

# An experimental study on draw solution performance in fertilizer drawn forward osmosis under Water Energy Food Nexus framework in Egypt

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Received 21 April 2020; Accepted 7 September 2020

# ABSTRACT

This research investigates the application of fertilizer drawn forward osmosis technique and its potential use in Egypt under the framework of the Water-Energy-Food Nexus. In this work, feed solution used is real brackish groundwater extracted from a well in Sinai, Egypt. Two sets of experiments have been conducted. The objective of having two separate scenarios is to provide informative assessment that is useful for the two main agriculture techniques, the conventional soil based one and the hydroponics technique. The first set examined three commonly used fertilizers in Egypt namely urea, di-ammonium phosphate and potassium nitrate to compare their performances. The second set examined standard hydroponic recipe, which is a mixture of nutrients, as a draw solution to fertilize crops in hydroponics systems. The nutrients mixture performance was tested and compared with that of the individual components at the same concentrations. Regarding the first set, di-ammonium phosphate resulted in the best performance as draw solute among the three tested draw solutes, where it exhibited a significant water flux equivalent to 13.8 LMH, a feed ions rejection reaching 98% and acceptable concentrations of draw solute ions in the final product water. For the second set, the hydroponic nutrients mixture exhibited better performance as draw solution compared with its individual macro-components. The use of the nutrient mixture as draw solute resulted in a flux of 11.7 LMH, 95% feed ions rejection compared with 9.2 LMH, 91%, and 10.03 LMH, 93% for its individual components. Mixing nutrients boosted the osmotic pressure and enhanced the driving force for fresh water permeation. Hence, it can be concluded that mixed nutrients have better performance than single fertilizers, not only for the enhanced desalination features and for water extraction performance but also because they provide a complete set of nutrients necessary for growing crops.

Keywords: Brackish water; Desalination; Forward osmosis; Hydroponics mixture; WEF Nexus

# 1. Introduction

Water–Energy–Food Nexus (WEF Nexus) has been recently developed as an efficient perception for explaining and describing the complicated and interconnected nature of our global resource systems, on which we rely to attain different social, economic and environmental goals [1]. Currently, there is a substantial stress on natural resources due to the unsustainable consumption and vast growth in population [2], which represents a threat on the environmental sustainability and economic development. Consequently, it is important to adapt conservation measures to natural resources use and eliminate occurrence of trade-offs [3].

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The existing water deficiency in Egypt is currently exceeding 13.5 billion m<sup>3</sup>/y (BCM/y) [4]. This deficiency is anticipated to elevate as a result of country's constant annual Nile water quota in addition to the rising land aridness which is one of the significant climate change impacts faced by the country [5]. The land aridness problem is keeping on increasing with the presence of negligible rainfall specially in the north coast area, which is another major symptom of climate change that recently affected the region [6,7]. Hence, it is crucial to develop an effective technique that can provide a sustainable alternative water supply without compromising non-renewable energy resources in addition to enhancing food production [8].

Desalination of brackish water using forward osmosis technology [9] is an emerging field of research [10–12]. One of its application, fertilizer drawn forward osmosis (FDFO), represents a potential alternative water supply for irrigation [13,14]. Adapting this technique, under the framework of the Water-Energy-Food "WEF" Nexus perspective, is very promising to overcome water scarcity challenges while preventing any trade-off with other sustainability pillars from occurrence. FDFO desalination can make irrigation water available at comparatively lower energy than the current desalination technologies [10,15]. As a low-energy technology [16], FDFO can be operated using renewable energy, which makes it suitable for inland and remote applications [17,18].

In this research, two sets of experiments have been conducted. First set represents a scenario of desalinating brackish water using the single commonly used fertilizers in Egypt and compare between their potentials as draw solutes. The second set represents a scenario of desalinating brackish water using hydroponics nutrients mixture as the draw solution, which is then compared with its individual macro-components as will be discussed in the next sections.

