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Organic fouling and osmotic backwashing in PRO

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ABSTRACT

The pressure-retarded osmosis process is the next generation seawater desalination technology and is considered as eco-friendly and economic renewable energy. As such, there are active studies of means of efficient cleaning to restore the membrane performance degraded due to the reversible membrane fouling that inevitably occurs after prolonged operation. This study evaluated the fouling rate by organic alginate, humic, and BSA (bovine serum albumin). Also, we focused on the comparison of cleaning methods which are physical flushing and osmotic backwashing (OB). For the comparison of the cleaning efficiency, we used alginate compound as a model substances representative of natural organic matter. Physical cleaning (PC) is the flushing method by flowing the distilled water on the membrane active and support layer in high velocity to remove the accumulated foulants on the membrane surface. OB is the method of backflow generated by osmosis to remove the accumulated foulants on/in the membrane active and support layer. The comparison indicated that OB resulted in higher membrane performance recovery than PC. To determine the optimum condition for higher membrane performance recovery from OB, the tests were performed at different concentrations of OB and cleaning speeds. The test indicated that the membrane performance recovery efficiency increased when the concentration increased to up to 1.7 M NaCl and when the cleaning speed increased by changing the feed flow rate at the constant concentration of 1.2 M NaCl.

Keywords: Physical cleaning; Osmotic backwashing; Membrane performance recovery

1. Introduction

Development of eco-friendly and economic alternative energy is urgently needed to meet the rapidly increasing demand for energy worldwide and overcome the shortcomings of fossil fuels. The power generation by salinity gradient is one of the alternative energy technologies and uses osmosis generated from salinity difference. Unlike solar energy and wind power, it is not affected by weather or seasonal factors. Moreover, its uses the unlimited seawater and

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thus continuous production is assured without the risk of exhaustion of resource, and the clean process emits of CO_2.

The reverse osmosis (RO) process is rapidly growing for desalination as it can obtain the water resource with the relatively low energy compared to the existing distillation-type seawater desalination process. The current RO process technology has been developed to its maximum level, and ways of combining the pressure-retarded osmosis (PRO) process to RO process are being studied to additionally lower the operating energy.

The PRO process is the same as the forward osmosis (FO) process which obtains the freshwater through the semi-permeable membrane using the natural osmosis from the difference of concentration. The energy is generated from the turbine which is rotated by increased flow rate by the difference of osmotic pressure. The factors affecting the membrane performance are the aging and fouling of the membrane. While the aging of membrane is the irreversible change of membrane performance caused by the deformation of the membrane, fouling of membrane is the apparent membrane performance change caused by the foulants affixed and accumulated inside and on the surface of the membrane. While the PRO process can generate the clean and renewable energy, the membrane fouling degrades the performance of the membrane [1–3].

The membrane performance change due to the fouling can be recovered through cleaning. In the FO process, the reversible fouling by the alginate organic material could show 98% recovery of permeated flux with only flushing of physical cleaning (PC) without the chemical cleaning process [4,5]. Comparison of FO process and RO process showed that the FO process resulted in higher flux recovery rate from similar flux reduction of the membrane. This is because the organic material adsorbed on the membrane surface can be more easily separated from the membrane surface than the RO process, in which the organic materials are compressed by the strong force, as the pressure applied to the membrane surface is lower than the RO process [4,6].

In a PRO process, the water permeability of the fouled membrane is degraded to lower the flux and thus the power density. After fouling, the flux and permeability decrease by around 46% and around 39%, respectively, and the power generation declines to lower the power density to around 26%. As the membrane performance can be significantly recovered by osmotic backwashing (OB), the power density can be recovered even to around 46% if the foulants accumulated in the porous support layer can be removed [1,7].

Since the fouling of the membrane can affect the membrane performance efficiency greatly, the membrane needs to be cleaned often.

