software which uses thermodynamic modeling based on published experimental data was used to predict the properties of solutions over a wide range of concentrations and temperature (McCutcheon et al., 2006). Solutions with an osmotic pressure less than 1 MPa (145 psi) at saturation concentration were eliminated. Based on these studies a list of inorganic fertilizers were analyzed using a modification of the flow diagram for draw solution selection that was developed by Achilli et al. (2010) The goal being to select inorganic fertilizer as draw solute that need not undergo an additional separation process and the product water received could provide nutrient rich water for irrigation. The other criterion was the commercial availability of the inorganic fertilizer in the form needed for testing and also the availability of its corresponding technical data (e.g., solubility, concentration/osmotic pressure relationship, and cost) necessary for desktop screening (Bowden et al., 2012).

**Forward osmosis membranes and their characteristics**

The FO membrane used in the experiments was procured from Hydration Technologies Inc. made up of cellulose triacetate (CTA) embedded with polyester screen mesh which act as a support layer. The membranes were selected based on their commercial success, high salt rejection (Rejection for 5,000 mg/L NaCl at 10 bar is 93%), and high water permeability. The membrane used had an active layer on one side and a non-active layer on the other side. The feed solution usually faces the active layer of the membrane in order to reject the salts in the feed. The membrane has a water permeability coefficient (A) of $3.07\times10^{-12}$ $ms^{-1}Pa^{-1}$, the thickness of the membrane is 93±3 μm.

**Solution chemistries:** Analytical grade chemicals of the selected fertilizers were used to make the draw solutions. For each inorganic fertilizer as draw solution test, different concentration of draw solute was evaluated.

**FO performance experiments**

All the experimental investigations for the FO process in this study were performed using a bench-scale cross flow filtration unit (Figure 1).

