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Impact of hydraulic pressure and pH on organic fouling in pressure retarded osmosis (PRO) process

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ABSTRACT

Pressure retarded osmosis (PRO) is a promising membrane-based process for producing clean and renewable energy. Since the major driving force is the salinity gradient between the feed and draw solutions, PRO can operate without a large environmental footprint. However, the performance of PRO can be severely limited by fouling, with organic fouling commonly deemed the main factor influencing PRO performance, since even a small amount of organic foulants can cause a significant flux decline. In spite of its importance, however, few studies have focused on PRO fouling. Therefore, the objectives of this study were to investigate the effect of hydraulic pressure as an influencing factor and to adjust the feed solution pH in order to alleviate fouling in the PRO process. Alginate was chosen as the model foulant due to its common existence in feed water. Based on our results, a higher hydraulic pressure caused an increase in the reverse solute flux, such that organic fouling became aggravated. In addition, the potential for fouling control by changing the feed solution pH was confirmed. As such, it is expected that this study would provide insight into PRO development in terms of the reduction of fouling.

Keywords: Pressure retarded osmosis (PRO); Organic fouling; Reverse solute flux; Feed solution pH; Hydraulic pressure

1. Introduction

Due to rapid population growth and industrial development, people in many countries suffer from a lack of energy resources. To overcome this shortage, resources that can sustainably produce clean energy, such as wind, hydro, solar, biomass, biofuel, and geothermal systems have received global attention [1–3]. Among these technologies, pressure retarded osmosis (PRO) is a promising membrane-based process that can generate power without causing environmental problems. In PRO, fresh water moves from a

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low-concentrated feed solution to a high-concentrated draw solution due to the osmotic pressure difference, and to convert mechanical energy to electric energy the increased volumetric flow runs a hydro-turbine [4,5]. A combination of seawater and river water has been applied in a PRO pilot plant in Norway by Statkraft [6]; however, the concentrated brine of reverse osmosis (RO) and wastewater effluent has recently received attention as the draw and feed solutions, respectively [7]. Utilization of the feed and draw solutions can be beneficial not only for PRO, but also for commercial RO plants. Prior to implementation, however, harmful effects on the marine environment caused by concentrated RO brine need to be minimized and intake costs reduced by re-using the wastewater discharge [8]. Since abundant water sources are commonly applied in PRO, the greatest advantages of this process is its sustainability as well as lack of carbon dioxide emissions [9].

Several drawbacks remain that hinder the commercialization of PRO processes. One significant problem is the lack of specialized PRO membrane modules. Even though a high performance has been observed in laboratory scale PRO membranes [10,11], there have been no adequate PRO membrane module developed yet. The requirement of separate pretreatment processes for the feed and draw solutions, and the development of an energy recovery device specialized for PRO are other obstacles [9]. In addition, the performance of PRO is severely limited by fouling, similar to that in membrane processes such as microfiltration (MF), ultrafiltration (UF), RO, and forward osmosis (FO) [12]. Among the fouling types, organic fouling plays a primary role in diminishing PRO performance PRO [13]. In terms of other membrane processes, considerable research has already been conducted to investigate the mechanisms and implications of organic fouling. For example, Lee and Elimelech [14] systematically investigated intermolecular adhesion forces between organic foulants in RO, and Lee et al. [15] identified the natural organic matter fouling in low-pressure membrane filtrations, MF, and UF. In addition, Mo et al. [16] and Kim et al. [17] investigated the relationships between organic fouling and feed solution pH in RO and FO processes, respectively.

However, fouling studies on PRO processes only originated in 2013 and as such remain in their initial stages. Relevant studies include that by Zhang et al. [18], who observed the mechanism of gypsum scaling, and a study by the Norwegian research institute, SINTEF [19], which investigated the effect of water quality and membrane type on the fouling by natural organic matter. In addition, She et al. [20] studied the effect of the hydraulic pressure and the selection of draw solution on organic fouling in PRO. However, even though PRO fouling is actively being studied, most research groups remain focused on the fouling occurrence itself, not fouling control or mitigation.