To continuously maintain the membrane performance, the chemical cleaning is essential. In the case of chemical cleaning, the flux recovery rate of the membrane generally increases as the higher concentration is used. However, there are cases in which the use of higher concentration does not affect the effectiveness of cleaning. If the chemical that does not react with the organic material is used, there will be no benefit of cleaning. Moreover, the foulants absorbed into the membrane layer or irreversible fouling cannot be removed [8]. Although frequent chemical cleaning may improve the membrane performance recovery efficiency, it will damage the membrane and cause additional cost. Therefore, the alternative cleaning methods are needed [9,10]. OB is carried out by reversing the water flux direction. OB was performed by switching the high/low concentration solution on the membrane orientation such that the active layer faced the high concentration solution and the support layer was toward the low concentration. PC is using the shear force on the membrane surface by increasing the cross-flow velocity [1,11]. As above reasons, we focus the chemical-free cleaning methods such as OB and PC in PRO system. This study compared how flux decrease by membrane fouling differed according to the type of organic materials and evaluated cleaning efficiency according to PC and OB in the PRO mode. The flushing cleaning is the PC method by flowing the membrane distilled water on the membrane active and support layer in high velocity to remove the foulants accumulated on the membrane surface. It was compared with OB which generates the flow in the reverse direction of water permeation generated during the PRO operation to remove the foulants on the active/support membrane surface. Also, this study intended to find the optimum condition by varying the concentration and speed of OB to analyze the OB in various aspects.

2. Material and methods

The foulants on the membrane surface and in the micro-pores of the membrane pollute the membrane to reduce the flux and degrade the permeation performance. As the result, higher pressure is needed, additional cleaning is needed to maintain the performance, and the membrane life shortens. For a long-term operation, maintaining the membrane performance for a long period is critical. This study compared the impact of flux reduction using the organic materials such as the alginate (Sigma–Aldrich, St. Louis, MO), humic (Sigma–Aldrich), and BSA (Sigma–Aldrich, St. Louis, MO) on membrane performance since the membrane performance and cleaning efficiency decreases as the membrane composition and adsorption are

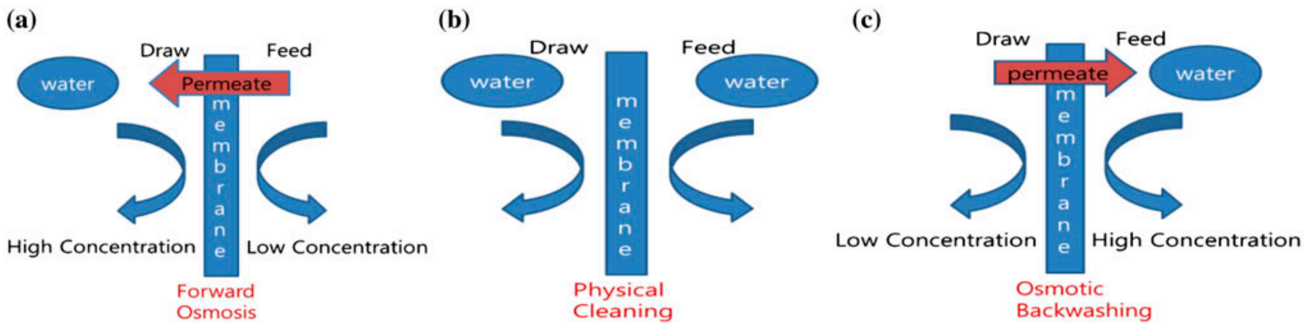

Fig. 1. Backwashing mechanism. (a) FO process (b) physical cleaning (PC), and (C) osmotic backwashing (OB).

stronger. It compared the flushing cleaning method, which flows distilled water on the membrane surface in high velocity to remove the foulants, with the OB which can clean even the membrane porous layer by generating the flux in reverse direction using the salinity gradient energy to check which method was more efficient for recovery of membrane performance.

Fig. 1(a) shows an FO process. When the low concentration solution is placed in the feed side and high concentration solution is placed in the draw side with a semi-permeable membrane between them, the osmotic pressure is generated so that only the solvent but not the solute permeates through the semi-permeable membrane. Fig. 1(b) shows a flushing cleaning, which is one of the PC methods, flowing the membrane-filtered water on the membrane surface in high velocity to remove the foulants affixed and accumulated on the membrane surface. Fig. 1(c) shows an OB. It arranges the concentration difference in the opposite way from the process (Fig. 1(a)) to clean even the inside of membrane by generating the flux in the reverse direction using the osmosis pressure by salinity gradient without changing the module.