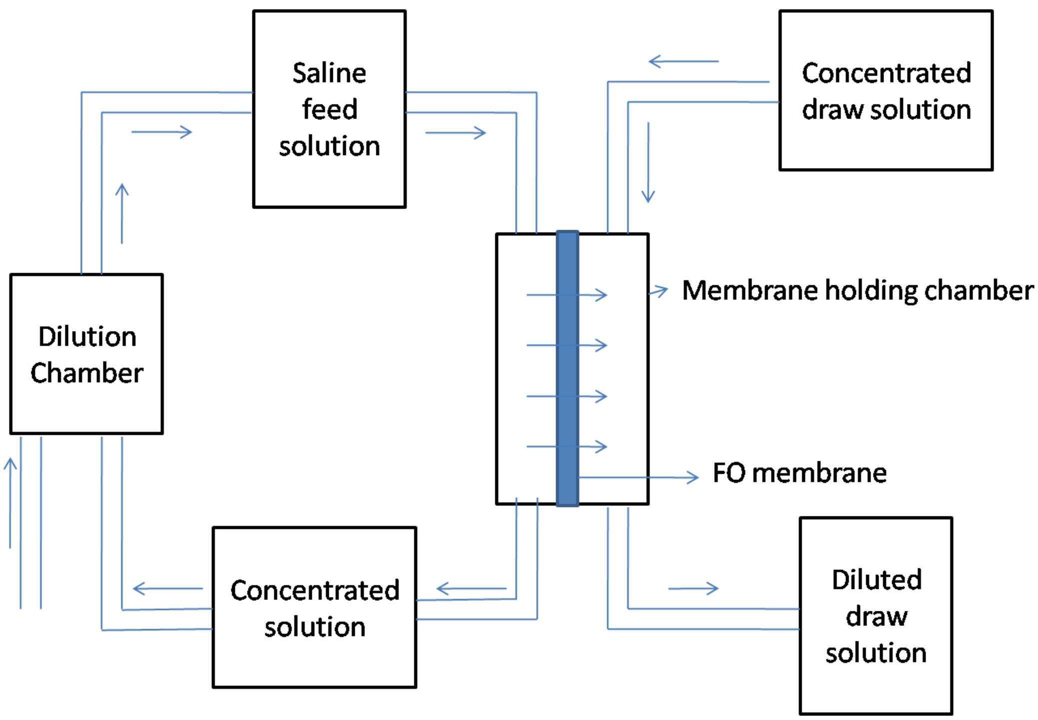



**Figure 1: Diagrammatic representative of Forward Osmosis setup**

The FO unit was a custom made glass chamber having two compartments with the dimensions 7.7 cm long, 2.6 cm width and 0.3 cm height. Two channels are provided on both sides of the membrane to allow feed water to flow on one side of the membrane and draw solution on the side of the membrane. The compartments were separated by asymmetrical CTA membrane of area 2.002 x $10^{-3}$ $m^2$. The membrane consists of an active layer formed above a support layer, where the active layer of the membrane faces the feed solution while the support layer of the membrane faces the draw solution. In order to obtain higher water flux and reduce strain on membrane, the feed and draw solution was circulated in the cell at a velocity of 21.4 cm/s. This gives a turbulent flow to feed and draw solution so that their concentration remains throughout homogeneous. Water flux across the membrane in the FO process was calculated from the change in the volume of the DS in the DS tank.

The water flux *Jw* (in $Lm^{-2}h^{-1}$) was calculated using the following relationship:

$J_v = \Delta V / A\Delta t$ (4)

Where $\Delta V$ (L) is the volume change of the feed solution over a predetermined time $\Delta t$(h) and *A* is the effective membrane surface area ($m^2$) (Ling, 2010)

The initial volume of both the DS and FS was kept 2.0 L each. The solutions after passing through the membrane were returned to their respective tanks. The water flux (*Jw*) was selected from the point at which a stable flux was observed from the plot of flux (*Jw*) versus time, which usually happened within the first 30 minutes of operation. Each experiment was carried out for duration of at least six hours for adequate diffusion of draw solutes and help effective monitoring of the reverse diffusion of draw solutes.

**Results**

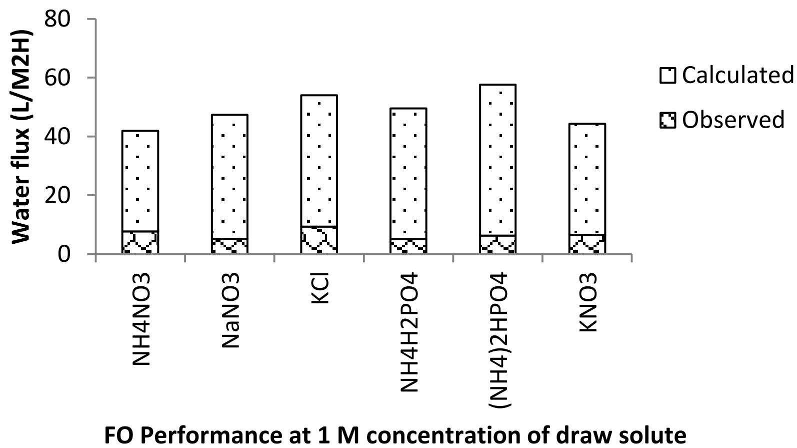
Six inorganic selected fertilizers (ammonium nitrate ($NH_4NO_3$), sodium nitrate ($NaNO_3$), potassium chloride (KCl), potassium nitrate ($KNO_3$), diammonium phosphate (DAP) and mono-ammonium phosphate (MAP) were tested as potential draw solute in FO desalination process. .These selected fertilizers were selected with the aim of providing nitrogen, phosphorus and potassium which are the main plant nutrition needed for agricultural production. In this work performance analysis was done on the basis of the expected and obtained experimental water flux. The water flux was tested at 1 M and 2 M concentration of draw solute. The calculated water flux at 1 M and 2 M concentration of draw solute is much higher than the osmotic pressure of sea water (28 Atms) hence ideal con of draw solute for FO process.

