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Investigation of Ammonium Sulfate/Ammonium Di-Hydrogen Phosphate fertilizers as Draw Solute for Forward Osmosis Desalination.

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ABSTRACT

Forward osmosis (FO) is an osmotically driven membrane process in which the driving force for separation is the difference in chemical potential between a concentrated draw solution and a broad range of aqueous solutions, including contaminated water.FO can be suitably used to desalinate water for irrigation, using fertilizer as draw agent where the desalinated water containing diluted draw solution can be directly applied for fertigation. This paper is concerned with the investigation of ammonium sulfate and ammonium di-hydrogen phosphate fertilizers and their blend as draw agents for forward osmosis desalination. By comparing the performance of the two compounds at different molar concentrations against distilled water feed water, it was found that 2 M ammonium sulfate solution gave the highest performance (12 L/m^2hr). The application of 2 M ammonium sulfate with real feed water from El-Salam canal in Sinai, Egypt and synthetic saline water was also investigated.

Keywords: Forward osmosis, Fertilizers, Draw agents, Brackish water, Fertigation.

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INTRODUCTION

The fresh water resources of the world are depleting, while world population is deemed to increase every year. This calls for science and technology to play a significant role in solving water scarcity issues, which are becoming increasingly evident in many parts of the world. Desalination technology in particular is expected to play a crucial role in solving the water issues in the future, because it can provide additional new water from an unlimited saline source on the planet. Current desalination technologies are prohibitively expensive and energy intensive. Reverse osmosis (RO), a commonly used desalination technology, is significantly more expensive than the standard treatment of fresh water for potable use. Less expensive methods of desalination are needed to make desalination technologies more competitive with fresh water treatment. Forward osmosis (FO) is an osmotically driven membrane process in which the driving force for separation is the difference in chemical potential between a concentrated draw solution and a broad range of aqueous solutions, including contaminated wastewater [1-3]. The process involves the permeation of water from a feed solution (FS) of low osmotic pressure across a semipermeable FO membrane, to a draw solution (DS) of high osmotic pressure. The FO membrane acts as a tight barrier to contaminant transport, including organic matter, dissolved and suspended solids.

One key component for successful development of FO technologies is the selection of an optimal DS. There are three main criteria for selecting a suitable DS for FO applications. First, the DS should have a relatively high osmotic pressure [4]. Second, the diluted DS should be able to be easily and economically re-concentrated and/or recovered [4, 5]. Lastly, the draw solute should exhibit minimized internal concentration polarization (ICP) in the FO processes. Many authors studied the use of FO desalinated for agricultural purpose. In such a situation, fertilizer can be used as a draw agent for FO process because the diluted DS can be directly applied for fertigation. This concept offers several novelties: firstly the cost of desalinated water remains very low, secondly DS does not need to undergo an additional separation process and thirdly the process provides nutrient rich water for irrigation of plants and crops. Besides, FO desalination has high recovery rate and high salt rejection rate [6, 7, 8], which will be an additional advantage for the irrigation application. The impact of such technology on the agriculture sector would be revolutionary for drought stricken countries where saline water is abundant in the form of sea water along the coastal areas and brackish groundwater in the inland areas [9, 10].

The objective of this study is to assess comparatively, the performance of fertilizers as DS for FO desalination. Ammonium sulfate (AS), ammonium di-hydrogen phosphate (ADHP) and their mixture were chosen for investigation, based on its higher osmotic pressure as obtained from literature (46.1 and 43.8 atm. respectively [11]).The study includes assessment of the osmotic potential of fertilizer solutions and carrying out basic FO experimental tests to evaluate their performance in terms of water flux and reverse solute flux. In addition, the optimum one was applied with real impaired feed water from El-Salam Canal water in Sinai, Egypt, and synthetic saline water at different concentrations.

MATERIALS AND METHODS

Experimental set-up:

A bench scale system was designed and constructed for this study with a membrane cell having two parallel channels. A schematic drawing of the designed system is illustrated in Figure (1).

