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Variations of graphene nanotube membrane support layer in outlet flux of PAFO system

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ABSTRACT

The PAFO system is a solution in the desalination of seawater using a hydraulic pressure of 5 bar, which competes with the FO system (direct osmosis). The project includes four stages of pilot construction, entrainment detection, graphene nanotube membrane synthesis and, finally, efficiency determination and outflow modeling of the PAFO system. High Flux is the most important parameter of the system test for practical application. According to the results, the highest flow of current (120 l / m2.hr) was calculated at the osmotic pressure of 55, indicating a 50% increase in the flow of water with KOH fertilizer as entrainment solution and membrane of low thickness backing layer. Outflow values were calculated using theoretical modeling (MATLAB software). The results show the consistency of the outflow with the flow of the proposed chi model.

KEY WORDS: Forward Osmosis; Flow; Drag solution; Support layer.

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Variaciones de la capa de soporte de membrana de nanotubos de grafeno en el flujo de salida del sistema PAFO

RESUMEN

El sistema PAFO es la solución en la desalinización de agua de mar utilizando una presión hidráulica de 5 bar, que compite con el sistema FO (ósmosis directa). El proyecto incluye cuatro etapas de construcción piloto, detección de solución de arrastre, síntesis de membrana de nanotubos de grafeno y, finalmente, determinación de eficiencia y modelado de flujo de salida del sistema PAFO. High Flux es el parámetro más importante de la prueba del sistema para una aplicación práctica. Según los resultados, se calculó el flujo más alto de corriente (120 l / m2.hr) en la presión osmótica de 55, lo que indica un aumento del 50% en el flujo de agua con fertilizante KOH como solución de arrastre y membrana de capa de soporte de bajo espesor. Los valores de flujo de salida se calcularon mediante el modelado teórico (software MATLAB). Los resultados muestran la consistencia del flujo de salida con el flujo del modelo de chi propuesto.

PALABRAS CLAVE: Osmosis adelante; flujo; solución de arrastre; capa de soporte.

Introduction

Osmosis is the transfer process of water through a semi-permeable membrane. In this process, water molecules are allowed and the solute molecules are returned. The osmotic force in the process is obtained from the drag solution and the final driving force is obtained from the difference between the osmotic pressure $\Delta\pi$and the hydraulic pressure Δp. The fundamental challenges of the forward osmosis process is an access to drag solution with high osmotic pressure and proper membrane.

Maryam Amini et al. 2012, used the forward osmosis system using NaCl solution as feed and drag solution. The results show an increase in water permeability and salt return. The water flux of $95(^{L}/_{m^2})$ was estimated (Maryam Amini et al. 2012).

Andrea Achilli et al. (2010), the process of forward osmosis analysis in this study involves the screening of 14 draw solutions and the study of water flow and salt diffusion. The best draw solutions were $CaCl_2$, $Ca(No_3)$, NaCl (Andrea Achilli et al. 2010).

Shrubphuntsho et al. (2011), in this research, the Fo system and agricultural fertilizers were used to desalinate seawater and agricultural uses. 9 fertilizers were selected as a drag solution from the relevant list, and their efficiency was evaluated by determining the pure water flux and return drag solution. According to the results, fertilizers with the highest solubility in water produce high osmotic pressure than seawater. The most appropriate drag solutions were introduced as $KCl–NaNo_3$ and KNO_3. Each kilogram of fertilizer separates about 11-29 liters of water from the sea (Shrubphuntsho et al. 2011).

Changquan Qiu et al. (2011), the forward osmotic membrane was successfully done using layer-by-layer (lbl) deposition, the results of bonded and non-bonded membranes were investigated using shape, water permeation structure, salt return, and solute flux. The water flux was estimated to be $100(^{L}/_{m^2.\,hr})$, which indicates high capability of lbl membranes for high flux (Changquan Qiu et al. 2011, 81).

Yan Kim et al. 2012, according to research on AFO process efficiency, showed that water flux is increased with the use of hydraulic pressure and solute return is reduced. Driving force control in AFO is easier than Fo, which leads to flexibility in system design and operation (Gaetanjlandin et al., 2013).

Sang Min et al. (2013), numerically predicted Foefficiency by the equilibrium copper equation for the feed and drag solution ratio associated with the water flux model. According to the results, a high concentration drag solution improves water flux. Water flux in opposite or reverse flow conditionis 10% higher than direct flow. A series of feed solution flow and parallel drag solution are effective in increasing water flux (Sang Min et al. 2013).

Gaetenjlandin et al. (2013), investigated the effect of hydraulic pressure on Fo. A 6 bar pressure on feed solution had doubled the water permeability. Moreover, salt diffusion was significantly reduced. This study investigates the limitations of the flow method to determine water permeability and membrane properties (Gaetenjlandin et al.2013).

Coworker et al. 2015, designed PVDF nanofibers for water desalination. Membranes prepared for drinking water.

Zhuqing et al. (2018), designed super-hydrophobic PVDF, containing nanofiber and fluoropropane and CNT (nanotubes), which were designed by electro method. The hydrophobic and mechanical properties were investigated by the concentration of CNTs. In another study, produced a thin film nanocomposite (TFN) containingsilica nanoparticles pores through interfacial polymerization. Huetal et al. made Go layer-by-layer (LbL) nano sheet son poly sulfane coated with polyamine and nano GO membrane benzene tricarbonyl trichloride binder and the outlet flux is estimated (Tiging et al. 2016).

David Chaen et al. 2015, investigated the simulation and modeling of nano graphene and outlet flux (Chaen et al. 2015).