Based on the above considerations, the purpose of this study was to investigate the effect of hydraulic pressure and feed solution pH on the mitigation of organic fouling in PRO, and alginate was chosen as the model foulant in these experiments. It is expected that the results of this study would be helpful for developing effective strategies for the control of PRO fouling.

2. Material and methods

2.1. Membranes

Commercialized FO membranes (OsMem™ CTA-ES, Hydration Technology Innovations, USA) were used for all PRO fouling experiments. The membrane consists of cellulose triacetate (CTA) having an embedded polyester screen support. The membrane has a solvent permeability coefficient (A) of 1.62×10^{-12} (m/s)/pa and a solute permeability coefficient (B) of 1.16×10^{-7} m/s. Membranes were kept in deionized water at 5℃ to extract glycerin and prevent dehydration prior to use.

2.2. Feed and draw solutions

To synthesize the wastewater effluent and RO brine, 10 mM NaCl and 1.2 M NaCl solutions were

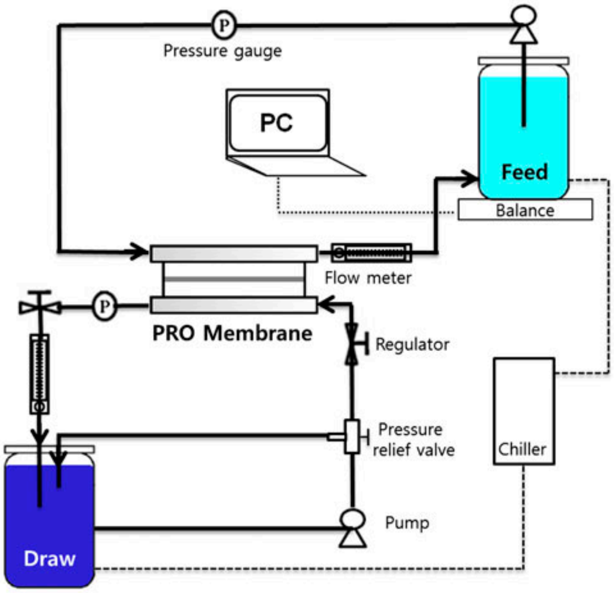

Fig. 1. Schematic diagram of the laboratory scale PRO test unit.

Table 1
Experimental conditions for organic fouling

Membrane type	CTA-ES
Membrane orientation	AL-DS*
Effective membrane area (cm^2)	19.46
Fees solution	10 mM NaCl, 1 mM $CaCl_2$, 200 mg/L Alginate
Draw solution	1.2 M NaCl
Hydraulic pressure (bar)	0/7.5/15
Feed solution pH	3/5.5/7/8.5/10
Temperature (°C)	25
Cross-flow velocity (cm/s)	10.68
Compaction time	2 h

*The active layer faced the draw solution, whereas the support layer faced the feed solution.

used as the feed and draw solutions, respectively. All solutions were prepared by dissolving sodium chloride in deionized water, at a conductivity of 0.8 μS/cm. Alginate extracted from brown algae (Sigma Aldrich, USA) was selected as the model organic foulant, since it is a major organic component in wastewater effluent [20]. Then, to realistically simulate the wastewater effluent, calcium chloride (Ca^{2+}) was added to the feed solution; phosphate-buffered saline was used to maintain the solution pH during all experiments.

2.3. PRO test unit

A schematic diagram of the laboratory scale PRO test unit is shown in Fig. 1. The flat-sheet PRO test unit has an effective membrane area of 19.46 cm^2. In PRO, spacers are commonly required at the feed side to overcome the hydraulic pressure from the draw side; here, fine-meshed RO permeate carriers were used. A gear pump (Cole-Parmer Instrument Company, USA) circulated the feed solution, and a high pressure pump (Joongwon SMET, Korea) pressurized the draw solution. The weight change of the feed solution was measured using a digital balance (Mettler Toledo, Switzerland), while the concentration change of the two solutions was measured using conductivity meters (Horiba, Japan). During the experiments, both solutions were maintained at a constant temperature (25 ± 1°C) using a water bath (AND, Korea). All data were monitored and collected using an automatic data acquisition system.

