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Using macromolecules as osmotically active compounds in osmosis followed by filtration (OF) system

S. Sarp[a], S. Lee[a], K. Park[b], M. Park[b], J.H. Kim[a], J. Cho[a,*]

[a]*Gwangju Institute of Science and Technology, School of Environmental Science and Engineering, Gwangju, Korea*
Tel. +82 62 715 2443; Fax: +82 62 715 2434; email: jwcho@gist.ac.kr
[b]*Daewoo Institute of Construction Technology, Suwon, Gyonggi-do, Korea*

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ABSTRACT

Finding a suitable osmostically active solute is the most important problem in forward osmosis (FO). Even though there are a number of osmotically active compounds that exist, the major problem occurs during the separation of product water from the solute. Osmotically active macromolecules (polyethylene glycol [PEG] and humic acid [HA]) were investigated in this research as possible draw solutes for FO. Cellulose triacetate FO membranes (Hydration Technology Innovations, LLC) and several ultrafiltration and nanofiltration membranes were used in osmosis and filtration steps of the system, respectively. Molecular weights (MW) of PEG were selected as 2 k, 10 k, and 20 kDa for 400 and 600 g/L concentrations. HA solutions were prepared in concentrations ranging from 200 to 800 g/L. Increased MW resulted in higher water permeation when PEGs were used. The relationship between the reflection coefficient and the viscosity was investigated for PEG/water separation by membrane filtration. The combined effect of the osmotic pressure and the viscosity of the PEG solutions was found to be greater than the effect of the reflection coefficient on the permeability.

Keywords: Forward osmosis; Polyethylene glycol; Humic acid; Reflection coefficient; Viscosity; Osmotic pressure; Permeability

1. Introduction

Membrane-based seawater desalination has been one of the most important freshwater production technologies, as it is a relatively low-energy process. However, increasing energy demands and the adverse effect of increasing CO_2 emissions are pushing scientists and engineers to establish a more energy-independent seawater desalination process. Forward osmosis (FO) has become an important study subject for the researchers in the last 5–10 years, as it theoretically offers a less energy-intensive process than reverse osmosis (RO), for seawater desalination. The working principle of FO is that water is transferred from a low osmotically active solution to a high osmotically active solution with no energy input. However, product water has to be separated from osmotically active solute (draw solution) in order to get usable/potable water.

Several research groups proposed different osmotically active solutes to validate the FO system as an energy-efficient process. Some of the important studies about FO systems are given in Table 1, which also

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*Corresponding author.

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Table 1
Draw solutions used for previous proposed FO systems and their drawbacks

Draw solution	Chemical formula	Molecular weight (g/mol)	Drawback	Ref.
Sulfur dioxide (volatile solutes)	SO_2	64.07	Heating for separation	[2]
Alcohols, sulfur dioxide	$–SO_2$	−64.07	Heating for separation	[6]
Aluminum sulfate	Al_2SO_4	342.15	Precipitation treatment	[4]
Potassium nitrate sulfur dioxide	KNO_3, SO_2	101.10, 64.07	–	[13]
Ammonium bicarbonate	NH_4HCO_3	79.06	Heating for separation Re-constitution	[12]
Ethanol	C_2H_6O	46.07	Diffusion of ethanol to feed side Loss of osmotic pressure	[11]
Hydrophilic magnetic nanoparticles	PEG-$(COOH)_2$ MNPs	–	Magnetic particle aggregation	[10]
Magnesium chloride	$MgCl_2$	95.21	High pressure requirement	[1]
Fertilizer	KCl, $NaNO_3$, KNO_3, etc.	74.55, 85.00, 101.10	Applicable only for fertigation	[17]

gives some brief information about the drawbacks of proposed systems. One of the most promising systems is the CO_2–NH_3 system, which can draw a high amount of water (up to 20 L/m^2/h (LMH), [21] from the feed side and can be separated with low heat requirements. However without waste heat available, this system is still more energy intensive than traditional RO systems.

In order to establish an economically feasible FO system, two separate processes should be considered: the first being the FO process and draw solution separation, and the second being the recovery process. An economically feasible FO process can be established by using membranes with high water permeability and draw solutions with high osmotic pressure.

However, finding a draw solution for an economically feasible separation and recovery system is not an easy task. Among several separation methods, membrane-based separation is still one of the most economical options, since it does not require any heat input. Therefore, we focused on the membrane-based draw solution separation and recovery process in our search for a suitable draw solution.