#### 2. Materials and methods

Bench-scale experiments were conducted using the fluxometer illustrated in Fig. 1. It consists mainly of two weigh scales connected to a data logger for continuous FS (feed solution), DS (draw solution) weight measurements, in addition to double-headed pump providing water flow rate of 0.22 L/min, Stenner Model 170DMP5 (USA brands). All experiments were conducted at constant temperature of 25°C. Temperature was maintained using heat exchanger Polyscience, model 9106 A (USA brands).

The primary volume of draw and feed solutions is 1 L per compartment; the increase in DS volume and reduction in FS volume was real time–monitored continuously and recorded in 3-minutes interval until the equilibrium between the osmotic pressures of the draw and feed solutions has been reached. Then average flux has been calculated based on the changes in volume between DS and FS. Mass transfer was conducted through commercial membrane provided by Porifira Co., (USA) with an area equal to  $1.257 \times 10^{-3} \,\mathrm{m}^2$ . Membrane properties are provided in Table 1. Before starting the experiments and during processing, membrane has been visually inspected for scaling that can affect membrane performance.

#### 2.1. Experimental plan

Two sets of experiments testing two scenarios have been conducted. First scenario has assessed the performance of three commonly used fertilizers in Egypt [20] as



Fig. 1. Fluxometer apparatus [19].

Table 1	
Porifera Co. membrane properties	[19]

Manufacturer	Porifera Inc.
Model	Roll-to-roll
Pure water permeability coefficient, A (L/m <sup>2</sup> h bar)	$2.2 \pm 0.01$
Salt permeability coefficient of active layer, <i>B</i> (m/s)	$1.6 \times 10^{-7}$
Total membrane thickness, (μm)	$70 \pm 10$
Structural parameter, S (μm)	$215 \pm 30$
Material of active layer	Polyamide (PA)
Material of support layer	Porous hydrophilic polymer

draw solutes to desalinate brackish water, which are urea (representing nitrogen), di-ammonium phosphate (DAP; representing phosphorus) and potassium nitrate (representing potassium). Feed solution samples were collected from an existing groundwater well located in Sinai, Egypt. The second scenario has investigated the performance of a standard hydroponics mixture of nutrients vs. the performance of its macro components as a potential DS. The performance in both scenarios has been assessed in terms of water flux, draw solute concentration in final product water and rejection of feed ions (Na<sup>+</sup> and Cl<sup>-</sup>). Fig. 2 summarizes the two scenarios.

# 2.2. Draw solution

A number of 15 experiments have been conducted in a duration of 6 h each, testing DAP, urea and potassium nitrate at concentrations equal to 1, 2, 3 M. All used chemicals are reagent grade provided by Sigma-Aldrich, Australia. In addition, a hydroponics standard mixture and its individual components have been also examined. Experiments are illustrated in Table 2.

A number of 24 samples were collected from both the draw and feed solutions. Both feed and draw solution samples were analyzed to determine the forward rejection of the feed solute ions via analyzing Na, Cl ions. To determine the draw solute concentration in final product water with subsequent dilution factor needed, N, P, K ions concentrations have been analyzed using photometer NOVA 60 Spectroquant.

Eq. (1) was utilized to calculate water flux  $J_w$  (in LMH) [21]:

$$J_{m} = \Delta V \times A \times t \tag{1}$$

where  $J_w$ : pure water flux (LMH);  $\Delta V$ : difference in draw solution volume before and after experiment (L); *A*: membrane area (m<sup>2</sup>); *t*: time (h).

# Scenario I

- Urea
- Di-Ammonium Phospahte (DAP)
- Potassium Nitrate

Fig. 2. Summary of the two experiment scenarios.

Physical and chemical properties of the three tested draw solutions have been gathered to assess their initial potential as draw solutes. Table 3 illustrates these physical and chemical properties [22].

Osmotic potential of each of these fertilizers was simulated at different concentrations using OLI Systems [22] (OLI Systems Inc., the USA) and illustrated in Fig. 3.

The selected hydroponics recipe consists of two tanks [23], A and B, each tank has a mixture of nutrients to be dissolved in water separately to avoid precipitation then the two compartments are to be mixed together and diluted to be applied to the hydroponics systems [24]. Table 4 indicates the composition of each tank in addition to their osmotic potential compared with the Osmotic potential of the brackish water [22,25].

