Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2019.22720

141 (2019) 1–7
February

Evaluation of maintenance chemical cleaning in seawater reverse osmosis pilot plant using hot wastewater from power plant

Ki Tae Park[a], JunYoung Park[b], Minjin Kim[a], Hyung Soo Kim, Poo Reum Kim, Ji-Hoon Kim[a,*]

[a]*Graduate School of Water Resources, Sungkyunkwan University, Suwon, Korea, Tel. +82-31-290-7647, Fax +82-31-290-7549, email: jjtt23@skku.edu (J.-H. Kim),*
[b]*Center of Built Environment, Sungkyunkwan University, Suwon, Korea*

Received 9 April 2018; Accepted 24 June 2018

ABSTRACT

As Independent water and power plant projects (IWPPs) connecting electricity generation and desalination is rapidly growing, interest in the SWRO (Seawater reverse osmosis) process is increasing. However, membrane fouling is an important problem in seawater reverse osmosis (SWRO) processes, because it was one of factors by increasing operating expenses. Many studies have been conducted to control this. However, only clean-in-place (CIP) is carried out. There is a need for practical maintenance cleaning. The objective of this study was to examine characteristics of membrane fouling by operating SWRO pilot plants using hot wastewater generated from power plants and derive maintenance chemical cleaning (MCC) applicable to these sites. Results of this study, depending on the operating conditions of the power plant, the influent water temperature showed a change of about 5ºC. This affected the operating pressure of the SWRO pilot plant and fluctuates by about be 7 kgf/cm on average. This variation in water temperature caused by characteristics of hot wastewater generated from power plant directly affected fouling on membrane. Results of MCC and cleaning wastewater showed that organic fouling was dominant. With increasing water temperature, the structure of protein was unfolded and its surface charge was converted to positive charge. Such protein with positively charged surface then formed insoluble aggregates through mutual bonding with negative charge of polysaccharide. This was considered the main cause of accelerated membrane fouling. In order to control membrane fouling, possible way of MCC method was derived for field application. It was performed under various conditions (only acid, acid-alkali, alkali-acid, or only alkali). As a result, alkali-acid cleaning was found to be an optimal protocol because the main cause of membrane fouling due to water temperature change was found to be organic foulants. Therefore, it is considered that MCC can be applied as a operational strategy for organic fouling control in a seawater desalination plant using feed water with frequent temperature changes in a power plant.

Keywords: Seawater desalination; Maintenance chemical cleaning; Membrane fouling; Chain segment binding

1. Introduction

Although desalination has attracted a great deal of attention to use sea water as an alternative water source due to water scarcity, it has limitations due to its strong dependence on energy cost. Independent water and power plant projects (IWPPs) connecting electricity generation and desalination have increased rapidly, especially Reverse osmosis (RO) is used in higher proportion as a desalination method than heat-based distillation. Despite its increasing use, RO process has some shortcomings. Particularly, membrane fouling in seawater reverse osmosis (SWRO) plants causes various problems such as decreased productivity and increased maintenance costs due to frequent chemical cleaning and wastewater treatment. The efficiency of membrane fouling control has been reported to be the most important issue because it directly affects membrane fouling. Many studies have been conducted on maintenance

*Corresponding author.

cleaning to control membrane fouling. Cleaning methods include physical, chemical, and physiochemical cleaning.

Physical cleaning can be performed with sponge ball [1], forward and reverse flushing [1], backwashing [2,3], and air flushing [4–6]. Chemical cleaning is the most common method. It is performed by selecting an optimal cleaning agent (NaOH, chelating agent, Citric acid, and HCl) according to fouling characteristics to dissolve foul ants attached to membrane surface. Physiochemical cleaning includes osmotic backwashing with hyper-saline solution [7], ultrasonic cleaning [8], and the use of magnetic water [9].

However, SWRO plants and facilities regularly control fouling only by chemical-in-place (CIP). There is a need for MCC applicable to these facilities. Thus, the objective of this study was to examine fouling characteristics in desalination processes using thermal discharge from power plants using a pilot plant with a production capacity of 100 m^3/d to derive a maintenance chemical cleaning (MCC) protocol applicable to this site.