The test was conducted in a lab. Applying OB and PC, cleaning efficiency was analyzed; Fig. 2 shows the test apparatus which was fabricated of stainless steel spacer to withstand the high pressure.

The cellulose triacetate Seapack flat membrane from HTI company was used for the separation membrane, and it was operated at the hydrostatic pressure of 20 bar for 6 h to observe the change of flux and power density due to membrane fouling. Then, the fouled membrane was cleaned by OB and PC, and the recovery of the membrane performance was observed

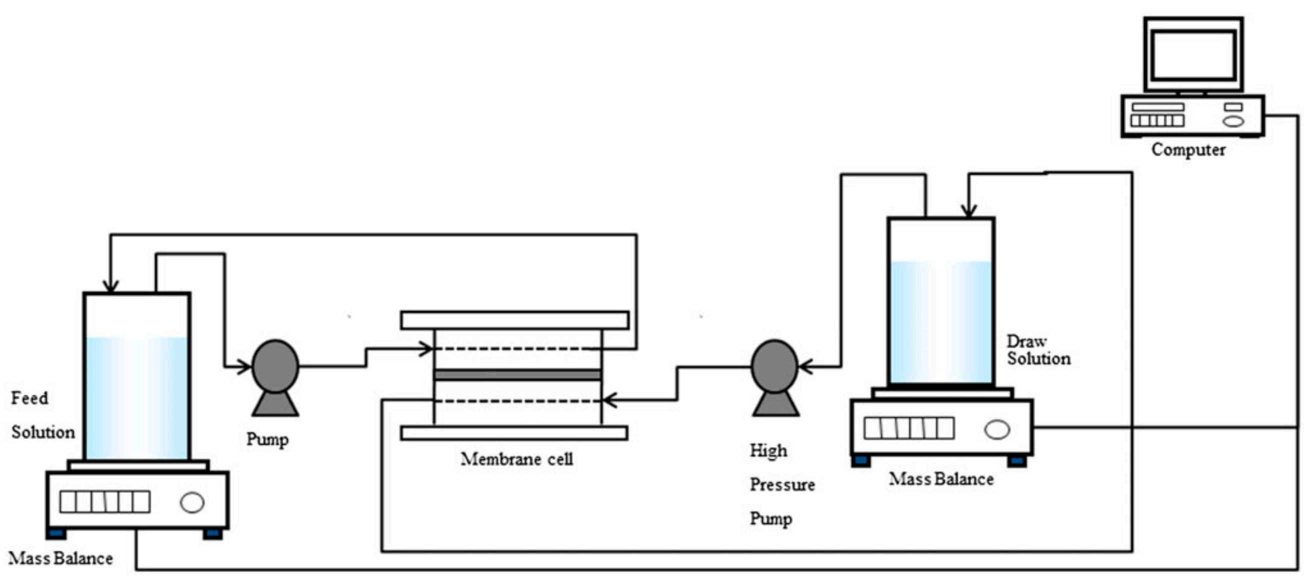

Fig. 2. Schematic of PRO system.

Table 1
Organic fouling experimental conditions

Items		Conditions		
Organic material		Alginate	Humic	BSA
Pressure, bar			20	
Operational time, h		25	23	19
Flow rate, L/h	Feed		30	
	Draw		90	
Solution	Feed, mg/L (TOC)	10	13.5	13.5
	Draw		1.2 M NaCl	

Table 2
Summary of experimental conditions

Items		Conditions
Effective membrane area, m^2		0.0064 (0.08 × 0.08)
Pressure, bar		20
Operational time, h		6
Flow rate, L/h	Feed	30
	Draw	90
Solution	Feed	44.3 mg/L (TOC) alginate
	Draw	1.2 M NaCl

Table 3
Cleaning conditions

Items		Conditions	
Cleaning type		OB	PC
Cleaning time, h		0.5	0.5
Solution	Feed	1.2 M NaCl	D.I water
	Draw	D.I water	D.I water
Flow rate, L/h	Feed	60	60
	Draw	60	60

Table 4
Conditions of OB by NaCl Concentration

Items	Conditions	
Cleaning type	OB	
Cleaning time, h	0.5	
Concentration	Feed direction	Draw direction
	1.7 M NaCl	D.I water
	1.2 M NaCl	D.I water
	1.0 M NaCl	D.I water
	0.6 M NaCl	D.I water

by measuring the flux. (Tables 1 and 2) show the organic fouling experimental conditions and summary of experimental conditions, while (Tables 3 and 4) shows the cleaning conditions and conditions of OB by NaCl concentration, respectively.