2.4. PRO fouling experiments

PRO fouling experiments were conducted using the laboratory scale PRO test unit described above. All chemicals, including the alginate stock solution, were added into the buffer solution to synthesize the feed and draw solutions and a new membrane coupon was exposed for 2 h at the given hydraulic pressure to ensure stabilization. During the experiments, the hydraulic pressure was gradually increased in order to prevent membrane deformation. The cross-flow velocity of both solutions was maintained at 10.68 cm/s, and each fouling test lasted more than 5 h, at an operating temperature of 25°C. In these experiments, the hydraulic pressure was varied from 0 to 15 bar, with the feed solution pH being varied from 3 to 10. Detailed experimental conditions are summarized at Table 1. The water flux (J_w) in all PRO fouling tests was evaluated based on the product of the water permeability coefficient (A) and the difference of osmotic pressure ($\Delta\pi$) and hydraulic pressure (Δp), as described in Eq. (1):

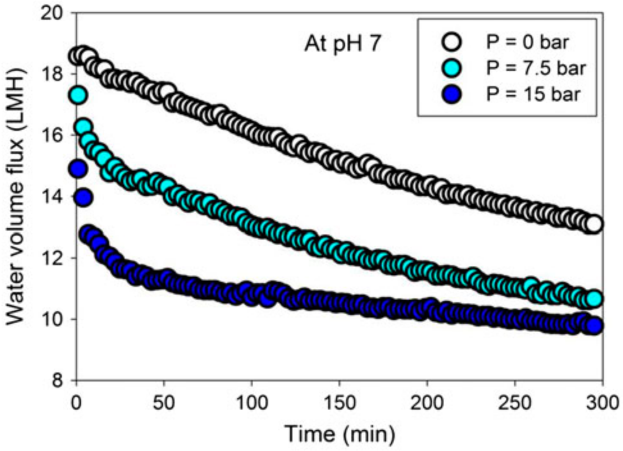

Fig. 2. Water flux decline due to organic fouling at various hydraulic pressures.

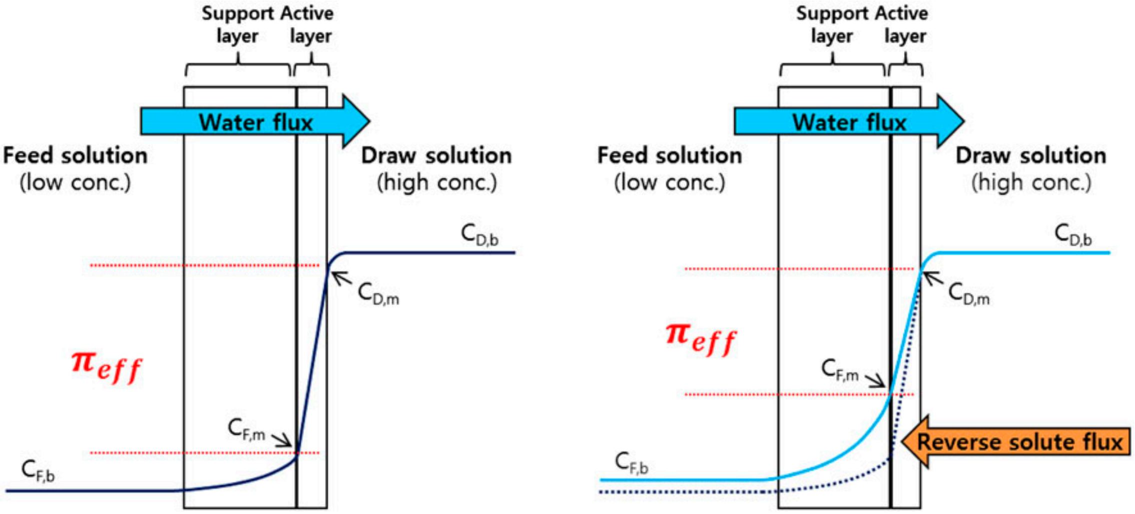

Fig. 3. Reduction of effective osmotic pressure due to increased reverse solute flux.