**Water flux:** it was calculated at a concentration of 1 M and 2 M con for the selected inorganic fertilizer. The feed solution in all the bench test was DI used under similar operating conditions. The findings were in accordance to Van't Hoff's (1887) equation given below

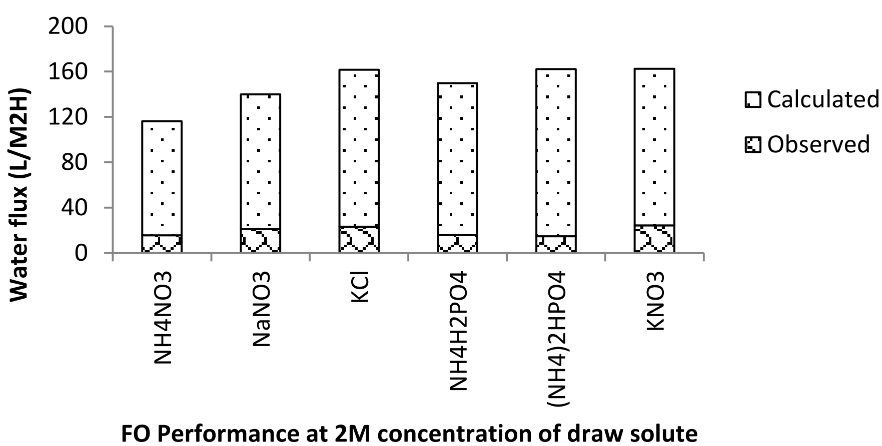
$\pi$=nMRT

where $\pi$ is the osmotic pressure in bars, M is the solute molar concentration in moles/liter, R is the universal gas constant (0.08314 L bar $mol^{-1}K^{-1}$), and T is the temperature in Kelvin.

The osmotic pressure which is the governing factor in FO is directly related to molar concentration (M) of the draw solute.




(Figure 2a)




(Figure 2b)

**Figure 2: Observed and calculated water flux at different draw solute concentration**

The water flux at 1 M con (Figure 2a) for the selected inorganic fertilizer as draw solute is highest for KCl (9.39 $L/M^2h$) followed by $NH_4NO_3$ (8.46 $L/M^2h$). The lowest water flux was observed in case of MAP (5.11 $L/M^2h$) and $NaNO_3$ (5.22 $L/M^2h$). Draw solute with lower molecular weight usually have higher diffusion (Valencia and González2010) resulting in higher water flux (Achilli et al., 2010; Qin et al., 2010) ultimately affecting the FO water flux. This increase in diffusion coefficient is expected to lower the solute resistivity within the membrane support layer ultimately reducing the ICP effects (McCutcheon and Elimelech, 2006). For the bench scale experiment using 2 M concentration (Figure 2b) for the selected inorganic fertilizers as draw solute $KNO_3$ (24.12 $L/M^2h$) show the highest water flux and KCl (23.22 $L/M^2h$), whereas DAP (14.76 $L/M^2h$) and $NH_4NO_3$ (15.48 $L/M^2h$) lowest water flux. Results have shown that water fluxes increase by increasing the DS concentration. These findings were similar to that of Xu et al., (2010), Choi et al., (2009), Achilli et al., (2009) and, McCutcheon and Elimelech (2006).

It is common in all the draw solute (1M and 2M) that the experimental water fluxes are much lower than the theoretical estimated (Figure 2) The difference in fluxes mainly attributed to CP effects especially dilutive ICP or solute dilution inside the support layer of the membrane (McCutcheon and Elimelech, 2006). ICP effect causes reduced osmotic pressure compared to the bulk solution (Bowden et al. 2012).