Table 5
Conditions of OB by feed flow rates

Items		Conditions
Feed		1.2 M NaCl
Draw		D.I water
Operation time, h		0.5
1 stage	Feed, L/h	30
	Draw, L/h	60
2 stage	Feed, L/h	60
	Draw, L/h	60
3 stage	Feed, L/h	120
	Draw, L/h	60

After comparing the PC and OB for membrane performance recovery efficiency, different OB concentrations and cleaning speeds of feed were tested to find the optimum condition. Table 5 shows the conditions of OB by feed flow rates.

3. Result and discussion

3.1. Organic fouling

Fig. 3 shows the membrane flux reduction from organic fouling using alginate, humic, and BSA. The result indicates that the alginate and humic showed similar flux reduction while the BSA sharply decreased the flux. BSA is one of the protein materials and has the higher viscosity than alginate or humic organic materials. The test showed that the cellulose triacetate Seapack flat membrane from HTI adsorbs the protein more easily. Membrane fouling and cleaning efficiency can be controlled by segmenting the membrane material and adsorption of organic materials [4]. To observe the membrane performance recovery rate according to membrane cleaning method, the alginate was selected for organic fouling to be used in comparison.

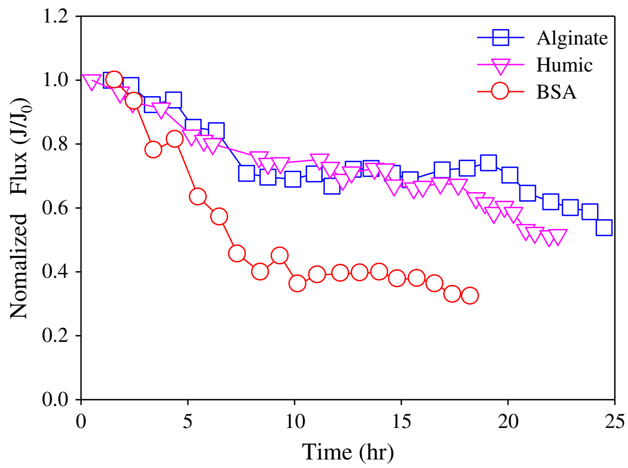

Fig. 3. Different organic fouling (alginate vs. humic vs. BSA) on PRO system. Experimental conditions: membrane —$W_{company}$ (Korea); p = 20 bar; operational $time_{avg}$ = 22 h; Q_{feed} = 30 L/h; Q_{draw} = 90 L/h; $feed_{solution}$ = 10, 13.5, and 13.5 mg/L (TOC); $draw_{solution}$ = 1.2 M NaCl.

3.2. Comparison of PC and OB

Fig. 4 shows the result of recovery of fouled membrane through PC and OB after the PRO operation. It shows that there was not much difference between PC and OB in membrane performance recovery initially. However, comparison of flux recovery to determine the membrane performance according to the cleaning method by supplying the alginate to the feed side at the same condition as prior to fouling showed that the velocity of membrane fouling after the PC was higher than that after the OB, indicating that it was more vulnerable to membrane fouling. Therefore, OB is better than PC in terms of cleaning efficiency in a prolonged operation.

Such result shows that the PC can provide sufficient shear force to remove the foulants accumulated on the surface but is limited in separating the organic materials adsorbed in the active/support of the membrane completely. On the other hand, OB can remove the foulants in the active/support of the membrane efficiently. Fig. 4 shows the membrane performance recovery of PC and OB.

3.3. Comparison of cleaning efficiency according to concentration of OB

Assuming that OB has better efficiency than PC, different conditions were applied in OB to find the best condition. The membrane performance recovery was measured by cleaning the membrane in OB at the concentration of 0.6, 1.0, 1.2, and 1.7 M NaCl each for 0.5 h. The result indicated that the membrane fouling reduction rate decreased as the concentration increased in a prolonged operation as shown in Fig. 5.