$$J_w = A(\Delta\pi - \Delta p). \tag{1}$$

3. Results and discussion

3.1. Effect of hydraulic pressure

Fig. 2 shows the water flux decline due to the organic fouling at various hydraulic pressure. As estimated from the water flux equation (Eq. (1)), the value of the initial water flux, at time zero, was low at a higher hydraulic pressure. A rapid flux drop at the initial stage was observed with a higher hydraulic pressure; specifically, the water flux decline was 18.58, 17.30 and 14.90 LMH as the hydraulic pressure was increased from 0 to 7.5 bar and 15 bar in the given experimental time. This result presented a different view against the work by She et al. [20], which concluded that less fouling was found according to an increase in the hydraulic pressure.

In this study, the change of reverse solute flux was mainly considered as being able to explain these experimental results. When the hydraulic pressure was increased, the reverse solute flux also increased, such that the organic fouling in PRO was aggravated. Notably, two different mechanisms, the concentration polarization (CP) and the cake enhanced osmotic pressure (CEOP) can be influenced by the reverse solute flux.

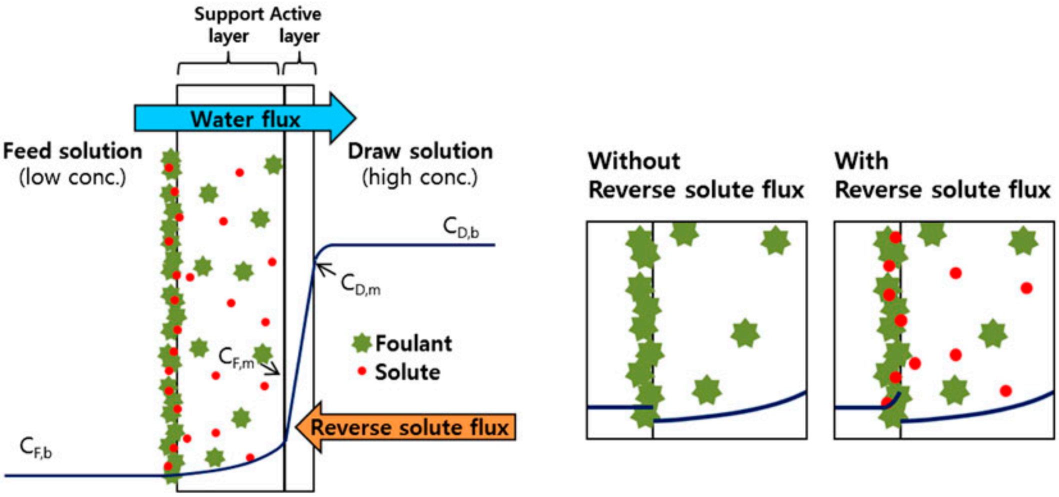

Fig. 4. Enhancement of CEOP by the captured reverse solutes.