Table 2 List of conducted experiments

Exp. No.	Draw solution
1	Di-ammonium phosphate (1 M)
2	Di-ammonium phosphate (2 M)
3	Di-ammonium phosphate (3 M)
4	Urea (1 M)
5	Urea (2 M)
6	Urea (3 M)
7	Potassium nitrate KNO <sub>3</sub> (1 M)
8	Potassium nitrate KNO <sub>3</sub> (2 M)
9	Potassium nitrate KNO <sub>3</sub> (3 M)
10	Hydroponics mixture – Tank A
11	Hydroponics mix Tank A – KNO <sub>3</sub> as
	individual component
12	Hydroponics mix Tank A – Ca(NO <sub>3</sub> ) <sub>2</sub> as
	individual component

# Scenario II

- Hydroponics Mixture
- Individual Macro Components

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Fig. 3. Osmotic potential simulation of urea, DAP and potassium nitrate.

Table 3							
Physical and	chemical p	properties	of the three	tested	draw	solutio	ns

Property	Urea	DAP	KNO <sub>3</sub>
Molecular weight	60.056 g/mol	132.056 g/mol	101.102 g/mol
pH	7.2 (10% solution)	8	7
Molecular formula	NH <sub>2</sub> CONH <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	KNO <sub>3</sub>
Osmotic pressure at 2 M	46.08	94.95	64.85
Physical description	Solid odorless white crystals or pellets	Crystals or crystalline powder	Colorless-to-white crystalline powder
Water solubility	545,000 mg/L (at 25°C)	69.5 g/100 g water at 25°C	38.3 g/100 g water at 25°C
Ionic strength	1.72 E-3	0.1	0.0336
Electric conductivity	4.96 E-3	21.47	14.9247

As per Table 4, due to the low concentrations of tank B and its subsequent low osmotic potential, it is concluded that tank A has the dominant osmotic impact of the mixture and tank B has negligible impact. In addition, mixing both tanks will result in precipitation, as previously mentioned. Hence, macro nutrients of Tank A have been used for conducting the experiments which are  $Ca(NO_3)_2$  and  $KNO_3$ . The performance of this mixture has been assessed compared with the individual performance of  $Ca(NO_3)_2$  and  $KNO_3$  at the same concentrations used in the hydroponics mixture which are 1.12 and 1.655 M, respectively. For the hydroponics mixture, the solution was prepared using DI water and a mixture with specific weights of each component of the nutrients recipe.

# 2.3. Feed solution

The feed solution used is real brackish groundwater sample collected from south Sinai with an estimated osmotic pressure of 2.44 atm [25], which is significantly lower than sea water that is estimated to have osmotic pressure of 55.5 atm [22]. Feed solution has the chemical composition presented in Table 5. Upon evaluation of the electric conductivity and total dissolved solids of the withdrawn sample in addition to the sodium adsorption ratio (SAR), this groundwater is inadequate to be utilized directly for agriculture as it has extremely concentrated sodium ions that is considered toxic to the plants [13].

#### 3. Results and discussion

3.1. Scenario I - individual assessment of DAP, urea and KNO<sub>3</sub> performance

3.1.1. Water flux

3.1.1.1. KNO3

Potassium nitrate flux has been determined at three different concentrations of 1, 2 and 3 M. The average flux has increased with the increase of DS concentration. As shown in Fig. 4, average flux was 5.71 LMH at 1 M and then it increased to 7.85 LMH then slightly elevated to reach 8.12 LMH at 3 M. This increase is attributed to the corresponding increase in osmotic pressure upon increase