The present study investigates and evaluates the efficiency of the PAFO systemin seawater salt desalination in various operating situations. In many studies, by building new membranes in forward osmosis systems, the water flux is raised successfully, but none of these plans were commercial. Consequently, changes in inlet pressure on feed solution, inlet water flow, concentration, flow direction, and membrane contact surfacelead to changes in osmotic pressure, concentration polarization, and osmotic pressure between the two solutions. Thus, providing information and collecting data for better design and operation in the future and making strong incentives for development of FO processes in a commercial scale are the main goals of this project, so the results are reported in real conditions using seawater (Persian Gulf) with very high EC.

1. Research method

Experimental studies were conducted in the HSE laboratory of the National Iranian Oil Company of the Pars Special Economic Energy Zoneduring 2016-2018. Determining FO efficiency is the result of the combination of tests. Drag and membrane were selected to determine pilot efficacy with 11 fertilizer solutions at a concentration of 50 mg/L as drag solution and sea water with EC=48000as feed solution. Graphene nanotube membranes were made by reducing the thickness of the support layer. Finally, the effects of nanomembranes made along with auxiliary pressure on the efficiency of the system were investigated.

1.1. Devices and equipment used

Tensiometer	model K20
Viscometer	ulv
EC-meter	conductivity module
Experimental laboratory precision of 0.1	CS Series
Maximum flow diaphragm pump of 100 and maximum pressure of 7 bar l/min	

Table 2-1: List of devices used

Material	Chemical formula
Graphene nanotube suspension	$CNT\text{-}NH_2$
Cyclohexane extra pure >99%	C_6H_{12}
Potash	KoH
Calcium nitrate	$Ca(No_3)_2$
Complete fertilizer	$N_{20} \times K_{20} \times P_{20}$
Complete fertilizer	$K_{40} \times P_{53}$
Urea phosphate	CH_4N_2O
Calcium chelate	OligoCalcium EDTA/Ca
High +Urea phosphate potash	CH_4N_2O + KoH
Calcium + High potash nitrate	KoH + $Ca(No_3)_2$
Calcium + High potash chelate	KoH + Oligo Calcium
Complete fertilizer Potash + 20x20x20	KoH + $N_{20}K_{20}P_{20}$
Complete fertilizer Potash + 34x52	KoH + $K_{40}P_{53}$

Table 2-2: Chemicals consumed

1.2. Pilot construction

In order to achieve the correct results of the laboratory pilot, PAFO was designed and constructed. Figure 1.2 shows a diagram of the PAFO system in the laboratory.

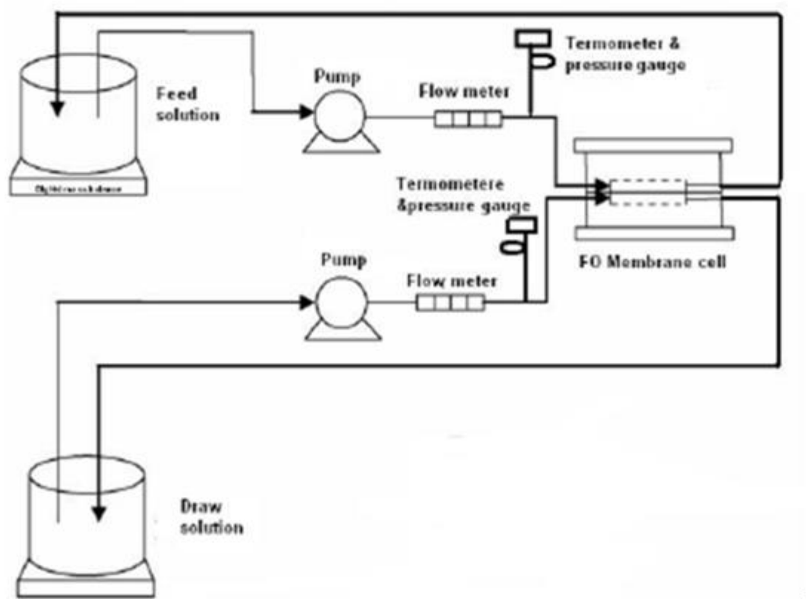


Figure 1.2: Diagram of forward osmosis system

- **Pilot specifications:**
- Plexiglas cell (3.75 m^2)
- Graphene nanotube membranes (15*25cm)
- Diaphragm pump for draw and feed solution flow (maximum flow of 100 l/min and maximum pressure of 7 bar)
- 200 liter tanks

Each piece of cell has an inlet tube and an outlet tube entering the flow through the piece to the diffusion channels, which are opposite to each other. Generally, the active layer that is brighter is towards the feed solution and back of membrane is towards the drag solution. Plexiglas membrane cell with the transverse flow consist of a series of symmetrical channels on each side. The dimensions of cell, length, width and depth, are 25cm, 15cm and 0.3cm, respectively, in the form of a hollow rectangle. Graphene nanotube membranes is made of thin support layer and has an effective surface of 139cm^2 mounted in a 139cm^{3}cell. Two diaphragm pumps are used for constant speed flow. The water velocity and drag solution are considered the same. The solution is rotating. The solution is passed from the feed solution to the drag solution until the osmotic pressure becomes equal on both sides.

1.3. Selecting drag solution

A list of fertilizers (synthetic or mineral) was investigated for selection. Selection criteria are solvability, generality of use, osmotic pressure, and diffusion coefficient. Chemical details are presented in Table 1-3. According to the table, most fertilizer shave osmotic pressure higher than seawater. In the initial screen,9 fertilizers were selected.

1.4. Inlet feed

Inlet feed in all phases was water of Persian Gulf with EC=48000.

1.5. Membrane synthesis

Membrane synthesis method with graphene nanotubes

1.6. Measuring method of parameters

1.6.1. Osmotic pressure

Due to the absence of osmotic pressure analyzer in Iranian laboratories, theoretical prediction method was used. Osmotic pressure is a function of dissolved solids concentration, the value of which is PSI=1.1−0.6 per TDS=100ppm.