Four methods (only acid, acid-alkali, alkali-acid, and only alkali) were evaluated as conditions for MCC. The aim of this study was to derive foul ants removal characteristics by analyzing cleaning efficiency and cleaning wastewater according to different MCC conditions.

2. Methods

2.1. Experimental apparatus and operating conditions

The pilot plant with a production capacity of 100 m^3/d is located in Gwangyang bay region (Fig. 1). Ultra-filtered (DOW, USA) hot wastewater from power plant was used as feed water. Feed water consisted of 1 pass inflow to a vessel by a high-pressure pump through a safety filter. ERI's pressure exchange (PX) type was installed as an energy recovery device (Fig. 2). With regard to RO membrane (LG Chem. Korea), seven elements (LG SW 440 GR, effective area of

Fig. 1. Location of the SWRO desalination plant and picture of the pilot plant.

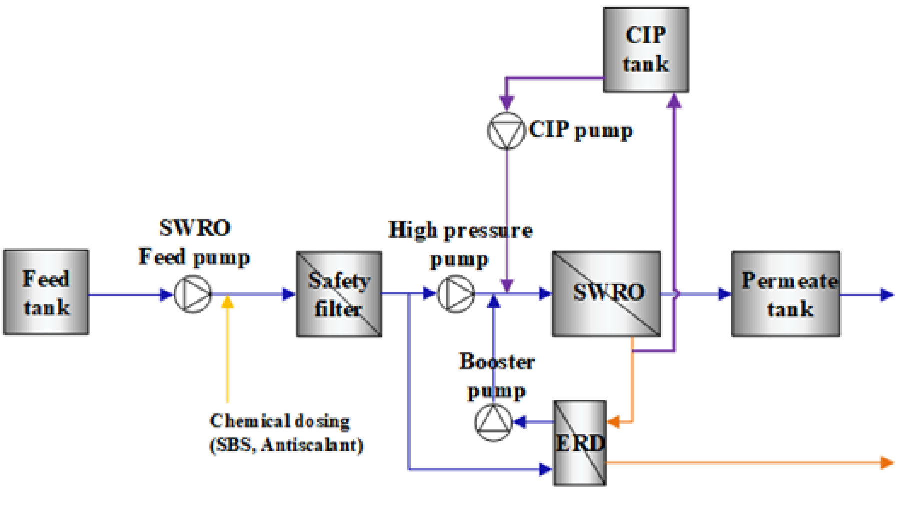

Fig. 2. Schematic of the pilot scale plant.

287 m^2) consisted of one vessel. Specifications of this membrane are shown in Table 1.

2.2. Efficiency evaluation of maintenance chemical cleaning

The cleaning efficiency of the MCC was evaluated by using the CIP line of SWRO process. Four methods were selected for cleaning conditions: only acid, acid-alkali, alkali-acid, and only alkali cleaning. Detailed methods and cleaning conditions are shown in Table 2. Permeate flux for measuring cleaning efficiency was normalized using Eq. (1) in consideration of feed water and operating conditions. MCC was performed when normalized permeate flux was decreased by 10% compared to the initial normalized flux. The volume of treated water and salt passage rate varied depending on SWRO operating conditions and membrane fouling. It is necessary to compare the volume of treated water and salt passage under standard conditions to effectively evaluate this pilot plant. In this paper, the measured permeate flow rate was standardized with respect to the operating pressure and the raw osmotic pressure at 25°C using the ASTM 4516-00 method [10]. The method is shown in Eq. (1).

$$Q_{p,s} = \frac{\left[P_{f,s} - \left(\frac{\left(P_{f,s} - P_{c,s}\right)}{2}\right) - P_{p,s} - \pi_{b,s} + \pi_{p,s}\right] TCF_s}{\left[P_{f,a} - \left(\frac{\left(P_{f,a} - P_{c,a}\right)}{2}\right) - P_{p,a} - \pi_{b,a} + \pi_{p,a} TCF_a\right]} \cdot Q_{p,a} \quad (1)$$

Table 1
Specifications of SWRO membrane

Model	LG 440 GR
Flow rate (m^3/d)	31.4
NaCl rejection (%)	99.85
Active area m^2	41
Feed spacer (mil)	28

where Q_p refers to permeate; P_f, P_c, and P_p refer to pressures (kPa) of feed, concentration, and permeate, respectively; π_b and π_p refer to osmotic pressures (kPa) of concentration and permeate, respectively; a and s refer to measured and normalized values, respectively. TCF, a temperature compensation coefficient, was calculated with the following formula: TFC = exp [3,020×(1/298.15–1/T)], where T was absolute temperature (K) [11]. Standardized salt passage (%SP) for SWRO process was calculated using Eq. (2).