Table 2
Reverse solute flux depending on the hydraulic pressure without the existence of alginate foulants

Hydraulic pressure (bar)	Reverse solute flux ($mmol/m^2$ h)
0	190
7.5	390
15	450

Table 3
Reverse solute flux depending on the hydraulic pressure with the existence of alginate foulants

Hydraulic pressure (bar)	Reverse solute flux ($mmol/m^2$ h)
0	30
7.5	70
15	80

In general, CP indicates the concentration or dilution of the solute near the membrane surface and finally reduces the driving force. In PRO, CP occurs both inside the porous layer and outside the membrane, referred to as internal CP (ICP) and external CP, respectively. When the hydraulic pressure was increased, the convective force caused by the pressure helped to increase the reverse solute flow from the draw side to the feed side. Due to this phenomenon, the feed solution concentration was increased and the ICP became more aggravated, ultimately reducing the effective osmotic pressure (π_{eff}) (Fig. 3). In Figs. 3 and 4, the C denotes the concentration, and the subscripts D, F, b, and m indicate the draw solution, feed solution, bulk region, and membrane surface, respectively.

To verify this assumption, the reverse solute flux was measured at various hydraulic pressures. Alginate foulants were not added to the feed solution at this time in order to separately consider the relationship between the reverse solute flux and hydraulic pressure. When the hydraulic pressure was increased from 0, to 7.5 and 15 bar, the reverse solute flux increased to 450 $mmol/m^2$ h (Table 2).

In addition, the reverse solute flux can influence the CEOP, i.e. the concentration increase at the membrane surface caused by the formation of fouling layer on the membrane. The accumulated fouling layer hinders the reverse solute flux and the captured salt ions would increase the CEOP, as described in Fig. 4.

This concept was subsequently verified by comparing the reverse solute flux under conditions of existence or non-existence of foulants. The values of the reverse solute flux at various hydraulic pressures obtained by adding the foulants into the feed solution are shown in Table 3. When the hydraulic pressure was increased from 0 to 7.5 bar and 15 bar, the reverse solute flux gradually increased from 30 to 70 $mmol/m^2$ h and 80 $mmol/m^2$ h. Even though the same hydraulic pressure was applied in Tables 2 and 3, much less reverse solute flux was detected in the case of non-presence of foulants. As such, these results confirmed that the reverse solute flux that permeated from the draw side could not reach the feed side due to interruption of the fouling layer.

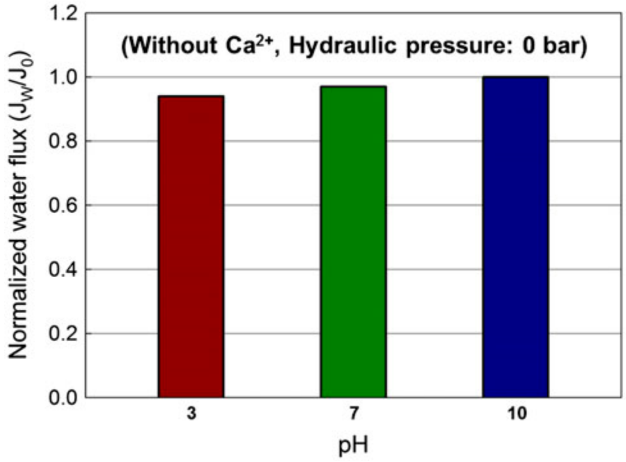

Fig. 5. Effect of feed solution pH on PRO organic fouling without the addition of Ca^{2+}.

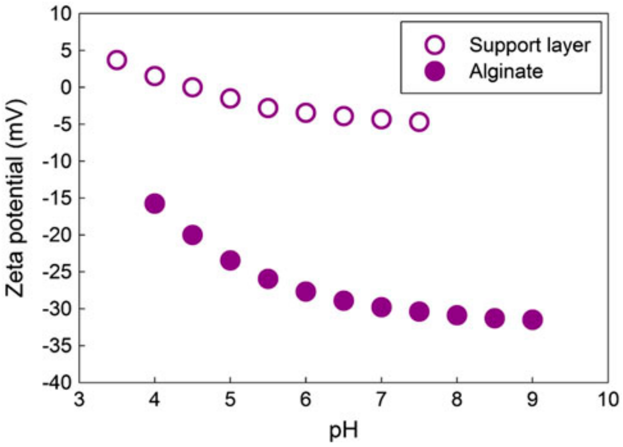

Fig. 6. Zeta potential profiles of membrane support layer and alginate.