Hence, we first focused on the linear flux Eq. (1) of water through a semi-permeable membrane, proposed by Kedem and Katchalsky [7].

$$J_v = L_p(\Delta P - \sigma\Delta\Pi) \tag{1}$$

In this equation, $\Delta\Pi$ represents the osmotic pressure difference of the solutions at the two sides of the membrane and σ represents the reflection coefficient of the solution/membrane system. L_p is the water permeability of the membrane and delta P is the pressure difference of the solutions at the two sides of the membrane. As it can be seen from the equation, three important parameters affect the flux; L_p, σ, and osmotic pressure difference. Since L_p is an independent membrane property, we selected osmotic pressure difference and σ as our core research parameters. Even though higher osmotic pressure draw solutions are essential for the FO process, this high osmotic pressure makes the separation process highly energy dependent. The only possible solution for this phenomenon is to use draw solution-membrane systems with very low reflection coefficients.

We used polyethylene glycol (PEG) as an osmotically active compound with high osmotic pressures, as it has a unique osmotic pressure—molarity relationship, where osmotic pressures of PEG solutions increase exponentially with molarity when high molecular weights (MW) are used [18]. Even though second-order van't Hoff's equation can be used to calculate the osmotic pressure of low and medium MW PEGs [15], osmotic pressure of 20 kDa MW PEG can also be calculated by the following Eq. (2) [18]:

$$\log(P) = 1.61 + [\mathrm{PEGwt}\%]^{0.21} \tag{2}$$

where P is the osmotic pressure of the 20 kDa PEG solution.

Wolfgang Bruns [20] suggested that the osmotic pressure of polymer solutions can be calculated accurately by considering third virial coefficient in third-order van't Hoff's Eq. (3):

$$\beta \Pi = \frac{c}{n} + A_2 c^2 + A_3 c^3 + \cdots \quad (3)$$

where β is $1/(kT)$, n is the number of structural units of a chain, and c is the concentration of the units. Therefore, this equation also suggests that a high number of structural units (high MW) result in a higher concentration value (when the molarity is considered), which increases the osmotic pressure polynomially. Hence, we decided to use high MW PEG solutions to achieve high osmotic pressure differences between the draw and the feed side of the membrane. Humic acid (HA) was also selected as an osmotically active solute for the same reasons.

The most important reason that we decided to use macromolecules (PEG and HA) as osmotically active compounds is the effect of high MW on the reflection coefficient. Kellen [8] compared several studies which investigated the relationship between the reflection coefficient and molecular radius of solutes (MW). It was seen that the reflection coefficient increases with the molecular radius of solutes (weight). In another research, Schultz et al. [19] showed that the reflection coefficient increases with the increase in ratio of solute radius to pore radius of the membrane. Also, in another aspect, Opong and Zydney [16] investigated the change in the reflection coefficient of bovine serum albumin with respect to mean bulk concentration with two different pore size membranes. They showed that the lower pore-sized membrane increased the decreasing rate of the reflection coefficient. Therefore, the reflection coefficient can be reduced by using smaller MWCO membranes when a higher MW solute is used. Hence, we selected high MW PEG and HA solutions and used low MWCO membranes in the filtration step in order to decrease the reflection coefficient.

Even though, according to Eq. (1), the low reflection coefficient ($\sigma < \Delta P/\Delta \Pi$) should be enough to get a positive water flux through the membrane on the filtration step, the effect of the viscosity should be taken into consideration. Therefore, following Eq. (4), was selected as a more realistic thermodynamic model of the permeability [14];

$$J_v = \frac{L_p}{\eta} \Delta P - \sigma \Delta \Pi \quad (4)$$

In this equation, η represents the viscosity of the solution. According to Fox and Flory [3], viscosities of macromolecules are related directly to their MW (Eq. (5)).

$$\log \eta = A + C M_w^{\frac{1}{2}} \quad (5)$$

where M_w is the weight average MW, and A and C are constants for a specified temperature.

Hence, we selected high MW PEG and HA solutions for the FO process, where we used commercialized FO membranes. We also used low MWCO membranes in the filtration step for the filtration of high MW PEG and HA in order to decrease the reflection coefficient.

2. Materials and methods

2.1. System configuration and equipment

Osmosis followed by filtration systems consists of two main parts (Figs. 1 and 3). The first part is the forward osmosis (FO) stage and second part is the filtration stage. The FO stage consists of one feed tank, one draw solution tank, two micro gear pumps (max press. 125 psi (8.62 bars), Cole-Palmer, USA), and one membrane cell (active area = 138.7 cm^2) (Fig. 1). The increase in the draw solution tank was measured by an electronic balance (AND, GF-6100) in order to calculate the permeability of the FO system (Fig. 2). The filtration stage consists of one draw solution tank, one product water tank, and one membrane cell (active area = 62.4 cm^2) (Fig. 3).