A study reported that the problem with OB was that it used the high concentration salts and accelerated CP to reduce the osmotic pressure could occur by the high concentration salts accumulated on the membrane and thus the membrane performance was not fully recovered and even lowered the efficiency [12]. Such result can be attributed to the fact that the transit flow sufficient enough for the CP generated in

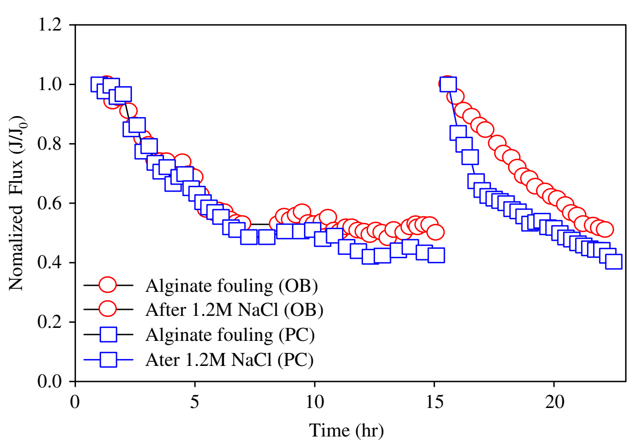

Fig. 4. Effect of cleaning type (OB vs. PC) on PRO system. Experimental conditions: membrane—$HTI_{company}$ (USA); cleaning time = 0.5 h; OB ($feed_{solution}$ = 1.2 M NaCl; $draw_{solution}$ = D.I water; $Q_{feed,\ draw}$ = 60 L/h); PC ($feed_{solution}$ = D.I water; $draw_{solution}$ = D.I water; $Q_{feed,\ draw}$ = 60 L/h).

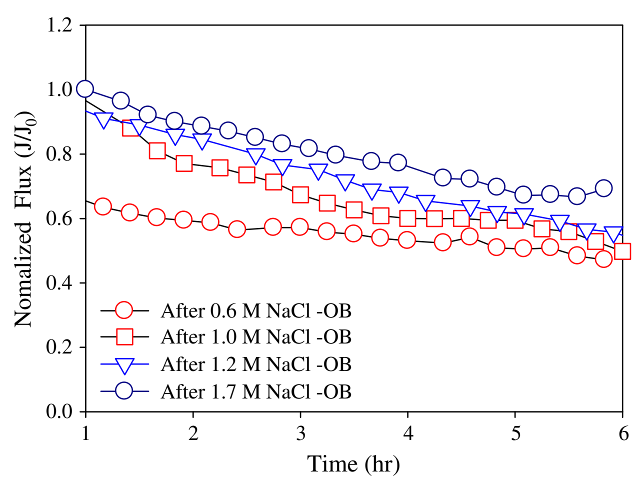

Fig. 5. Effect of OB by NaCl concentration. Experimental conditions: membrane—$HTI_{company}$ (USA); cleaning time = 0.5 h; OB ($feed_{direction}$ = 1.7, 1.2, 1.0, and 0.6 M NaCl; $draw_{direction}$ = D.I water).

the permeation side to reduce the osmotic pressure and separate the organic material was not generated. However, observation of membrane performance recovery with flux test after cleaning the membrane at a high concentration of up to 1.7 M NaCl for 0.5 h indicates that the secondary reduction of cleaning efficiency has no major impact. As the difference of osmotic pressures increase, the reverse flow increases remove more of initial CP layer to dilute it and the sufficient force is supplied to separate more foulants by reducing the amount adsorbed in the micro-pores of the support membrane. That increases the efficiency of recovering the membrane performance. In another study, comparison of CP layer removal methods in an RO process indicates that it is gradually diluted after partial removal of the CP layer [13,14]. That means that the cleaning efficiency improves when the initial CP layer removal rate is high as the osmotic pressure needed for OB increases. The pressure and feed flow rates have less impact on concentration on initial CP layer removal [13,15].