1.6.2. Diffusion coefficient

To measure the diffusion coefficient, first, the surface tension must be calculated. Surface tension was measured at temperature of 20 °C using plate or ring method according to National Iranian Standard 2976. The diffusion coefficient was determined by formulaic calculations.

S= diffusion coefficient

Yc= Surface tension of cyclohexane (mN/m)

Yf=Surface tension of fertilizer solution (mN/m)

Y= Interfacial tension of foam solution and cyclohexane (mN/m)

(1-2) S=Yc-Yf-Y

(National Iranian Standard 3778)

1.6.3. Viscosity

The viscosity of the solutions in torque was measured between 10 and 100 by Brookfield apparatus.

1.6.4. Water flux

Water flux was consistently recorded by the laboratory scale from the difference of the initial and final weights as the amount of water flux over time.

1.6.5. Water permeability coefficient (A)

A is the membrane water permeability coefficient. Increased permeability increases the flux water during operation of Fo and PAFo systems.

$$A = J_w / (\Delta\pi + \Delta P) \quad (2.2)$$

J_w=Water flux ($L/m^2.hr$)

$\Delta\pi$= Osmotic pressure difference

ΔP= Hydraulic pressure difference

A solution with zero osmotic pressure (distilled water) was used for in vitro measurement. The system was designed in a way to fix the hydraulic pressure and current. Data were collected every 5 minutes and 3 averages were determined.

1.6.6. Permeability coefficient of solute (B)

B is the permeability coefficient of the solute (drag material). Diffusion indicates the inverted solute. In the PAFo process, the value of parameter B must be limited.

(2.3) $J_s = B\Delta C$

ΔC= Concentration differences over the membrane

J_s= Drag solution or drag solute flux $^{gr}/_{m^2.hr}$

B= Permeability of the solute

(2.4) $B = \exp\frac{J_w}{K} \times J_w\frac{1-R}{R}$

If overlooking the concentration polarization in above flow, the feed solution B is equal to zero

(2.5) $B = J_w\frac{1-R}{R}$

C_P and C_F= Solute concentration in the feed and permeation solution

1.6.7. Water flux modeling

1.6.7.1. Osmosis

Osmosis is the spontaneous transfer of molecules from a dilute solution to a concentrated solution. The semi-permeable membrane allows the passage of solvent molecules, but it doesn't allow the passage of solute. Osmotic pressure is a function of the number of solute molecules(n), solvent volume (V), temperature (T), and ideal gas constant (R).

$\pi_{=\frac{n}{v}.iRT}$(2.6)

(Sang Min et al. 2013, 27).

1.6.7.2. Water flux equations

Equation for FO systems with zero hydraulic pressure adjustment is zero. Lee et al. developed the water flux equation based on resistance method against fouling and internal and external concentration polarization for the FO system.

In the FO system, the feed water is in contact with active membrane layer and drag solution is in contact with the support layer. The equation is as follows:

(2.7) $J_w = A(\pi + B/A)e^{-(J_w/k_m)} - (\pi + B/A).e^{(J_w/k_{ECP})}$

(Sang Min et al. 2013, 27)

A, B= Water and salt permeability coefficient

K_m, K_{ECP}= External concentration polarization (ECP) and internal concentration polarization (ICP)

K_m= Mass transfer coefficient

K_m= D/S=D.E/&.T (2.8)

(Sang Min et al. 2013, 27)

D= Drag material diffusion coefficient

S= Structure parameter

E= Membrane porosity

&=Layer thickness

T= Membrane curvature

1.6.7.4. General equation for FO water flux system

General equation for water flux in forward osmosis is obtained by Lee et al. and the modified equation by Mica Cheaon.

(2.9) $J_w = A\left[(\pi_D \exp(-J_w K_a) - \pi_F \exp({}^{J_w}/_{k_b})\right]$ Type equation here.

(Sang Min et al. 2013, 27)

J_w= Water flux

A= Pure membrane water permeability

π_D=Osmotic pressure of drag solution

π_F= Osmotic pressure of feed solution

k_a= Soluble specific resistance coefficient (solute resistance to diffusion to the pores)

k_b= Mass transfer coefficient

-$k_a$calculation (soluble specific resistance coefficient)

(2.10) $$k_a = \frac{t\tau}{D\epsilon} s = \frac{t\tau}{\varepsilon}$$

(Sang Min et al. 2013, 27)

t= Membrane layer thickness

τ= Membrane curvature

ε= Pores

D= Drag strength diffusion coefficient

s= Membrane structure parameter

As a result, with respect to substitution of a membrane structural parameter in the equation, ka is obtained:

(2.11) $$k_a = \frac{s}{D}$$

(Sang Min et al. 2013, 27)

Dis drag solution diffusion coefficient measured by Tensiometer and s is the membrane structure parameter, and in the FO system, s can be estimated for the system. Parameters is constant for each membrane in different states.

Structure parameter s calculations

(2.12) $$s = \left(\frac{D}{J_w}\right) \times Ln\left({(B + A \times \pi_D)} \big/ {(\beta + J_w + A \times \pi_F)} \right)$$

(Yan Kim et al. 2012)

D= Drag strength diffusion coefficient

π_D=Osmotic pressure of drag solution

π_F= Osmotic pressure of feed solution

A= Water permeability coefficient

β= Salt permeability coefficient

Membrane structure parameter (s)indicates the resistance of the membrane support layer in diffusion of solute. According to the research, it was found that with a decrease in parameter s, the water flux is increased.