2.2. Membrane and osmotically active compound selection

Three different types of draw solutions: $MgCl_2$ (99%, Sigma-Aldrich), PEG (Sigma-Aldrich), and HA (Humic acid sodium salt, Technical grade, Sigma-Aldrich) and two different FO membranes (high permeability-no support layer and low permeability-with support layer) were used for the FO stage. Selected draw solution concentrations were as follows: $MgCl_2$ (95 g/L), PEG (2 kDa—600 g/L, 10 kDa—400 and

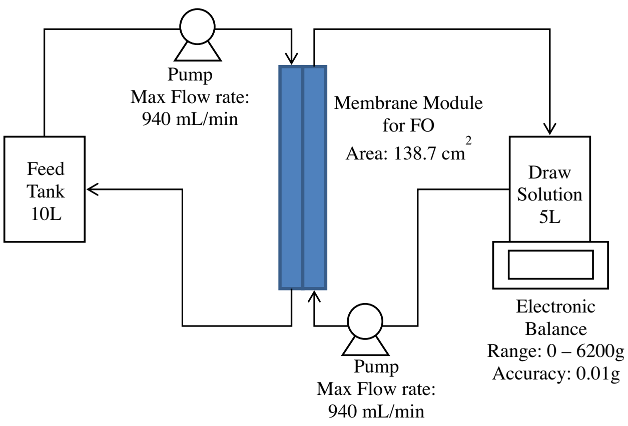

Fig. 1. Schematic of FO part of the system.

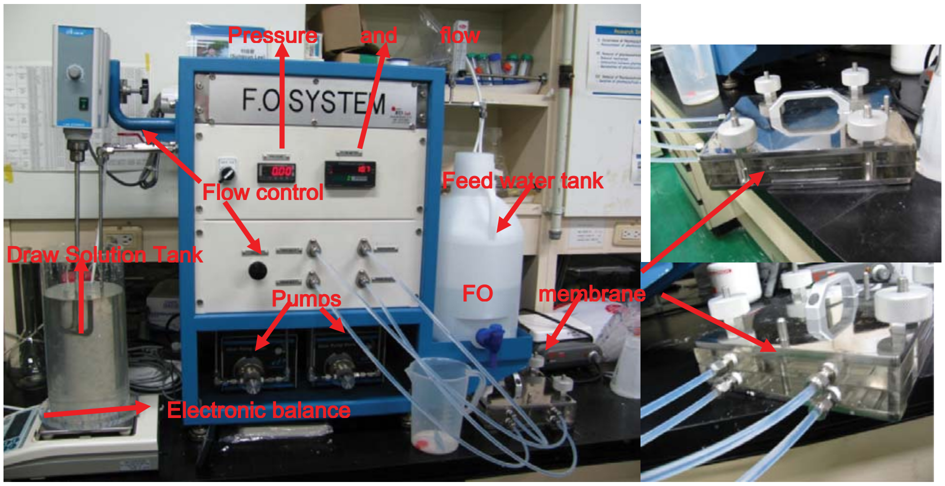

Fig. 2. Picture of the FO system that was designed and constructed for the project.

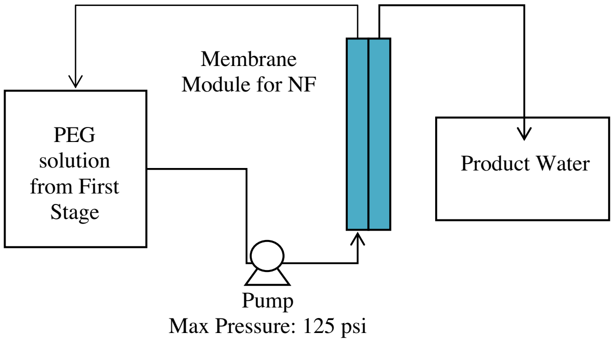

Fig. 3. Schematic of filtration part of the system.

Table 2
Selected solutes and their concentrations for draw solution preparations

Draw solution	$MgCl_2$	PEG 2 kDa	PEG 10 kDa	PEG 20 kDa	HA
Concentration (g/L)	95	600	400	400	200
					400
			600	600	600
					800

600 g/L, and 20 kDa—400 and 600 g/L), and HA (200, 300, 400, 600, and 800 g/L) (Table 2).