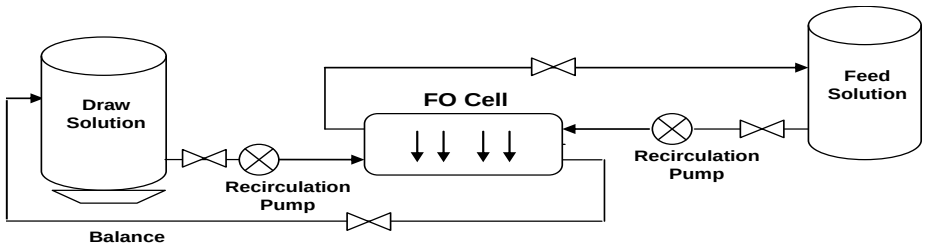

Figure 1: Closed-loop bench-scale forward osmosis experimental setup.

Feed and draw solutions were re-circulated from their respective tanks at 0.857 l/min through the FO membrane cell and back to the tanks using a piston dosing pump positive stroke spring return. The membrane cell consists of CFO42 stainless steel 316 FO style cell with active membrane area 56 cm^2, cell has symmetric channels on both sides of the membrane, each channel with dimensions of 2, 115, and 55 mm for height, length and width, respectively. The draw and feed solutions flowed counter-currently in each channel on both sides of the membrane, both of which were controlled independently by a micro pump (ETATRON D.S. S.P.A.). The DS tank will be placed on an analytical balance (Vibra, Pine Brook, NJ), and the rate of change of the DS weight was recorded and used for calculation of water flux through the membrane. The conductivity meter Myronn L Ultrameter was used for TDS measurements.

Materials:

Chemicals:

Ammonium sulfate (AS) and ammonium di-hydrogen phosphate (ADHP) were used as laboratory reagent with minimum assay of 98.5%. Sodium chloride (NaCl) (Alpha chemika) had minimum assay of 99.9 %.

Membranes:

FO thin film woven membrane from Hydration Technology Innovations Company (HTI) was used, this membranes made of cellulose triacetate (CTA) embedded about a polyester mesh. This type of membrane has a thickness of around or less than 50 µm, moreover it is relatively smooth and hydrophilic [8]. The HTI membranes have been used in a number of studies, and are currently viewed as the best available membranes for FO applications [12, 13]; typical characteristics of these types of membranes are shown in table (1).

Table 1: Typical Membrane Characteristics

Item	Description
Thickness	50 µm
The water contact angles (active layer)	61.3°±0.8°
The water contact angles (support layer)	66.4°±1.3°
water permeability coefficient	1.07×10−12 m/s Pa
sodium chloride permeability coefficient	6.54×10−8 m/s

It is known that membrane orientation plays a significant role in FO applications. In this study, the membrane active layer facing feed was adopted in order to avoid aggravated fouling due to pore-clogging in the support layer if the reverse membrane orientation were to be adopted [14]. Virgin membrane coupons were cut to size and stored in distilled water over night prior to use in each experiment.

Feed and draw solutions:

Distilled water was used as FS for the evaluation of the performance of the selected fertilizers at different molarities. While, for the application of the optimum one, two types of FS were examined, first, water from El-Salam Canal in Sinai, Egypt, and the second was synthetic brackish and sea water at concentrations of 5000, 10000 and 35000 mg/L NaCl. Table (2) represents the analysis of El-Salam canal water FS. On the other side, mainly ammonium sulfate (AS) and ammonium di-hydrogen phosphate (ADHP) were used to prepare the DS.

Table 2: Analysis of El-Salam canal water

Element to be analyzed	Results	Units
- Colour	17	mg/L Pt Co
- Turbidity	4.2	N.T.U
- Odour	Odourless	-
- pH	7.84	-
- Total dissolved solids [TDS]	1540	mg/L
- COD	76	mg/L
- BOD	40	mg/L

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RESULTS AND DISCUSSIONS

AS performance:

Figure (2) shows water flux as a function of time for AS at concentrations of 0.25 to 2.5 M. It was observed that higher water flux value was obtained at higher concentrations till 2 M then the water flux decreased at 2.5 M. the highest value for water flux was found to be 12 L\m^{2}hr. It was also observed that at all concentrations, the water flux increases with time till it reaches its maximum value at about 120 min. then it start to decrease gradually.