-$\mathbf{k_b}$calculation (mass transfer coefficient)

(2.13) $$k_b = \frac{shD}{d_h}$$

(Sang Min et al. 2013, 27)

Sh= Sherwood number

D= Drag strength diffusion coefficient

d_h=Hydraulic diameter

Sherwood number, known as mass transfer Nuselet number, is a non-dimensional number in the mass transfer science that indicates the mass transfer rate from convection to mass permeability.

$$\frac{Mass\ transfer\ coefficient}{Diffusion\ transfer\ coefficient}$$

- Sherwood number calculation

(2.14) $$sh = 1.85\left[Re \times Sc \times \frac{d_h}{L}\right]^{0.33} \quad \rightarrow \quad Re \leq 2100$$

(Inger Lise et al., 2013: 5)

(2.15) $$sh = 1.85[Re^{0.75} \times Sc^{0.33}] \quad \rightarrow \quad Re \geq 2100$$

(Inger Lise et al., 2013: 5)

(2.16) $$Re = \frac{d_h V \rho}{u}$$

(Inger Lace et al., 2013: 5)

Sc= Schmidt number

Re= Reynolds number

$\frac{\rho}{u}$= Kinematic viscosity

D_h= Hydraulic diameter

(2.17) $$d_h = \frac{4\times\text{Soaked area}}{Soaked\ area}\text{Type equation here.}$$

(Inger Lace et al. 2013, 5)

-Schmidt number calculation (**Wilhelm Schmidt**)

A non-dimensional number that indicates theratio of the momentum diffusion (viscosity) to the mass diffusion (diffusion coefficient).

(2.18) $$\frac{u}{D} = \frac{Dynamic\ viscosity}{Diffisuion\ coefficient} = \frac{\left(Pa.s\ \ or\ \ \text{N}.\frac{s}{m^2}\right)}{(m^2/s)}$$

(Inger Lise et al., 2013)

1.6.7.5. Water flux model in PAFO system

Achilli et al (2010) presented a new equation for PAFO (FO and RO hybrid system)

(19-2) $$J_w = A\left(\Delta p + \left(\pi_D \exp\left(-\frac{J_w}{k_d}\right) - \pi_F \exp\left(\frac{J_w}{k_F}\right)\right)\right)$$

(Inger Lise et al., 2013)

(20-2) $$J_w = A(\pi - \pi) + \ \Delta p\text{Type equation here.}$$

(Inger Lise et al., 2013)

A= Membrane water permeability coefficient

Δp= System hydraulic pressure

π_D= Osmotic pressure of draw solution

π_F= Feed osmotic pressure

$k_F$and$k_d$areequal to k or 1/k in equation, respectively.

2. Results

2.1. Primary evaluation of flux system

After pilot startup, the outlet flux from the pilot is reduced after a 2-hour period, because the drag solution became thinner and the feed solution became thicker over time. The water transfer from the feed water to the drag solution occurs by the osmotic process reach the osmotic equilibrium (zero osmotic gradient).

Flux changes over time are in accordance to curve 3.1.

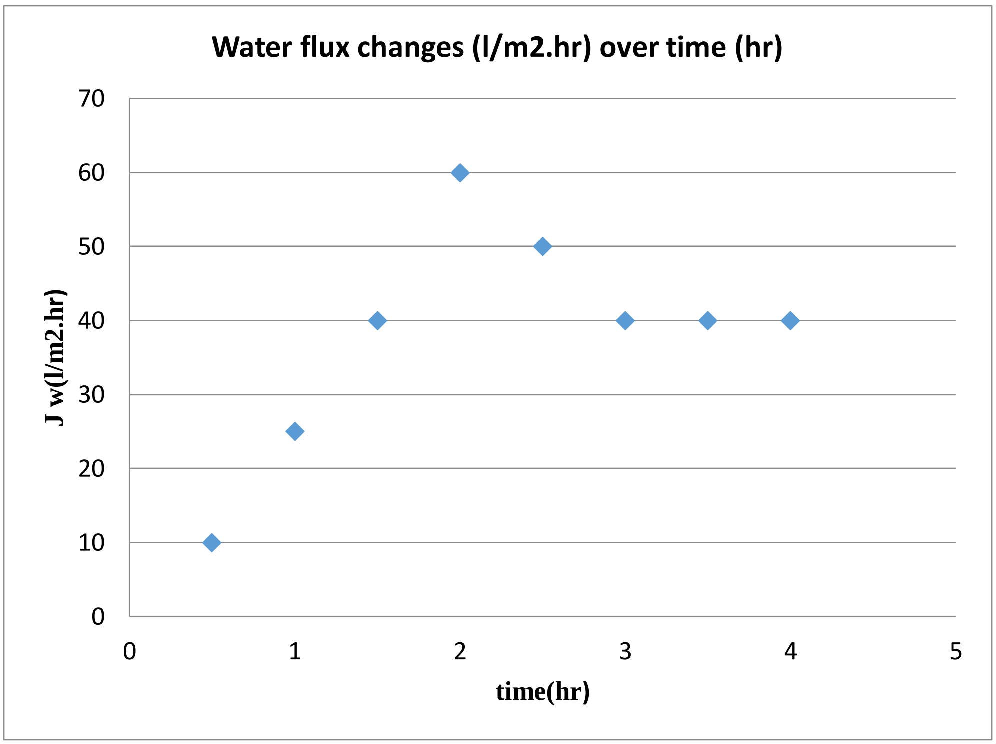


Figure 3.1: Water flux changes over time in FO system

2.2. Results of the effect of osmotic pressure on flux (J_w)

Details of chemical fertilizers used are presented in Table 3.1, and the drag soltion in this project was prepared by dissolving fertilizer compounds in distilled water at a concentration of 50 mg/L.