$$\%SP_s = \frac{EPS_a}{EPF_s} \cdot \frac{TCF_a}{TCF_s} \cdot \frac{C_{b,s}}{C_{b,a}} \cdot \frac{C_{f,a}}{C_{f,a}} \cdot \%SP_a \quad (2)$$

EPF (element permeate flow rate) refers to the permeate rate for average RO element.

C_b and C_f refer to concentrations of concentrated water and feed, respectively, with a and s (measured and normalized values, respectively). The concentration of concentrated water is expressed as mean value measured by the measuring instrument. It is calculated by recovery rate Y (flow rate ratio of treated water/inlet water) based on the following formula: $C_b = C_f \times In[(1/(1-Y))/Y]$. The recovery rate of MCC was calculated using Eq. (3) as shown below. J_c refers to flux after MCC while J_0 refers to the initial flux.

$$\text{Flux recovery} = \frac{J_C}{J_o} \quad \text{Eq. (3)}$$

2.3. Analytical methods

With regard to water quality analysis, conductivity (Burkert, Germany), turbidity (Hach, USA), pH (GF Piping systems, USA) of feed and permeate, and ORP (GF Piping systems, USA) of the inlet water were measured by on-line measuring instrument. Operating pressures of SWRO were measured and stored by a pressure gauge (Rosemount, USA) in real-time. In addition, TOC (Total organic carbon) was measured with a TOC analyzer (TOC-VCSN, Shimadzu, Kyoto, Japan) to examine concentrations of organic matter in cleaning wastewater after MCC for each condition. Cation concentrations were analyzed using an atomic absorption spectrometer (AA6501F, Shimadzu, Japan) and an ion chromatograph (DX-100, Dionex Corp., Sunnyvale, CA, USA).

Table 2
Procedure of MCC protocol

Item	Procedure
Mode 1[1] (Acid cleaning)	15 min rinsing (by permeate, 2 m^3) → 2 h cleaning after adjusted to pH 3 (by H_2SO_4) → 15 min flushing (feed water) → filtration
Mode 2[2] (Acid-Alkali cleaning)	15 min rinsing (by permeate, 2 m^3) → 1 h cleaning after adjusted to pH 3 (by H_2SO_4) → 1 h cleaning after adjusted to pH 11 (by NaOH) → Neutralization after adjusted to pH 7 (by H_2SO_4) → 15 min flushing (feed water) → filtration
Mode 3[3] (Alkali-Acid cleaning)	15 min rinsing (by permeate, 2 m^3) → 1 h cleaning after adjusted to pH 11 (by NaOH) → 1 h cleaning after adjusted to pH 3 (by H_2SO_4) → 15 min flushing (feed water) → filtration
Mode 4[4] (Alkali cleaning)	15 min rinsing (by permeate, 2 m^3) → 2 h cleaning after adjusted to pH 11 (by NaOH) → Neutralization after adjusted to pH 7 (by H_2SO_4) → 15 min flushing (feed water) → filtration

[1]Mode 1: Only acid cleaning
[2]Mode 2: Acid cleaning after alkali cleaning
[3]Mode 3: Alkali cleaning after acid cleaning
[4]Mode 4: Only alkali cleaning