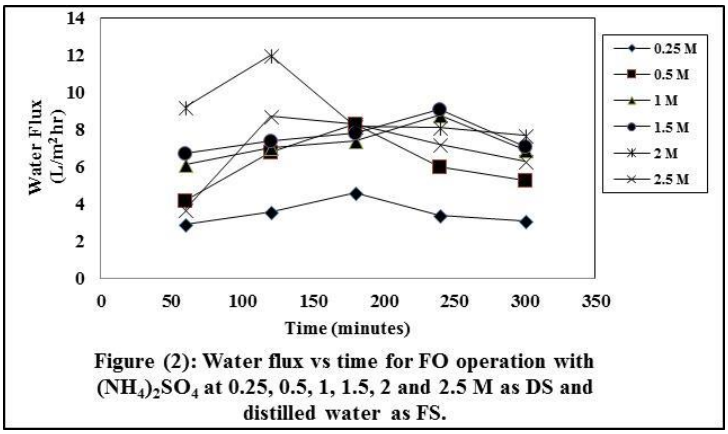

Figure (2): Water flux vs time for FO operation with $(NH_4)_2SO_4$ at 0.25, 0.5, 1, 1.5, 2 and 2.5 M as DS and distilled water as FS.

The increasing of water flux with increasing DS concentrations and behavior of flux change with permeation time can be illustrated well from literature. Arkhangelsky et al., indicated that water flux did not increased linear by increasing DS concentration [15], similar observations were reported earlier and the ICP effect was suggested to be responsible for this phenomenon [16, 17, 18]. This is due to the fact that the effect of ICP on the water flux was more severe at higher DS concentrations due to the accumulation of salt ions within the membrane support layer that facing the DS. Zhao et al., explained the behavior of flux decline with time, they demonstrated that coupled adverse effects of ICP and membrane fouling can severely reduce the osmotic water flux and increased mass transfer resistance as the feed water becomes more concentrated due to water permeation from FS to DS and reverse salt diffusion from DS to FS [7].

Figure (3) demonstrates the effect of FO permeation time on reverse salt flux at AS concentrations from 0.25 to 2.5 M. It was found that at the highest reverse salt flux (0.5 mol\m^{2}hr) was observed at 2.5 M concentration of AS and 120 min. permeation time then decreased by time from 0.5 mol./m^{2}hr to 0.3 at 300 min. While at the other concentrations, the reverse salt flux was found to be low (0.05-0.2 mol\m^{2}hr) and was approximately constant with time. Generally, it is clear that as the ammonium sulfate concentration increases, the reverse salt flux increases.

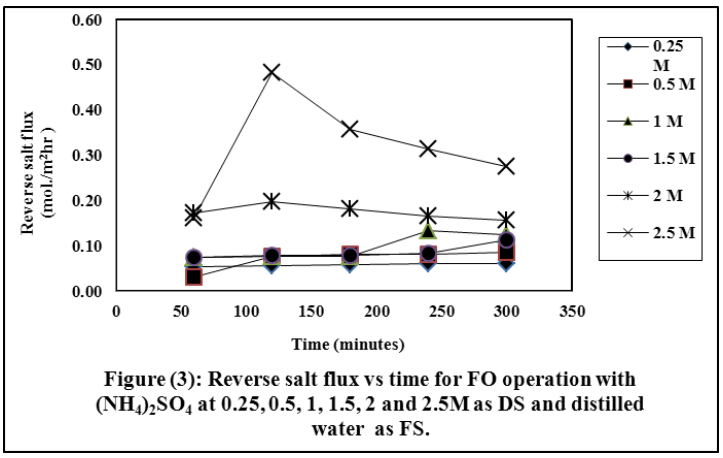

Figure (3): Reverse salt flux vs time for FO operation with $(NH_4)_2SO_4$ at 0.25, 0.5, 1, 1.5, 2 and 2.5M as DS and distilled water as FS.