Table 3.1: Chemical physical properties of fertilizers

No	Fertilizer	Chemical formula	Concentration $({}^{mg}/_{l})$	EC n $({}^{S}/_{cm})$	π Osmotic pressure (bar)	Diffusion coefficient (D)
1	Potash	KoH	50 mg/l	92000	55	1.1
2	Calcium nitrate	$Ca(No_3)_2$	50 mg/l	116000	70	1/31
3	Complete fertilizer	$N_{20} \times K_{20} \times P_{20}$	50 mg/l	65000	35	1/04
4	Complete fertilizer	$K_{40} \times P_{53}$	50 mg/l	65000	39	1/04
5	Urea phosphate	CH_4N_2O	50	15000	9	1.91
6	Calcium chelate	OligoCalcium EDTA/Ca	50 mg/l	23000	14	1.06
7	Urea phosphate +High potash	CH_4N_2O + KoH	25+25 mg/l	57000	34	1.91
8	High potash + Calcium nitrate	KoH + $Ca(No_3)_2$	25+25 mg/l	114000	68	1.06
9	High potash + Calcium chelate	KoH + Oligo Calcium	25+25 mg/l	79000	47	1.04
10	Complete fertilizer 20x20x20 +Potash	KoH + $N_{20}K_{20}P_{20}$	25+25 mg/l	111000	67	1
11	Complete fertilizer 34x52 + Potash	KoH + $K_{40}P_{53}$	25+25 mg/l	90000	54	1.38

Ca(NO3)2 has the highest osmotic pressure at a concentration of 50 mg/L equal to 70 bar and the urea phosphate at osmotic pressure of 9 bar has the minimum osmotic pressure. According to the table, most selected fertilizers have higher osmotic pressure than seawater. According to the results presented in the table, the calcium nitrate has the highest diffusion coefficient of 1.31 and the complete fertilizers have the lowest diffusion coefficient of 1.04. This indicates a correlation between the diffusion coefficient and high osmotic pressure. Draw solutions with high diffusion coefficient and high osmotic pressure have higher water flux.

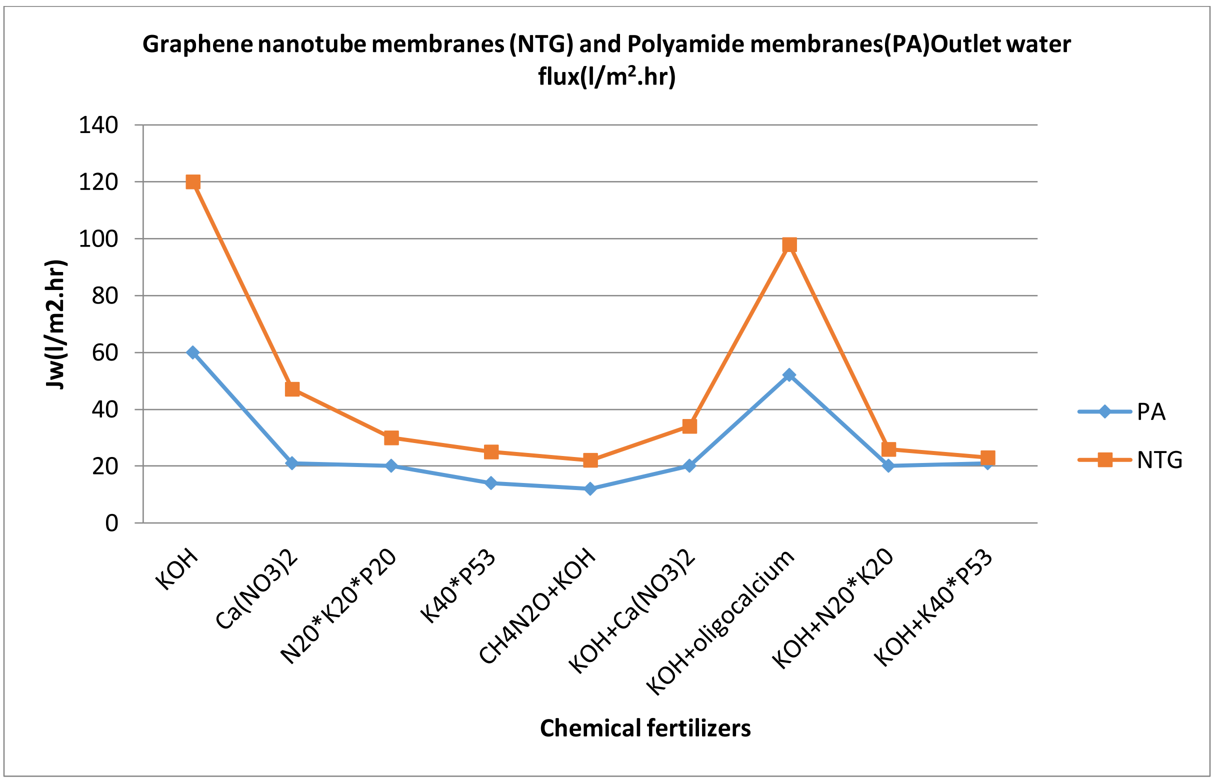


Figure 3.2: Outlet water flux values J_w(l/m^2.hr) with drag solutions of PAFO system

Outlet water flux for draw solutions are presented in Figure 3.2. The lowest and highest fluxes of 120 (l/m^2.hr) and 22(l/m^2.hr) are at osmotic pressure of 55 bar and 34 bar, respectively. In this project, the same concentration is considered. It can be said that pure water flux is a function of the concentration and osmotic pressure of the draw solution. There is a linear correlation coefficient between water flux and predicted osmotic pressure. Some fertilizers have low correlation coefficient. Among the selected fertilizers, the fertilizer with higher molecular weight has the greatest impact on internal polarization and flux reduction. The abnormal relationship of osmotic pressure of drag solution and water flux in the forward osmosis process indicates internal polarization in the water flux flow. The internal polarization reduces flux and pressure across membranes.