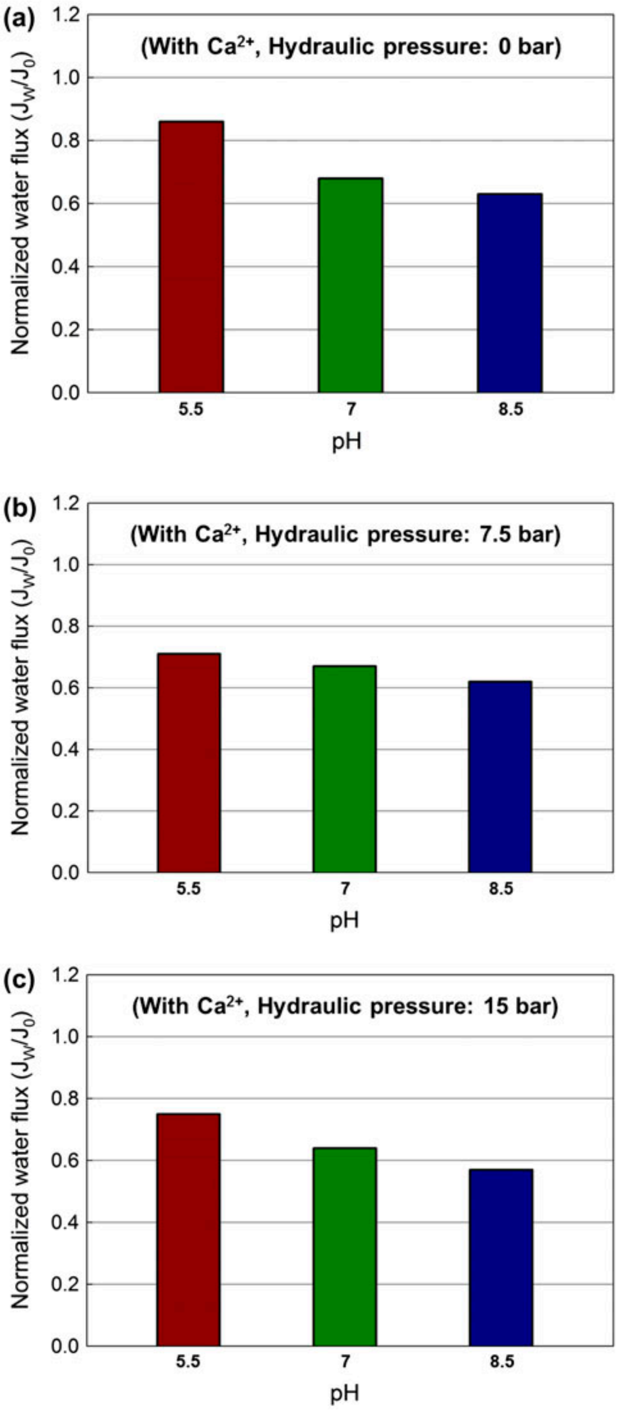

Fig. 7. Effect of feed solution pH on PRO organic fouling at various hydraulic pressures with the addition of Ca^{2+}. The hydraulic pressures were (a) 0 bar, (b) 7.5 bar, and (c) 10 bar.

3.2. *Effect of feed solution pH*

In previous studies, it was found that alginate has a negative charge at a neutral pH due to its deprotonated carboxylic functional groups and that it forms gels with alkaline earth metals such as Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, in a so-called egg box effect [21,22].

To examine the effects of alkaline earth metals, experiments were conducted by dividing them into two categories: Whether or not divalent ions were added into the feed solution. Here, calcium ions (Ca^{2+}) were selected from among the divalent ions mentioned above. The effect of feed solution pH on organic fouling in PRO is illustrated in Fig. 5. The normalized water flux slightly increased by an increase in the feed solution pH from 3 to 10.