The second stage of the process was performed in order to recover/remove draw solution, and five different types of membranes were used: FO (CTA FO—low permeability (090128) and high permeability (081118), Hydration Tech., Inc., Albany, OR), ultrafiltration (UF) (GM—MWCO = 8,000 Da, GEWater, USA), nanofiltration (NF) (NE 40—MWCO = 1,000 Da, NE 70—MWCO = 350 Da, and NE 90—MWCO = 200 Da, Woongjin Chemical, Korea), Ceramic (ZiO_2—MWCO = 3,000 Da and 8,000 Da, TAMI Industries, France), and RO (FL—MWCO = 70 Da). MWCO data of the membranes were supplied by the producer companies.

3. Results and discussion

3.1. FO tests with DI water

As a preliminary test, a low permeability FO membrane was tested with 20 kDa PEG solution, and little higher than 1 LMH flux was observed. The viscosity of the 20 kDa PEG solution was very high and it was concluded that because of this very high viscosity, the PEG solution cannot interact with the feed solution properly. Therefore, the high permeability FO membrane was installed in order to increase interaction between the draw and the feed solutions. Water flux (2.9 LMH) was observed with the high permeability FO membrane when 400 g/L 20 kDa PEG was used. It was concluded that even with the high permeability FO membrane, the interaction between the draw and the feed solutions was not enough to get a high flux. Therefore, the concentration of 20 kDa PEG was increased to 600 g/L, when the high permeability CTA FO membrane was used, and it was found that the flux was improved up to 6.3 LMH.

In order to decrease viscosity and get higher fluxes a 10 kDa PEG solution was selected. When 400 g/L 10 kDa PEG solution was used, 3.5 LMH water flow was achieved. The concentration of 10 kDa PEG was increased to 600 g/L and the water flux through CTA FO membrane was improved up to 4.2 LMH. It was concluded that 20 kDa PEG presented a better osmotic pressure gradient, as expected, than a 10 kDa PEG solution, in given concentrations. Even though the flux was still relatively low, it represented a valuable candidate for an economically feasible FO system.

In order to investigate other macro molecular candidates for an FO draw solution, HA was selected for the further tests. The concentration range of HA was selected to be from 200 to 800 g/L. The HA powder was simply dissolved into DI water in order to get the desired HA solutions. After the preliminary tests, it was found out that the impurities in the HA powder cause a non-dissolved portion of residues in the solution. Therefore, mash-type filters were used to eliminate these impurities prior to the FO tests. The HA solution was found to be less effective even at high concentrations when compared with the PEG solutions. Maximum flux was achieved by 800 g/L HA solution and found to be 3.0 LMH.

3.2. FO tests with seawater

In order to confirm that the 10 kDa PEG solution can receive water from seawater, the feed solution was changed from DI water to seawater. The 600 g/L 10 kDa PEG solution was used with the high permeability FO membrane. Around 2.9 LMH water flux was observed in this configuration. Even though the flux was considerably low, it could still be an alternative if the water could be subtracted from PEG solution. The 20 kDa PEG solution with 600 g/L concentration also gave 4.0 LMH flux when seawater was used as feed solution. Other draw solutions did not give any flux during seawater FO tests.

Table 3
The summary of the FO tests with DI water and seawater.

Membrane	Draw solution		Flux (LMH)	
			Feed: DI	Feed: seawater
FL	$MgCl_2$	95 g/L (1 M)	0.5	0.0
NE 90	$MgCl_2$	95 g/L (1 M)	0.8	0.0
	2 kDa PEG	600 g/L (0.3 M)	0.4	0.0
	20 kDa PEG	400 g/L (0.02 M)	1.1	0.0
CTA	10 kDa PEG	400 g/L (0.04 M)	3.5	0.0
		600 g/L (0.06 M)	4.2	2.9
	20 kDa PEG	400 g/L (0.02 M)	2.9	−0.5
		600 g/L (0.03 M)	6.3	4.0
	HA	200 g/L	1.2	0.0
		300 g/L	1.5	0.0
		400 g/L	1.8	0.0
		600 g/L	3.4	0.0
		800 g/L	3.0	−1.9

The HA solutions were also found to be ineffective when seawater was used as a feed solution, and no flux was observed. The summary of the FO tests is given in Table 3.

3.3. UF/NF filtration tests for water recovery

In order to separate water from PEG solutions, 10 kDa PEG solutions (200 and 600 g/L) were tested with two types of membranes (NE70 and NE90).

The NE40 and NE90 membranes were tried, with pressures up to 170 psi (11.72 bars), and no permeate flow was observed. Also a high permeability FO membrane was tried with pressures up to 170 psi (11.72 bars), and again, no permeate flow was observed.