In Table 3.2. Outlet flux of the system with graphene nanotube membranes and reverse osmosis membranes are presented.

Table 3.2: Outlet flux of the system with NTG and PA membranes

No	Fertilizer	RO membrane flux $J_w \left(L/_{m^2.hr}\right)$	Graphene nanotube membrane flux $J_w \left(L/_{m^2.hr}\right)$
1	Potash	60	120
2	Calcium nitrate	21	47
3	Complete fertilizer $N_{20} \times K_{20} \times P_{20}$	20	30
4	Urea phosphate + high potash	12	22
5	High potash + calcium nitrate	20	34
6	Potash + calcium chelate	52	98
7	Complete fertilizer + potash $N_{20} \times K_{20} \times P_{20}$	20	26
8	Complete fertilizer + potash $N_{40} \times P_{53}$	21	23
9	Complete fertilizer $N_{40} \times P_{53}$	14	25

According to the table, the highest outlet flux with PA and graphene nanotube membranes is 60 (l/m2.hr)and 120(l/m^2.hr)respectively.

PAFO against FO systems is a new solution with an aim of putting pressure on the feed solution to increase water permeability through membranes. Once a 5 bar pressure is applied on a feed solution, the permeability and flux is multiplied compared to the FO system. The results of research from 2010 to 2017 on the outlet flux from osmotic systems with different membranes are presented in Table 3.3, indicating the high importance in choice of membrane in these systems.

Highest water flux with nanographene membranes is estimated up to 50-300 (l/m^2.hr).

Table 3.3: Research results of FO system

System	Type of membranes	Drag solution	Flux	Reference
FO	LbL(PAH/PSS)	MgCL2	100	Changquan Qiuetal (2011)
MBR		MgSO4	6.3	Kiwa Water Research (2009)
Fo	CTA	Fertilizer	5-10	Andereaachili-Tzahi (2010)
AFO	CTA	Sea water	8	Gaetenjlandin-Arne (2013)
FO	CTA	Sea water	2-6	Shrubphuntsho-Hokyonshon (2011)
FO	TFN	Sea water	95	Maryamamini-Mohsenjahanshahi (2012)
RO	GO nano	-	80-276	Glenn L-Martin Hall (2013)
FO	-	Graphen hydrogel	2	Yaozengling Giu-Kunwang (2012)
RO	GO nano	-	50-300	Shahin Homaegohar (2017)

2.3. Calculation results of water permeability (A)

Water permeability values are presented in Table 3.4. The maximum water permeability is 8.6 (l/m^2.hr) and minimum water permeability is 0.9 (l/m^2.hr). According to the results, the maximum graphene nanotube membrane permeability coefficient is approximately increased by 50% compared to the maximum RO membrane permeability coefficient.

Table 3.4: PA membrane and thin graphene nanotube membrane permeability A values

No	Fertilizer	$\Pi_F - \Pi_D$ (bar)	P_H (bar)	Membrane permeability coefficient Ro(A)	Graphene nanotube membrane permeability coefficient(A)
1	Potash	103	5	4.3	8.6
2	Calcium nitrate	25	5	0.7	1.56
3	Complete fertilizer $N_{20} \times K_{20} \times P_{20}$	10	5	1.33	2
4	Urea phosphate + high potash	11	5	0.75	1.43
5	High potash + calcium nitrate	20	5	0.71	1.36
6	Potash + calcium chelate	2	5	7.41	13
7	Complete fertilizer + potash $N_{20} \times K_{20} \times P_{20}$	22	5	1.42	2.30
8	Potash + complete fertilizer $N_{40} \times P_{53}$	9	5	0.77	0.9
9	Complete fertilizer $N_{40} \times P_{53}$	106	5	1.27	2.9

Water permeability is improved in new membrane. Increased hydrophilicity of membranes and the existence of nanotubes as water passage channel are the main causes of this increase. The results of water permeability variations with osmotic pressure and hydraulic pressure are similar to the changes in Gaetenjlandin-Arne et al. (2013) in the evaluation project of the effects of hydraulic pressure on forward osmosis system.

2.4. Results of B/A values

Permeability values of the solute are presented in Table 3-5. The maximum and minimum permeability values (B) equal to 120 ($l/m^2.hr$) are calculated with potash fertilizer and potash fertilizer.

According to the results, the minimum graphene nanotube membrane permeability coefficient of solute (B)is approximately decreased by 50% compared to the minimum RO membrane permeability coefficient.

This indicates proper efficiency of graphene nanofiber membranes with low-thickness support layer.

Table 3.5: Comparing permeability values of solute (B) and B/A ratio and return percentage (PA membranes and thin graphene nanotube membranes)

Fertilizer	R% (PA)	R% (NTG)	B (PA)	B (NTG)	$^B/_A$ (PA)	$^B/_A$ (NTG)
KoH	30	50	121	120	28	13
$Ca(No_3)_2$	47	65	23	24	33	16
$N_{20} \times K_{20} \times P_{20}$	18	30	91	69	35	34
$K_{40} \times P_{53}$	20	30	56	58	44	21
CH_3N_2O + KoH	17	21	37	82	52	57
KoH + $Ca(No_3)_2$	50	63	20	20	28	14