	Tank A		Tank B
Nutrient	Quantity	Nutrient	Quantity
$Ca(NO_3)_2 \cdot 3H_2O$	184.0 g	KH <sub>2</sub> PO <sub>4</sub>	51.5 g
NH <sub>4</sub> NO <sub>3</sub>	14.4 g	MgSO <sub>4</sub> ·7H <sub>2</sub> O	93.1 g
KNO <sub>3</sub>	167.3 g	MnSO <sub>4</sub> ·H <sub>2</sub> O	0.290 g
10% Iron-DTPA Sprint 330	3.8 g	H <sub>3</sub> BO <sub>3</sub>	0.352 g
		Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O	0.023 g
		ZnSO <sub>4</sub> ·7H <sub>2</sub> O	0.217 g
		CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.035 g
Osmotic pressure	127.36 atm (OLI Systems Inc., 2019)	Osmotic pressure	53.7836 atm (OLI Systems Inc., 2019)
Osmotic pressure Tank A + Tank B (1:1) mixture		129.727 atm (OLI Systems Inc., 2019)	
Osmotic pressure of the brackish water used (salinity 3,000 ppm)		2.44 atm [25]	

Table 4 Hydroponic nutrients mixture tested as draw solution

Table 5

Real brackish groundwater sample analysis from El Tor, Sinai, Egypt (Nasr and Sewilam [7])

Raw GW sample characteristics	Ion concentration
Na <sup>+</sup>	669.99 mg/L
Cl-	1,041.25 mg/L
NH <sup>4+</sup>	2.1 mg/L
SO <sub>4</sub> <sup>2-</sup>	2,224.8 mg/L
Ca <sup>2+</sup>	564.8 mg/L
$Mg^{2+}$	215.4 mg/L
K <sup>+</sup>	41.73 mg/L
Fe <sup>3+</sup>	0.036 mg/L
Mn <sup>2+</sup>	0.016 mg/L
NO <sub>3</sub>	29.75 mg/L
HCO <sub>3</sub>	17.08 mg/L
$CO_{3}^{2-}$	0 mg/L
EC	7.32 mS/cm
TDS	3.66 g/L
pH	6.5

in the DS concentration. However, the increase of flux due to increasing the concentration to 3 M was not significant compared with the increase resulted from raising concentration from 1 to 2 M. This can be attributed to the increase in concentration polarization [26] occurring due to increasing solute concentrations. In addition, it can be noticed that the change in water flux was stable starting from the second hour of the experiment.

#### 3.1.1.2. Urea

Upon testing urea, relatively low flux compared with potassium nitrate has been observed; average flux value is only 2.56 LMH at 1 M DS, 3.53 LMH at 2 M and increased to 4.39 LMH at 3 M (Fig. 5). The reason of this low flux is the relatively low osmotic pressure of urea that resulted in lowering the driving force based on osmotic pressure

difference between the draw and the feed solutions. This low osmotic potential of urea is attributed to the few number of species formed upon dissociation in water [13,27].

#### 3.1.1.3. Di-ammonium phosphate

During the experiments, it has been observed that water flux was varying and did not reach the plateau phase till the 5th hour. Although these experiments were repeated several times to crosscheck the behavior of DAP as DS, similar results were obtained every time. From the graph below, it can be concluded that DAP has the highest flux compared with potassium nitrate and urea, resulting in average flux of 5.37 LMH at 1 M concentration, 7.42 at 2 M and 9.53 LMH at 3 M concentration (Fig. 6). This is attributed to the fact that DAP has the highest osmotic pressure compared to the other tested draw solutions.

Fig. 7 illustrates a comparison between the fluxes obtained at different molarities for the three tested fertilizers. Di-ammonium phosphate has the highest water flux among the three fertilizers, which is attributed to having the highest osmotic potential compared with potassium nitrate and urea. Urea exhibited the lowest flux rates due to its relatively low osmotic potential and few species formed.

#### 3.1.2. Draw solute concentration in final product water

Draw solute ions in the final water product were analyzed using NOVA 60 Spectroquant and the results are illustrated in Fig. 8. Based on these concentrations, the required dilution factors prior being utilized for direct fertigation are estimated (Fig. 9).