**Performance ratio (PR):** Performance of inorganic fertilizers in FO (the performance test) was performed at 1 M and 2 M concentration of selected inorganic fertilizers as draw solute (table 1). Distilled water was used as feed solution under similar operating conditions. The results are shown under table 1. Performance ratio is the percentage ratio of the experimental water flux and estimated or theoretical water flux calculated based on the bulk osmotic pressure (Achilli et al., 2009). It indicates the percentage of the effective bulk osmotic pressure difference that is effectively generating water flux across FO membrane (McCutcheon et al., 2006). Among all the six tested fertilizers $NH_4NO_3$ (22.73) show the highest performance ratio at 1 M draw solute followed by KCl (21.03), $KNO_3$ (17.34), $NaNO_3$ (12.39), DAP (12.19) and MAP (11.49). The water extraction capacities of the fertilizers were observed to depend inversely on the molecular weight and directly on osmotic pressure and concentration of the draw solutes. These finds were according to (McCutcheon et al., 2005; Ling and Chung, 2011). The osmotic pressure of a specific draw solution depends on the draw solution's characteristics, including size and charge; selection of a draw solution with charged ions and a low molecular weight is desirable to achieve high osmotic pressure and water flux.

**Table 1: Performance ratio of selected inorganic fertilizers using DI as feed solution**

| Draw solution | Chemical formula | Molecular weight | Concentration | π (atm) | Performance ratio (%) |
|---|---|---|---|---|---|
| Ammonium nitrate | $NH_4NO_3$ | 80.04 | 1M | 33.7 | 22.73 |
| | | | 2M | 64.9 | 15.39 |
| Sodium nitrate | $NaNO_3$ | 85 | 1M | 41.5 | 12.39 |
| | | | 2M | 81.1 | 17.92 |
| Potassium chloride | KCl | 74.6 | 1M | 44 | 21.03 |
| | | | 2M | 80.1 | 16.77 |
| Mono-ammonium phosphate (MAP) | $NH_4H_2PO_4$ | 115 | 1M | 43.8 | 11.49 |
| | | | 2M | 86.3 | 11.84 |
| Diammonium phosphate (DAP) | $(NH_4)_2HPO_4$ | 132.1 | 1M | 50.6 | 12.19 |
| | | | 2M | 95 | 10.02 |
| Potassium nitrate | $KNO_3$ | 101.1 | 1M | 37.2 | 17.34 |
| | | | 2M | 59.9 | 17.43 |

It was noted that the low molecular weight compounds show better performance than higher molecular weight compounds. These findings were similar to Achilli (2010) work that at similar concentration the low molecular weight compound shows better results. In case of 2 M concentration of draw solute concentration the performance ratio is different in most of the cases and do not follow the above trend. The performance ratio decrease in the order of $NaNO_3$ (17.92), $KNO_3$ (17.43), KCl (16.77), $NH_4NO_3$ (15.39), MAP (11.8) and DAP (10.02).

The osmotic pressure of sea water vary from 26- 28atm (3.5% w/w sodium chloride solution) depending on its total dissolved solids (Ling, and Chung 2011).It is expected that water will continue to move from the saline feed water to draw solution chamber as long as there is a difference of osmotic potential between them. Because of the higher osmotic pressure of draw solute used, the draw solution possesses the osmotic power to draw pure water from the saline feed water leaving behind salts. This process will take place up to a where net osmotic pressure becomes equal and water movement will cease. All the fertilizers has different solution chemistry, therefore different fertilizers will achieve osmotic equilibrium at different molar concentrations and this depends largely on the molecular weight of the draw solution. Based on the theoretical calculations, all soluble fertilizers can extract water from brackish water as long as it can generate osmotic potential higher than the saline feed water (Phuntsho et al., 2011).

## Conclusion

The concept of low energy FO was used for water desalination using fertilizer as draw solute. The idea behind the use fertilizer as draw solute was that the desalinated water can be directly used for irrigation. All the fertilizers possessed different osmotic pressure and among the selected fertilizer the highest osmotic pressure was shown by and possesses the lowest osmotic pressure of. The highest water flux was noted in $KNO_3$ and KCl at 1 M and 2 M concentration respectively of draw solute. With the increase in concentration of draw solute the water flux also increase although no correlation was found between them. It was noted that the experimental water flux was much lower than the observed water flux in all the selected draw solute. The reason behind the difference in experimental and observed water flux being the ICP effect in the asymmetrical FO membrane.

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