The membrane performance degradation by CP, which is a kind of secondary membrane fouling, can be observed using the high concentration salts in a lab. However, when OB is applied using the seawater and freshwater that can be obtained from PRO operation, the salt concentration is less than 1.7 M NaCl. Thus, the pretreatment process before cleaning can be combined to make membrane cleaning more efficient.

3.4. Comparison of membrane performance recoveries according to ob flow rate

Membrane cleaning is an essential step for recovering the membrane performance. The organic material accumulated on the membrane surface can be removed and diluted by the cross-flow in the feed side. Generation of both cross-flow and backflow can increase the cleaning efficiency to ensure successful cleaning [16].

Fig. 6 shows the result of setting the concentration of OB constant, flowing 1.2 M NaCl at 0.5, 1, and 2 LPM in the feed side and setting the flow rate in the draw side constant at 1 LPM. It indicates that the cleaning efficiency increased as the cleaning speed in the feed side increased. That is attributed to the increased cross-flow due to the higher cleaning speed in addition to the backflow generated by OB increasing the efficiency of removal of foulants in the micro-pores of the membrane. Fouling of membrane occurs more in the support layer having a thicker membrane than the active layer having a thinner membrane. It is estimated that, if the flow rate high concentration solution in the feed side is increased, there is the added flushing effect of the cleaning water in contact with the surface of the support layer to increase the efficiency of OB.

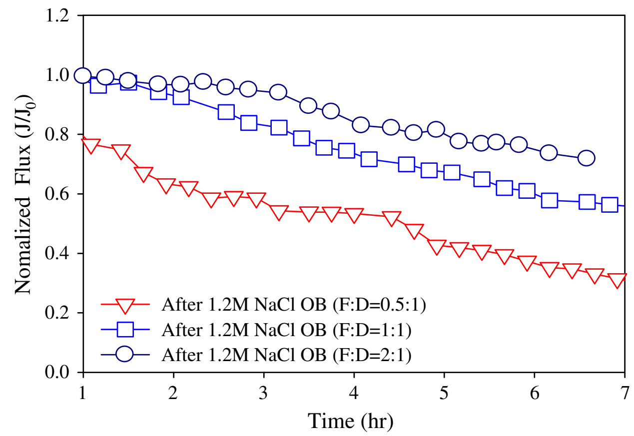

Fig. 6. Effect of OB by feed flow rates. Experimental conditions: membrane—$HTI_{company}$ (USA); cleaning time = 0.5 h; OB ($feed_{flow\ rates}$ = 30, 60, and 120 L/h; $draw_{flow\ rates}$ = 60, 60, and 60 L/h).

4. Conclusions

(1) Since adsorption of membrane and foulants significantly degrade membrane performance after membrane fouling, different cleaning method should be selected according to the foulants type in order to increase the cleaning efficiency. Therefore, if the correlation between the membrane and foulants can be segmented through testing, the additional cost of cleaning can be reduced.

(2) Both PC and OB can be used as an effective way to recover the membrane initial flux in the PRO.

(3) However, the fouling rate of the PRO membrane after PC is estimated to be faster than OB, thus the OB that can more effectively remove the foulants in the micro-pores of the membrane support layer is judged to be better than the PC in cleaning method.

(4) The measurement of flux recovery by varying the concentration of OB indicates that the membrane performance recovery efficiency is higher as the osmotic pressure difference is greater by increasing the concentration of OB solution at the condition of up 1.7 M NaCl salt concentration for 0.5 h. Although the additional testing can observe the secondary CP of membrane after OB, the salt concentration within the

tested condition can be attained for OB cleaning using the available seawater and freshwater resources during PRO operation. Thus, if the OB is applied with the pretreatment process, the efficient cleaning can be assured.

(5) If the difference of efficiency of OB cleaning using the external seawater is minor within the 1.7 M NaCl salt concentration, increasing the concentration of cleaning water is judged to be unnecessary since it violates the objective of testing to find the eco-friendly and economic cleaning method.

(6) More cross-flow and backflow are generated when the flow rate of the feed side with high concentration washing water is increased while the flow rate in the permeation side is fixed during the OB, thus flushing cleaning is more effective by removing more foulants on the membrane surface of the support layer to increase the efficiency of the membrane performance recovery.

Acknowledgments

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