This tendency can be explained by the zeta potential difference between the membrane support layer and alginate [23]. As shown in Fig. 6, the zeta potential values of both the membrane support layer and alginate became more negatively charged at a higher feed solution pH. The intensified repulsive force interrupted interactions among the alginate molecules and their deposition on the membrane surface. For this reason, there was less fouling under alkaline conditions.

However, the opposite trend was observed when divalent cations existed in the feed solution. In Fig. 7, the normalized water flux decreased by increasing the solution pH in all cases of hydraulic pressure, with an especially rapid drop in normalized water flux found when no hydraulic pressure was applied.

The severe fouling at a higher solution pH can be described as being due to the following mechanisms. The carboxylic functional groups in the alginate were deprotonated at higher pH and the alginate molecules became more negatively charged. Since the negatively charged alginate molecules had more opportunities to combine with divalent cations (Ca^{2+}), a longer and thicker alginate chain was developed, as illustrated in Fig. 8 [21]. Due to the intensified egg box effect, alginate fouling in PRO process became more aggravated at a higher pH.

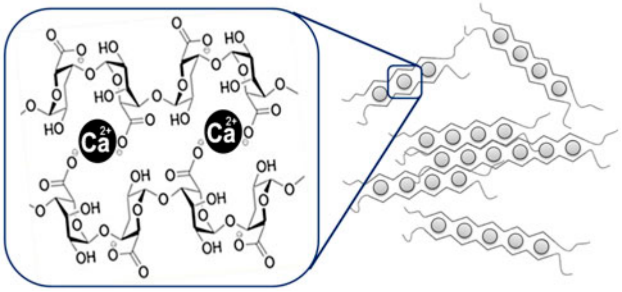

Fig. 8. Illustration of aggravation of egg box effect due to divalent ions. Figure adopted from Ref. [21].

4. Conclusions

The impact of hydraulic pressure and feed solution pH on organic fouling in the PRO process was systematically investigated in this study. It was revealed that the increased reverse solute flux due to the increase of hydraulic pressure aggravated the ICP and CEOP phenomenon, such that the driving force of PRO was highly decreased. In addition, the potential for mitigating organic fouling in PRO by adjusting the feed solution pH was confirmed. Here, acidic conditions were found to be beneficial for alleviating PRO fouling when divalent ions exist, whereas alkaline conditions are better in the absence of divalent ions.

Even though the effect of hydraulic pressure and feed solution pH was studied as an important influencing factor on organic fouling in PRO, further research should be performed to determine the specific operating conditions required to mitigate and ultimately control fouling. Fouling experiments need to be conducted under more specified conditions—not only at varying hydraulic pressures and solution pHs, but also with different foulant and solution concentrations. In addition, simulation-based studies used to generalize the experimental results and select efficient control periods and durations are required. Despite the need for further works, this study provides insights into the future direction for PRO development, especially in terms of the mitigation and control of PRO fouling.

Acknowledgments

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References

[1] T.-S. Chung, X. Li, R.C. Ong, Q. Ge, H. Wang, G. Han, Emerging forward osmosis (FO) technologies and challenges ahead for clean water and clean energy applications, Current Opinion Chem. Eng. 1 (2012) 246–257.

[2] S. Weitemeyer, D. Kleinhans, T. Vogt, C. Agert, Integration of renewable energy sources in future power systems: The role of storage, Renewable Energy 75 (2015) 14–20.

[3] J. Maisonneuve, P. Pillay, C.B. Laflamme, Pressure-retarded osmotic power system model considering non-ideal effects, Renewable Energy 75 (2015) 416–424.

[4] K. Touati, T. Schiestel, Evaluation of the potential of osmotic energy as renewable energy source in realistic conditions, Energy Procedia 42 (2013) 261–269.