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These results are in good finding with Yong et al.[19]; they studied the coupled reverse draw solute permeation and water flux in forward osmosis with neutral draw solutes, they concluded that reverse salt flux was increased by increasing of water flux. Also, the same results were obtained by Phillip et al. [20].

ADHP performance:

Figure (4) shows water flux as a function of time for ADHP at concentrations of 0.25 to 2 M. It was observed that higher water flux value was obtained at concentration of 1 M then the water flux decreased by increasing the concentration in which the highest value for water flux was found to be 9 L\m^{2}hr. It was also observed that at all concentrations, the water flux increases with time till it reaches its maximum value at about 60 min. then it slightly decreases with time.

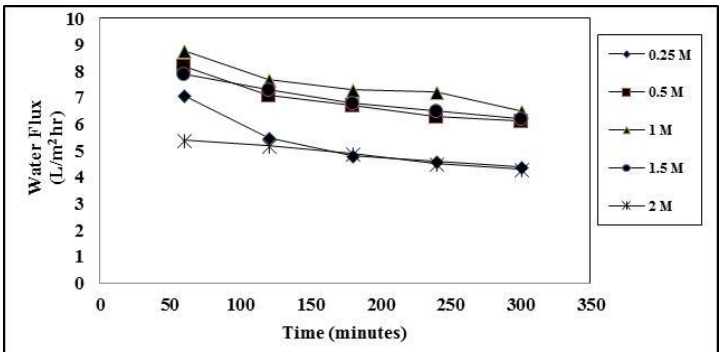

Figure (4): Water flux vs time for FO operation with $NH_4H_2PO_4$ at 0.25, 0.5, 1, 1.5 and 2 M as DS and distilled water as FS.

As indicated above, the behavior of water flux with DS change can be attributed to the effect of ICP on the water flux at higher DS concentrations, in addition, the coupled adverse effects of ICP and membrane fouling that can severely reduce the osmotic water flux and increased mass transfer resistance as the feed water becomes more concentrated due to water permeation from FS to DS and reverse salt diffusion from DS to FS [7].

Figure (5) demonstrates the effect of FO permeation time on reverse salt flux at ADHP concentrations from 0.25 to 2.0 M. It was found that the highest reverse salt flux (0.2 mol\m^{2}hr) was observed at 2 M concentration of ADHP and 120 min. permeation time then decreased by time from 0.2 mol./m^{2}hr to 0.15 at 300 min. While, at the other concentrations, the reverse salt flux values were found to be low (0.03-0.13 mol\m^{2}hr) and were approximately constant with time. The increasing of reverse salt flux may be attributed to the increasing of osmotic driving force. Generally, it is clear that as the ADHP concentration increases, the reverse salt flux increases.

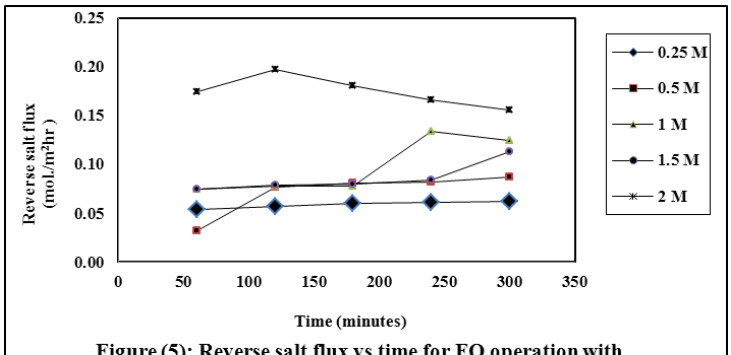

Figure (5): Reverse salt flux vs time for FO operation with $NH_4H_2PO_4$ at 0.5, 1, 1.5 and 2M as DS and distilled water as FS.