As an example of the maximum allowable NPK concentrations for crops and selecting potatoes for being one of the crops with relatively high tolerance of nutrients concentration in soil, the NPK concentrations are 0.15, 0.12 and 0.19 g/L, respectively [28]. Thus, individual fertilizers tested as draw solutes to desalinate the selected brackish water sample will need further dilution. The dilution factor will exceed 10, as per Fig. 9. Urea showed the highest solute concentration in product water, which is a result of the relatively low osmotic pressure and the subsequent



Fig. 4. Water flux of  $KNO_3$  as DS.



Fig. 5. Water flux of urea as DS.



Fig. 6. Water flux of DAP as DS.



2 M

Urea

Draw Solutes Molarity (M)

3M

1 M

2M

DAP

3M

Fig. 7. Average flux comparison between  $KNO_{3'}$  DAP and urea.

1 M

2 M

KNO

3M

1 M



Fig. 8. N, P, K concentrations in the final produced water.



Fig. 9. Required dilution factor.

low water flux that caused limited dilution of the draw solution. Both KNO<sub>3</sub> and DAP exhibited lower solute concentrations, which is attributed to the relatively high flux that caused solute dilution. Solute concentration is inversely proportional to the original solute concentration, which is matching with the increasing water flux.

# 3.1.3. Forward rejection of feed Na<sup>+</sup> and Cl<sup>-</sup> ions

Ion rejection values of Na<sup>+</sup> and Cl<sup>-</sup> ions for both DAP and KNO<sub>3</sub> are remarkably higher than urea that exhibited rejection between 74% and 82% as illustrated in Fig. 10 comparing the performance of the three types of fertilizers tested at 1, 2 and 3 M concentrations. The increase in rejection is proportional to the increase in osmotic pressure difference between the feed and draw solutions that depends

on the type and concentration of the draw solute used. Hence, the low feed ions rejection of urea is attributed to its low osmotic potential compared with the other two fertilizers used. Moreover, there is another significant reason, which is the membrane surface charge. Upon investigating the behavior of DAP and KNO3/ Na+ rejection tends to increase as draw solution volume increases, meanwhile, this results in decrease in Cl- rejection. This can be justified with alteration of the membrane surface charge which is basically negative, due to the decrease in pH and the formation of H<sup>+</sup> ions with the DS concentration increase, H<sup>+</sup> ions are attracted to the negative surface and alter its charge, resulting in changing in surface overall charge to positive. This enhances the rejection of Na<sup>+</sup> and negatively affects Cl<sup>-</sup> ions that become attracted to the new positive charge formed on the membrane surface. On the other hand, while investigating



Fig. 10. Forward rejection of feed Na<sup>+</sup> and Cl<sup>-</sup> ions at different DS types and concentrations.



Fig. 11. Water flux of the hydroponics mix vs. its individual macro components.

urea behavior, unlike DAP and KNO<sub>3</sub>, increasing urea concentration increases the pH and subsequent OH<sup>-</sup>, which does not alter the surface charge of the membrane resulting in decreased Na<sup>+</sup> ions rejection and enhancement of Cl<sup>-</sup> rejection.

# 3.2. Scenario II: the hydroponics mixture and its individual components

#### 3.2.1. Water flux

From Fig. 11, it can be observed that the flux of the mixture is significantly higher than that of the individual components. The average flux of hydroponics mixture is 11.7 LMH compared with calcium nitrate, which has the lowest average value of 9.2 LMH and potassium nitrate with flux rate of 10.03 LMH. The increase in both osmotic pressure and water flux in the hydroponics nutrient mixture can be attributed to the alteration in the ions species generated [27] as a result of this blend. The higher the number of species formed, the higher the osmotic pressure followed by an increase in water flux.

#### 3.2.2. Draw solute concentration in final product water

Draw solute ions were analyzed for the selected hydroponics mixture (Fig. 12), in addition to its individual components in order to compare their dilution requirements (Fig. 13). From Fig. 12, it can be concluded that solutes ions concentrations have decreased significantly in case of the hydroponics mixture compared with its individual components. This leads to lowering the dilution requirements to be ranging from 3 to 5 times compared with a factor of more than 20 times in case of individual components (Fig. 13). This significant change in solutes behavior in case of being utilized as a mixture can be attributed to change in species formation and in ions diffusivity, especially that this nutrients mixture had common nitrate ions that can alter the behavior of draw solute due to the common ion effect.