For the 20 kDa PEG solutions (for 200 and 600 g/L concentrations) GM, NE40, NE70, and ceramic membranes were used. The 200 g/L 20 kDa PEG solution was removed from the product water with almost all membranes tested. The NE 40 and NE 70 membranes removed 97% of the PEG with 110 psi (7.58 bars). The GM membrane removed only 80% of the PEG from the product water at the same pressure. For the 600 g/L 20 kDa PEG solutions, no flux was observed when the NE 40 membrane was used with the pressures up to 120 psi (8.27 bars).

The effect of the MWCO/MW ratio on the reflection coefficient was seen when we compared the permeate flux values from the GM and NE (40 and 70) membranes. The NE40 and NE70 membranes had lower MWCO values than the GM membrane, and yet they both provided higher permeate fluxes for the same PEG (20 kDa) concentration. On the other hand when we increased the PEG concentrations, osmotic pressures became too high to be compensated by the reflection coefficients. Therefore, no permeate flux was observed for the filtration of high PEG concentration solutions.

The 3,000 Da MWCO ceramic membrane did not give any permeate flux. The 8,000 Da MWCO ceramic membrane gave around 10 LMH permeate flux but when the 20 kDa PEG removal was checked, it was seen that only 25–30% of the PEG was removed by the 8,000 Da MWCO ceramic membrane. Therefore, it was concluded that the water recovery from the PEG solutions is not a feasible option for FO-based water treatment.

Table 4
UF/NF filtration test results

Membrane	Draw solution	Pressure (psi)	Flux (LMH)[1]	Removal (%)	DI flux reference (LMH)
GM	20 kDa PEG 200 g/L (0.01 M)	110	4.4	80	22 at 40 psi (2.76 bars)
NE40	20 kDa PEG 200 g/L (0.01 M)	110	8.4	97	20 at 40 psi
	20 kDa PEG 600g/L (0.03 M)	120	0	–	
NE 70	20 kDa PEG 200 g/L (0.01 M)	110	5.5	97	26 at 40 psi
	20 kDa PEG 600 g/L (0.03 M)	170	0	–	
NE 90	10 kDa PEG 500 g/L (0.05 M)	170	0	–	26 at 40 psi
Ceramic (3,000 Da)	20 kDa PEG 600 g/L (0.03 M)	170	0	–	–
Ceramic (8,000 Da)	20 kDa PEG 600 g/L (0.03 M)	170	10	25-30	–

For the HA solutions, all membranes were tested up to 170 psi (11.72 bars) and no flux was observed during the tests. A summary of the results is given in Table 4 for each case.

4. Conclusions

The PEG solutions with high MW and high concentrations were found to be somewhat effective for forward osmosis. The 20 kDa PEG solution at 600 g/L concentration gave 6.3 LMH water flux when DI water was used as a feed solution, and 4.0 LMH water flux when seawater was used as a feed solution. Even though the water flux values were not high compared with the CO_2–NH_3 system (up to 20 LMH, [21], they were still feasible as no energy input was required. The HA solutions did not give high water fluxes when DI water was used as a feed solution, compared with the PEG solution. Also the HA solutions did not give any water flux when seawater was used as feed solution. Therefore, HA was found to be an ineffective osmotically active compound when compared with PEG and other salt solutions.

High concentration PEG solutions were then tested for the removal of the osmotically active compounds from the product water. Even though the low concentration solutions of PEG were removed effectively by NF and FO membranes, no permeate flux was observed for the concentrations which are required for seawater FO. The removal of the HA solutions was also insufficient and no permeate flux was observed even at the high pressures.

We have showed in Section 3.3 that the reflection coefficient is an effective parameter for filtration of the high osmotic pressure solutions. However, the viscosity of the solution is higher when high MW macromolecules are used (Eq. (5)) and when the concentration is higher. Increased concentration of PEG also caused an increase in the osmotic pressure of the draw solution. This combined effect of high viscosity and high osmotic pressure for high concentration PEG solutions overcame the positive effect of the reflection coefficient on the filtration step and no permeate flux was observed. Therefore, in order to get positive permeate flux from the draw solution recovery system, optimization of the concentration of draw solute and more specialized membranes are required. Using low viscosity polymers may also be another solution for this limitation. The viscosity of the macromolecules can be reduced by increasing the branching in the polymeric structure. Dendrimers can be given as examples for these types of macromolecules [5]. Dendrimers can also be engineered to specified properties, such as viscosity and osmotic pressure [9].

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