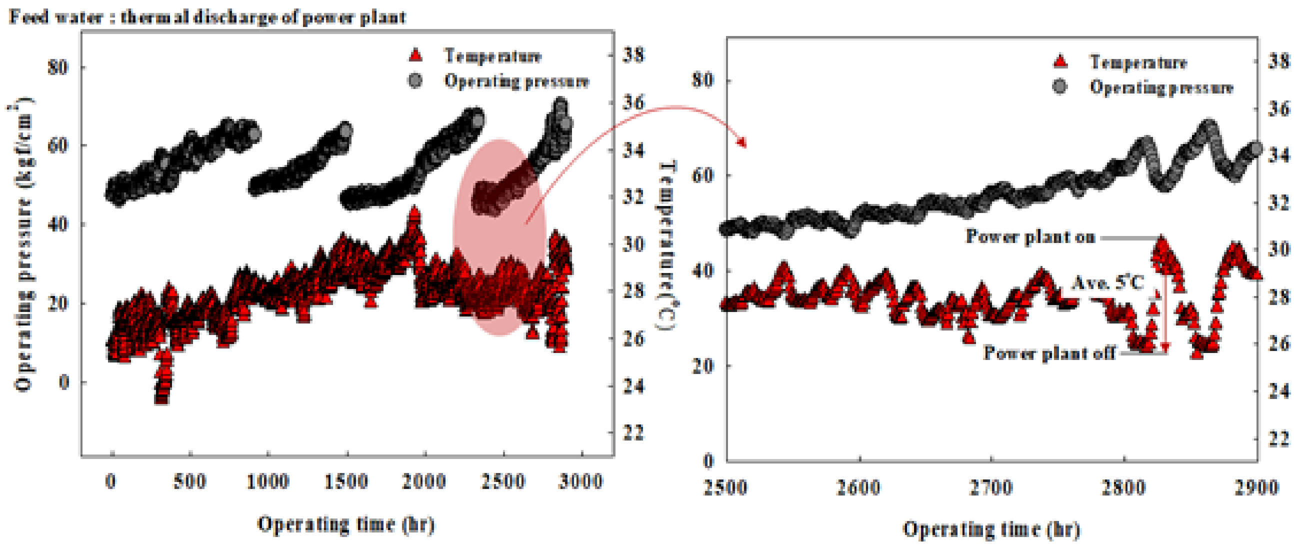

Fig. 3. Operating results of pilot plant according to temperature changes of feed water.

3. Results and discussion

3.1 Operating result of SWRO pilot plant using hot wastewater from power plant

The SWRO pilot plant was located in Gwangyang bay region. Feed water was hot wastewater generated from the power plant. It was operated at fixed recovery rate of 45% during this study. Regarding feed water quality, electrical conductivity ranged from 43.9 to 51.1 ms/cm (average, 47.4 ms/cm). Water temperature ranged from 12.5 to 27.0°C (average, 19.4°C) as shown in Table 3. Due to characteristic of hot wastewater, the average difference in feed water temperature was 5°C according to on/off of the power plant. The average fluctuation in operating pressure was measured to be 7 kg f/cm due to differences in water temperature.

These feed water temperature changes showed characteristic of membrane fouling different from that when feed water temperature was constant. The decreasing rate of normalized permeate was 1.84 L/h at constant water temperature. The normalized permeate rate reduction rate was 1.84 /h and 2.11 L/h, respectively, when the feed water temperature condition was constant or not in the pilot plant. The water temperature fluctuation of the influent water showed about 14.6% higher than that of the other cases. Results of pilot plant operations when the power plant was shut down to maintain a constant temperature of inlet water (a) or when the temperature of inlet water varied by repetition of on/off (b) are shown in Fig. 4. These results might be due to interactions of biopolymers such as polysaccharide and protein. It has been reported that polysaccharide and protein are induced by various non-covalent interactions such as static electricity, H-bond, hydrophobicity, and steric interaction [12]. Interactions between polysaccharide and protein at various temperatures are schematically shown in Fig. 5. Temperature is an important determinant of protein structure. As the temperature rises, the protein structure unfolded and becomes electrically coupled with the polysaccharide [13]. It has been reported that such induced complex can form insoluble "protein-polysaccharide" aggregates due to increased charge neutralization [14]. The results of the pilot plant operation also showed that the normalized permeate flow decreased drastically when the influent water temperature was changed. The main cause of the membrane contamination was considered to be insoluble complex due to protein structural deformation. Protein structure changed with increasing water temperature. Insoluble aggregates formed by interactions between protein and polysaccharide were the main reason for rapidly reducing normalized permeate flow.