# 3.2.3. Forward rejection of feed Na<sup>+</sup> and Cl<sup>-</sup> ions

Rejection results are summarized in Fig. 14, where calcium nitrate showed higher rejection percentage compared with potassium nitrate that had rejection of 91% for Na<sup>+</sup> and 88% for Cl<sup>-</sup>. The hydroponics mixture exhibited the highest feed ions rejection compared with its individual components with 95% for Na<sup>+</sup> and 93% for Cl<sup>-</sup>. This is attributed to the increase in the driving force resulted from the increase in osmotic pressure difference. This is matching with the fact that the hydroponics mixture has the highest osmotic potential followed by that of calcium nitrate then the component with the least osmotic potential which is the potassium nitrate. In addition, this phenomenon can be related to the membrane surface charge [29]. pH of the three DSs are acidic, with formation of H<sup>+</sup>



Fig. 12. Draw solutes concentration in the final water product.



Fig. 13. Required dilution factor.



Fig. 14. Forward rejection of FS Na<sup>+</sup> and Cl<sup>-</sup> ions for hydroponics mix vs. its components.

ions that are attracted to the negative charges on the membrane surface with subsequent alteration of these negative to positive charges that repel the Na<sup>+</sup> ions resulting in enhancement of its rejection, while attract the negative chloride ions Cl<sup>-</sup> and reduce their rejection.

#### 4. Conclusion and recommendations

The first scenario compared the performance of individual fertilizers representing the core macro-pollutants for crops nutrition N, P, K represented in commonly used fertilizers in Egypt, which are urea, di-ammonium phosphate and potassium nitrate, respectively. DAP showed the highest water flux rate compared with the other two single fertilizers reaching 13.8 LMH, feed ions rejection reaching 98% and acceptable concentrations of draw solute ions in the final product. On the other hand, urea exhibited poor performance as a DS with a water flux as low as 2.2 LMH, low feed ions rejection equivalent to 78%, in addition to high DS solute in the final water product of 4.3 g/L, which agrees with Phuntsho et al. [30], and Nasr and Sewilam [31] findings. Hence, urea solely is not a recommended draw solute for this application. In the second scenario, macronutrients of hydroponics standard recipe were tested compared with its individual macro components at the same concentrations. Water flux of hydroponics mixture reached 14.35 LMH compared with calcium nitrate, which had the lowest value of 9.1 LMH and potassium nitrate with flux equivalent to 12.15 LMH. Final concentrations of draw solute ions in the final product were also tested. Nutrients mixture results exhibited a significant improvement in terms of the needed dilution to meet the crops fertigation requirement compared with the individual recipe components. For example, for nitrogen concentrations, dilution factor needed dropped from 22.6 to 5.3 when the hydroponics mixture was utilized.

Based on the conducted research and its conclusion, for single fertilizers, it is crucial to select a draw solute with high molecular weight and larger number of species formation due to their vital impact on the performance during the

desalination process. On the other hand, fertilizer blending is recommended over the individual nutrients. Not only due to the ability of the mixture to meet plant nutritional requirements without the need for further addition of more fertilizers but also due to the higher osmotic potential of the mixture and its ability to mitigate a major forward osmosis limitation, which is the need of product water dilution. However, it is advised to conduct a preliminary simulation to test the osmotic potential for each hydroponic recipe before testing to predict its adequacy as a draw solution and study its ingredients before blending to prevent salts precipitation due to the common ion effect. Regarding testing other hydroponics mixtures, creating nutrients recipes tailored to fit the Egyptian crops nutritional requirements can be very useful as an adaptation measure for climate change to boost crops productivity without compromising energy sustainability nor freshwater consumption in addition to overcome the challenge of the increasing land aridness.

In summary, adapting forward osmosis desalination to produce diluted hydroponics nutrients mixtures for food production is a promising plan to tackle water, energy and food challenges in Egypt. However, further research is needed to develop the FDFO technique in order to overcome its limitation regarding the after-treatment dilution needs.

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