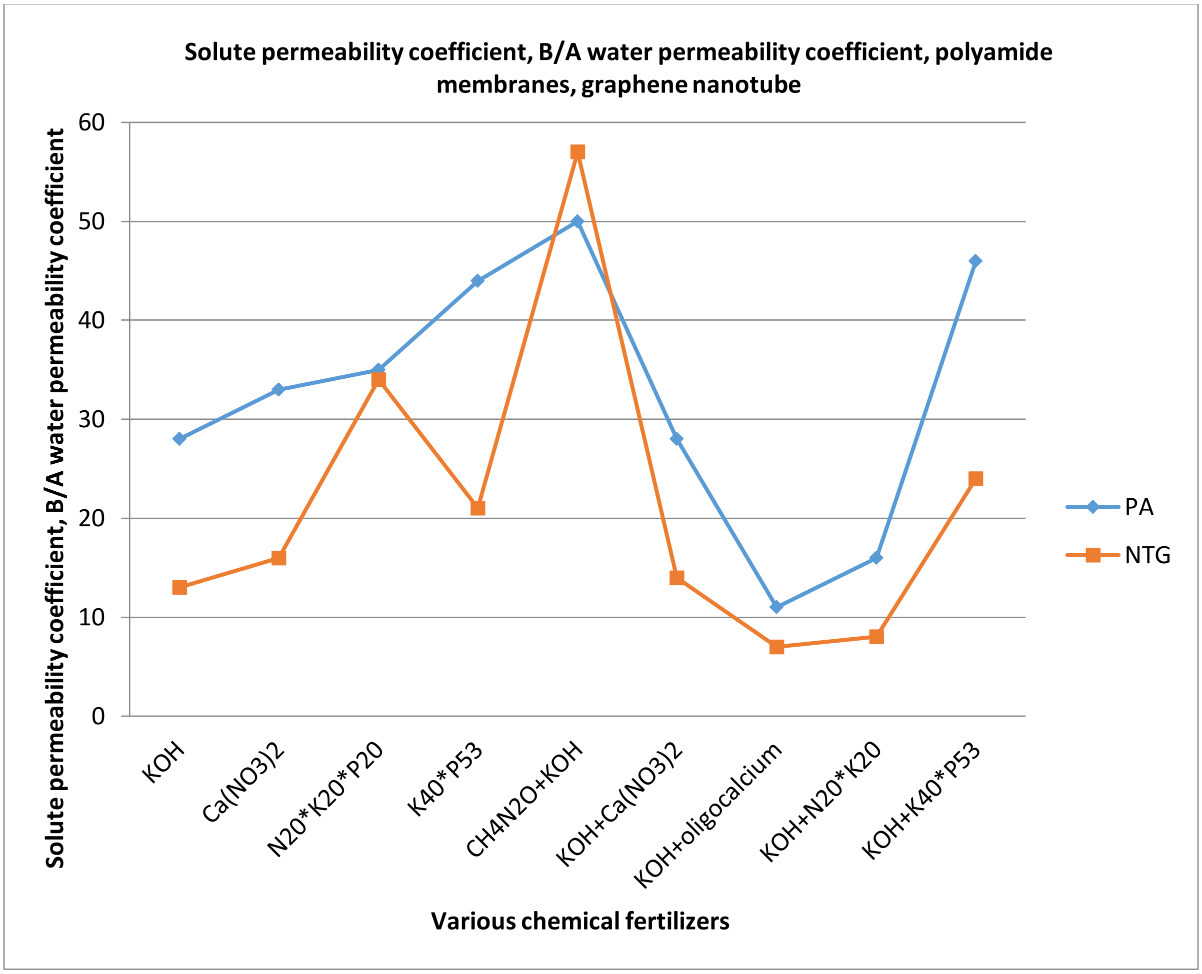
KoH + Oligo Calcium	38	50	84	98	11	7
KoH + $N_{20}K_{20}P_{20}$	46	58	23	19	16	8
KoH + $K_{40}P_{53}$	37	51	35	22	46	24

According to research, water permeability and flux of graphene nanotubes depends on the chemistry and geometric shape of the nanotubes, hydrated radius, and the properties of the transition ions. The critical diameter for salt return is between 0.6 and 0.8 nm. It is also found in the hydrogenated graphene membranes, salt return is higher than hydroxyl graphene membranes.

B/A represents the return flux of solute. Evaluation of B/A efficiency of drag solutions is essential, because it reduces the quality of production of concentrated solution. B/A of drag solution variable depends on the type of drag solution and the capacity of ions in the solution. Among the non-composted fertilizers, KOH has the lowest B/A. This fertilizer contains univalent elements, while in case of bivalent elements, B/A of higher values are created. Thus, it can be concluded that fertilizers with univalent ions are a priority for the PAFO system. It should be noted that the ratio of B⁄A in graphene nanotube membranes is lower than other membranes, including cellulose acetate.

In contrast to expectations, increased hydraulic pressure followed by decreased B/A. This ratio is reduced with graphene nanofibers membranes. A decrease is caused by different factors and it can be estimated that with increased hydraulic pressure and increased permeability, the concentration polarization in the membranes is increased, but after a short period of time, a high osmotic pressure on the other side of the membrane reduces the polarization. These two phenomena on both sides of the membrane prevent an increase in B/A.

In Figure 3.3, a comparison of B/A ratio with PA membrane and graphene nanotube are presented.



Curve 3.3: Comparing B/A ratio of PA membrane and thin graphene nanotube membrane

The results of changes in water permeability with osmotic pressure and hydraulic pressure are similar to the changes in Gaetenjlandin et al. (2013) in the evaluation project of the effects of hydraulic pressure on forward osmosis system. We need to know that PA membranes have no proper efficiency to be used in forward osmosis systems. A few studies and examinations have been done in this field. In PA membranes, the internal polarization of solute is high and internal polarization reduces the osmotic pressure difference and causes a severe limitation in the water flux. Although forward osmosis commercial membranes are developed by hydration technology and water permeability (A) is almost equal to 1 ($l/m^2.hr$), but the water flux is still low and equal to 9 ($l/m^2.hr$).