[5] A. Achilli, T.Y. Cath, A.E. Childress, Power generation with pressure retarded osmosis: An experimental and theoretical investigation, J. Membr. Sci. 343 (2009) 42–52.

[6] Statkraft, Crown Princess of Norway to Open the World's First Osmotic Power Plant, 2009. Available from: <http://www.statkraft.com>.

[7] J. Kim, M. Park, S.A. Snyder, J.H. Kim, Reverse osmosis (RO) and pressure retarded osmosis (PRO) hybrid processes: Model-based scenario study, Desalination 322 (2013) 121–130.

[8] Y.M. Kim, S.J. Kim, Y.S. Kim, S. Lee, I.S. Kim, J.H. Kim, Overview of systems engineering approaches for a large-scale seawater desalination plant with a reverse osmosis network, Desalination 238 (2009) 312–332.

[9] J. Kim, J. Lee, J.H. Kim, Overview of pressure-retarded osmosis (PRO) process and hybrid application to sea water reverse osmosis process, Desalin. Water Treat. 43 (2012) 193–200.

[10] G. Han, S. Zhang, X. Li, T.-S. Chung, High performance thin film composite pressure retarded osmosis (PRO) membranes for renewable salinity-gradient energy generation, J. Membr. Sci. 440 (2013) 108–121.

[11] S. Chou, R. Wang, L. Shi, Q. She, C. Tang, A.G. Fane, Thin-film composite hollow fiber membranes for pressure retarded osmosis (PRO) process with high power density, J. Membr. Sci. 389 (2012) 25–33.

[12] N.Y. Yip, M. Elimelech, Influence of natural organic matter fouling and osmotic backwash on pressure retarded osmosis energy production from natural salinity gradients, Environ. Sci. Technol. 47 (2013) 12607–12616.

[13] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes, J. Membr. Sci. 132 (1997) 159–181.

[14] S. Lee, M. Elimelech, Relating organic fouling of reverse osmosis membranes to intermolecular adhesion forces, Environ. Sci. Technol. 40 (2006) 980–987.

[15] N. Lee, G. Amy, J.-P. Croué, H. Buisson, Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM), Water Res. 38 (2004) 4511–4523.

[16] H. Mo, K.G. Tay, H.Y. Ng, Fouling of reverse osmosis membrane by protein (BSA): Effects of pH, calcium, magnesium, ionic strength and temperature, J. Membr. Sci. 315 (2008) 28–35.

[17] Y. Kim, M. Elimelech, H.K. Shon, S. Hong, Combined organic and colloidal fouling in forward osmosis: Fouling reversibility and the role of applied pressure, J. Membr. Sci. 460 (2014) 206–212.

[18] M. Zhang, D. Hou, Q. She, C.Y. Tang, Gypsum scaling in pressure retarded osmosis: Experiments, mechanisms and implications, Water Res. 48 (2014) 387–395.

[19] W.R. Thelin, E. Sivertsen, T. Holt, G. Brekke, Natural organic matter fouling in pressure retarded osmosis, J. Membr. Sci. 438 (2013) 46–56.

[20] Q. She, Y.K.W. Wong, S. Zhao, C.Y. Tang, Organic fouling in pressure retarded osmosis: Experiments, mechanisms and implications, J. Membr. Sci. 428 (2013) 181–189.

[21] K. Kashima, M. Imai, Advanced Membrane Material from Marine Biological Polymer and Sensitive Molecular-size Recognition for Promising Separation Technology, INTECH Open Access Publisher, 2012.

[22] Y. Fang, S. Al-Assaf, G.O. Phillips, K. Nishinari, T. Funami, P.A. Williams, L. Li, Multiple steps and critical behaviors of the binding of calcium to alginate, J. Phys. Chem. B 111 (2007) 2456–2462.

[23] M. Xie, W.E. Price, L.D. Nghiem, Rejection of pharmaceutically active compounds by forward osmosis: Role of solution pH and membrane orientation, Sep. Purif. Technol. 93 (2012) 107–114.