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Mixture of AS (1M) and ADHP (M) performance

The flux performance of the mixture of 1M AS and 1M ADHP was presented in Figure (6). It was observed that the maximum flux was about 11 L\m^{2}hr after 120 min. permeation time, and then the flux decreased slightly with time till 10 L\m^{2}hr.

Figure (7) illustrates the effect of FO permeation time on reverse salt flux and salt rejection for mixture of ADHP (1M) and AS (1M). It was found that the highest reverse salt flux (0.2 mol\m^{2}hr) was observed at 2 M concentration of ADHP and 120 min. permeation time then decreased by time from 0.2 mol./m^{2}hr to 0.15 at 300 min. In addition, the salt rejection was decreased slightly by time from 99.9 to 99.4 %.

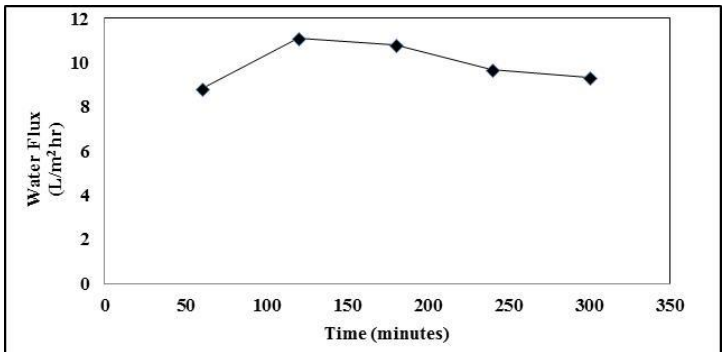

Figure (6): Water flux vs time for FO operation with mixture of 1M $(NH_4)_2SO_4$ and 1M $NH_4H_2PO_4$ as DS and distilled water as FS.

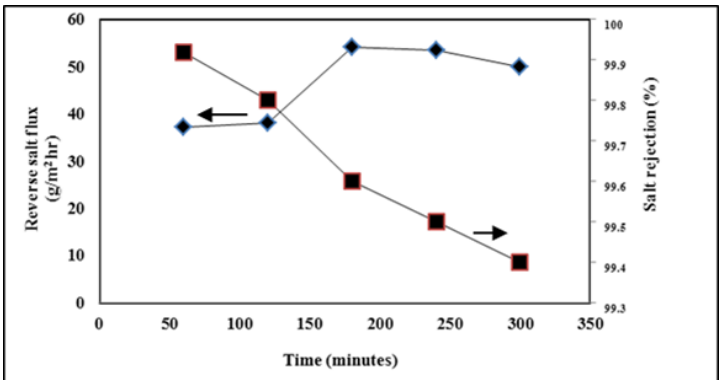

Figure (7): Reverse salt flux and salt rejection vs time for FO operation with mixture of 1M $(NH_4)_2SO_4$ and 1M $NH_4H_2PO_4$ as DS and distilled water as FS.

According to the previous results, 2 M AS solution that gave the highest performance was selected for applications.

Ammonium sulfate application:

Application with El-Salam canal water:

The effect of FO permeation time on water flux for El-Salam canal water as FS against 2 M AS as DS was represented in Figure (8). The results were compared with AS performance using distilled water at the same conditions. It was observed that by using of El-Salam canal water as FS the flux increased to reach 9.3 L/m^{2}hr at 120 min. then decreased gradually by time to 7.5 L/m^{2}hr after 300 min. Also it was found that the FO performance with El-Salam canal water FS is lower than that obtained with using distilled water wherever the

optimum flux with El-Salam canal water was 9.3 L/m^{2}hr while with distilled water was 12 L/m^{2}hr at 120 min. This can be attributed to the decreasing of osmotic driving force due to the increasing of FS concentration.