In recent studies and developments, the thin film composite (TFC) membranes are made. The permeability of these membranes is over 1($l/m^2.hr$), which approximately had doubled water flux, but due to the high costs, these membranes are limited, while graphene membranes are not expensive and are affordable.

According to Andrea Achilli et al. (2010), in the field of forward osmosis (FO) using membranes cellulose triacetate, water flux is reported to be equal to 5-10 (l/m2.hr), 8 (l/m2.hr), 6 (l/m2.hr), which also indicates low water flux with cellulose membranes in comparison with the present project (Achilli, 2010).

Changquan et al. (2011), in this study, the forward osmotic membrane synthesis with layer-by-layer membrane and electrolytes was conducted. Water flux is 100 (l/m2.hr) and permeability is 6 (l/m2.hr), indicating the capability of lbl membranes for high flux.

In comparison with results of this project, where seawater and fertilizer were used as feed solution and drag solution, the water flux is 120(l/m^2.hr) and maximum permeability is 8.6 l/m2.hr, which indicates a few percent increase in the water flux with the graphene nanotube membranes in this research.

According to the results, water flux, water permeability, and salt return are improved in the low-thickness support layer nanographene membranes. Such membranes have a great potential for being used in the forward osmosis process, which is due to the increased and improved structural properties. The internal nanotubes and inner pores of nanotube are the solvent crossing paths, which cross the water without pressure.

According to the research conducted at the Babol Noshirvani University, entitled "Nanocomposite Membrane Preparation for Forward Osmosis by Surface Polymerization 2012", salt water was used as drag and feed solution. The produced water flux was estimated to be 95 (l/m^2.hr). In this research the drag and feed solutions do not show the real conditions, because brine osmotic pressure is very different from the seawater osmotic pressure, while in the present project, the seawater with EC of 48000and chemical fertilizer solution have been used as a solution, indicating the real conditions in water treatment. Furthermore, the thickness of membrane support layer has been modified to change and improve the membrane properties, indicating improved water flux of 120(l/m^2.hr) in comparison with project of the Babol Noshirvani University.

2.5. Modeling the outlet flux of the PAFO system

Theoretical modeling of PAFO was performed, and the results of the laboratory measurements were compared with the predicted model. The outlet results are presented in Figure 3.4. The theoretical flux was calculated by Chi equation for PAFO system using MATLAB software.

Table 3.6: Theoretical flux values of the PAFO system

Pilot flux (l/m2.hr)	Modeling predicted flux (l/m2.hr)
120	103
47	35
25	20
30	23
23	20
34	25
98	81
33	24
26	19

According to the diagram below, in all cases, PAFO efficiency is higher than the results of the predicted model.

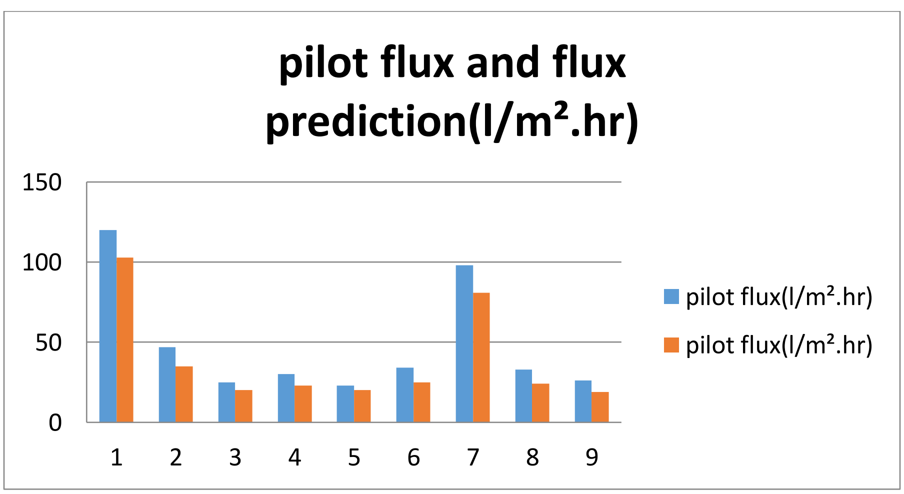


Figure 3.4. Comparing testing and modeling pilot flux

According to the results presented in Table 3-6, the measurements are partly consisted with predictions on developed water flux modeling the process.

The important cases in modeling osmotic systems are membrane orientation and membrane deformation and varied membrane structure parameter. The flux increase rate in the PAFO process is clearly different based on membranes in the research. PAFO modeling with TFC membranes was not confirmed in comparison with laboratory observations due to the membrane malfunction. Thus, it is suggested to define and analyze the membrane structure for proper modeling of these systems.

Conclusion

This study is a main framework for assessment of PAFO system and effective factors on the water flux of this this system. The system efficiency was examined by fertilizer as a drag solution and graphene nanotube membrane with thickness ssupport layer. High flux is the most important parameter to cofirm FO technology for practical application. According to this study, KOH fertilizer of 55 barosmotic pressure and diffusion coefficient of 1.31 has the highest water flux of 120 ($^{L}/_{m^2.\,hr}$)According to the results, the maximum graphene nanotube membrane permeability coefficient is approximately increased by 50% compared to the maximum PA membrane permeability coefficient. According to the results, the minimum graphene nanotube membrane permeability coefficient of solute (B)is approximately decreased by 50% compared to the minimum PA membrane permeability coefficient, which indicates proper efficiency of graphene nanofiber membranes. The PAFO system overcomes the FO system and makes up the limitations of this system, such low flux. The increased hydraulic pressure and decreased thickness of support layer in the graphene nanotube membranes synthesis significantly affects the outlet flux of the PAFO system. In fact, the PAFO system is the application of the FO+RO hybrid system, which is specially designed for high recovery.

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