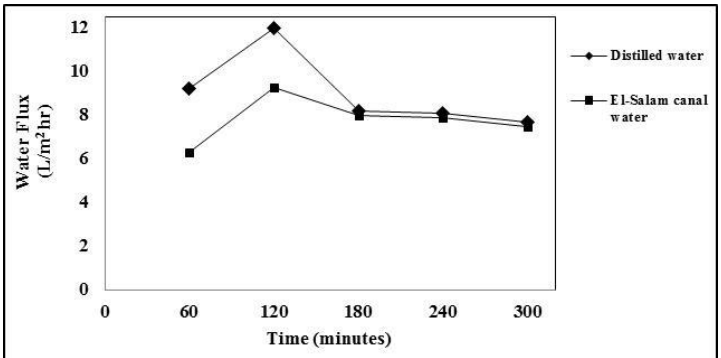

Figure (8): Water flux vs time for FO operation with 2M $(NH_4)_2SO_4$ as DS and El-Salam canal water as FS.

Figure (9) illustrate the reverse salt flux as a function of time for El-Salam canal water FS as comparing with distilled water FS. It was observed that the performance with El-Salam canal water FS was worse than that obtained with distilled water, where, in spite of decreasing osmotic driving force by increasing of FS concentrations, the reverse salt flux with El-Salam canal water was found to be higher than that obtained with distilled water. In which, it was increased from 0.37 mol./m^{2}hr at 60 min. to 0.82 at 180 min., then decreased gradually to 0.73 after 300 min., while with distilled water FS the reverse salt flux was ranged from 0.197 mol./m^{2}hr to 0.156 for time between 60 min. and 300 min. respectively.

The salt rejection with El-Salam canal water was found to be 98.9% after 300 min., while with distilled water was 99.8%.

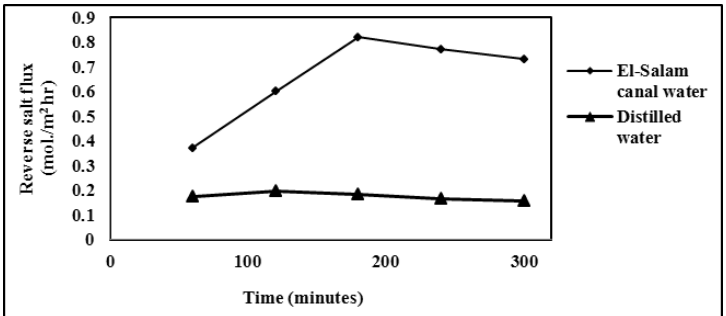

Figure (9): Reverse salt flux vs time for FO operation with 2M $(NH_4)_2SO_4$ as DS and El-Salam canal water as FS.

The results are in good finding with Cui et al.[21]; they studied the removal of heavy metal ions by forward osmosis process, they also demonstrated the effect of FS concentrations on FO performance, they concluded that water flux was decreased with increasing of feed concentration due to the decrease in osmotic pressure difference between the draw and feed solutions. In addition, they concluded that increasing of feed concentrations would enhance the diffusion of heavy metal ions. However, the increase in feed concentrations would increase the feed osmotic pressure and reduce the overall driving force for water transport. As a result, there was an insignificant reduction in the solute rejection and increase in reverse salt flux.

Application with Synthetic brackish and sea water

Figure (10) shows water flux as a function of time for the 2M AS DS with synthetic brackish and sea water at concentrations of 5000, 10000 and 35000 mg/L as FS. The results were compared with AS

performance with distilled water at the same conditions. It was observed that the water flux with 5000 mg/L FS increased from 8.4 L/m^{2}hr at 60 min. to 10.5 at 120 min. then decreased by time to 7.1 L/m^{2}hr after 300 min., for 10000 mg/l FS it was increased slightly from 7.5 at 60 min. to 8.6 at 120 min., then it decreased gradually to 7 L/m^{2}hr after 300 min. With 35000 mg/L FS the same trend was obtained, in which, the flux was increased from 6.3 at 60 min. to 7.6 at 120 min., then decreased gradually to 6.5 L/m^{2}hr after 300 min. Comparing with the performance of distilled water, the flux was found to be decreased by increasing the salinity of FS in which the maximum water flux (12 L/m^{2}hr) was obtained at 120 min. by using distilled water as feed solution. As discussed above, this can be explained by decreasing of osmotic driving force.

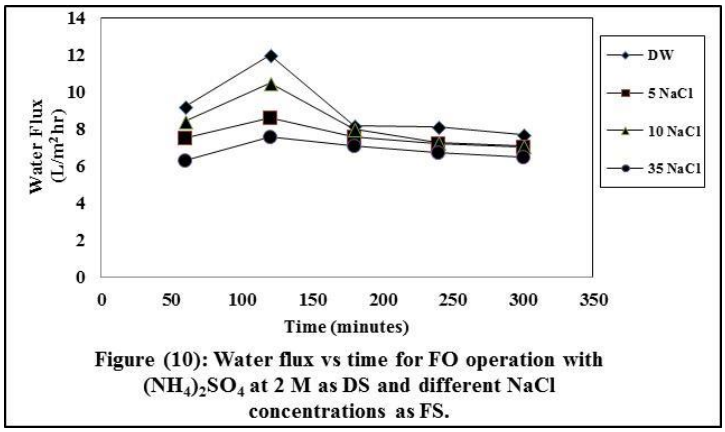

Figure (10): Water flux vs time for FO operation with $(NH_4)_2SO_4$ at 2 M as DS and different NaCl concentrations as FS.

Figure (11) illustrates the reverse salt flux as a function of time for synthetic saline water FS as comparing with distilled water FS. It was found that the reverse salt flux was increased significantly by increasing FS salinity up to 10000 mg/L, and then tend to decreased by increasing FS concentration to 35000 mg/L.

As demonstrated above, the increasing of reverse salt flux by increasing the concentration up to 10000 mg/L may be due to the increasing of feed osmotic pressure and reduction of overall driving force for water transport [21].While, further decreasing in reverse salt flux by increasing the concentration up to 35000 mg/L may be explain by increasing of ICP by increasing of feed concentrations [7].

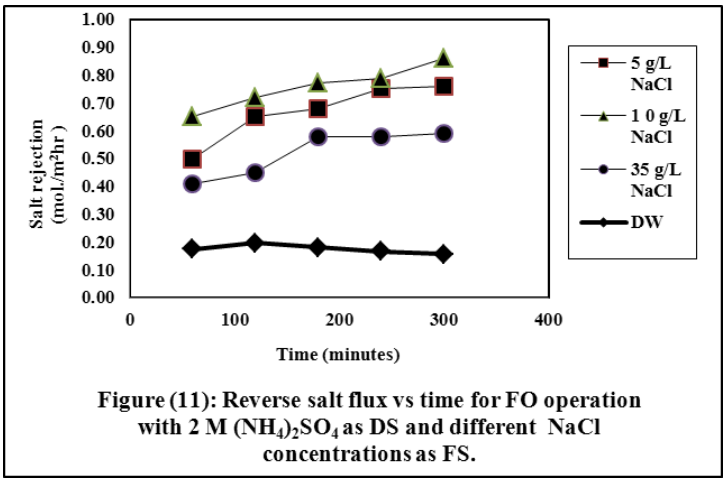

Figure (11): Reverse salt flux vs time for FO operation with 2 M $(NH_4)_2SO_4$ as DS and different NaCl concentrations as FS.

The salt rejection for 5000, 10000 and 35000 mg/L FS concentrations were found to be decreased slightly from 99.9, 99.8 and 99.88% at 60 min. to 98.9, 98.8 and 99.2% at 300 min., while for distilled water FS, decreased from 99.99 to 99.77 %.

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CONCLUSIONS

It can be concluded from the above results that; the AS performance gave maximum overall water flux of 12 L/m^2hr at 2 M while, with respect to ADHP the highest value for water flux was found to be 9 L\$m^2$h. Also, it was found that 2 M AS solution gave the highest performance; accordingly it was selected for FO application. Finley, by application of 2 M AS draw solution with El-Salam Canal water and synthetic saline water FS the same trend was obtained, where water flux was decreased as compared with distilled water base line performance, while reverse salt flux was increased.

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