Table 3
Analysis results of feed water quality during operation

Parameter (unit)	Max.	Min.	Mean
pH (–)	7.85	8.40	8.14
Temperature	27.0	12.5	19.4
Conductivity (mS/cm)	51.1	43.9	47.4
TOC (mg/L)	1.2	0.9	1.0
UV254 (cm^{-1})	0.01	0.007	0.013
SDI15	1.4	1.1	1.2

3.2. Evaluation of MCC efficiency though normalized permeate flow

MCC was conducted with the CIP system using NaOH and H_2SO_4 when normalized permeate flow showed 10% decline (Normalized permeate flow: about 4.2 m^3/h). Cleaning sequences were performed as shown in Table 3. MCC performance result by mode, decline rates of Normalized permeate were 2.16, 1.56, 1.43, and 1.76 L/h, respectively (Fig. 6). Cleaning recovery rates calculated with Eq. (3) also were 97.2, 108.8, 110.0, and 107.1%, respectively (Fig. 7)

On the basis of previous studies, it is known that cleaning order affects recovery rate. It has been reported that acid cleaning after alkali cleaning is effective for organic fouling [15–20]. This can be explained by the effect of membrane

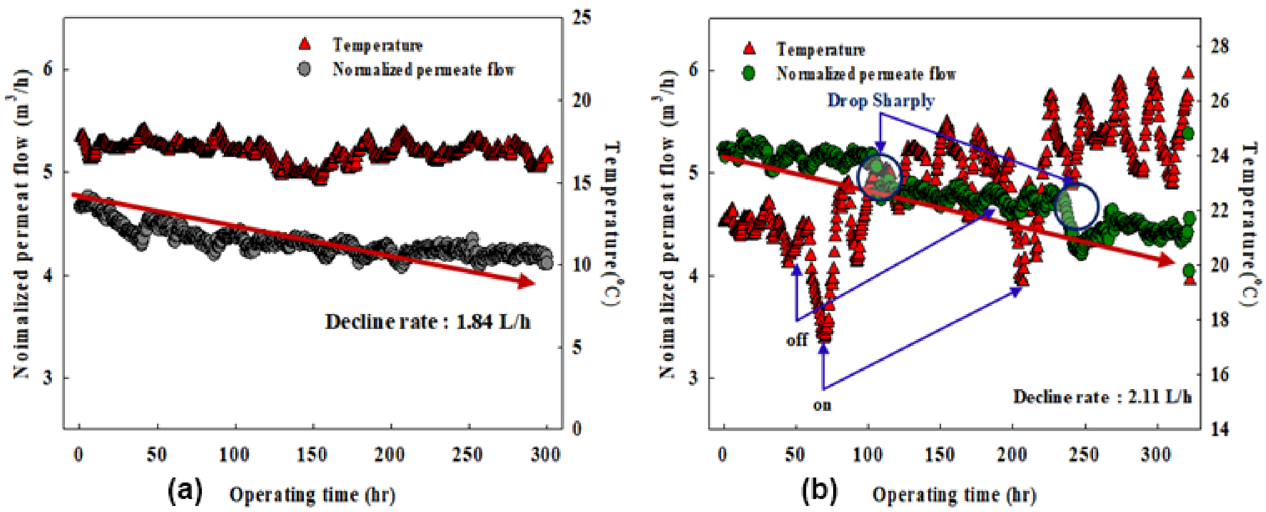

Fig. 4. Operation results of SWRO according to the operating characteristics of the power plant. (a) Operating results at a constant water temperature with the power plant shut down, (b) Operating results by variation of water temperature with on/off state of the power plant and normalized permeate flow.

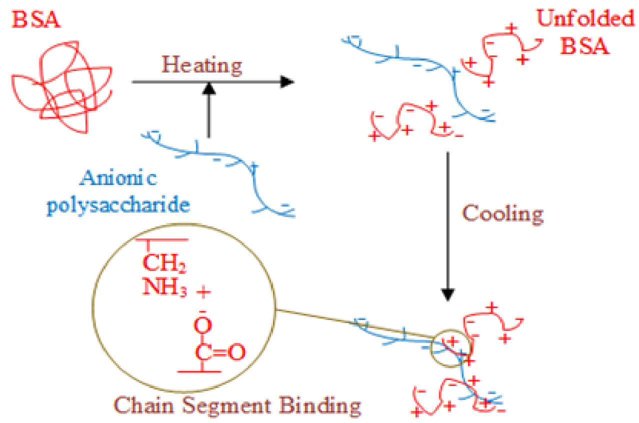

Fig. 5. Interactions between polysaccharide and protein at various temperatures.

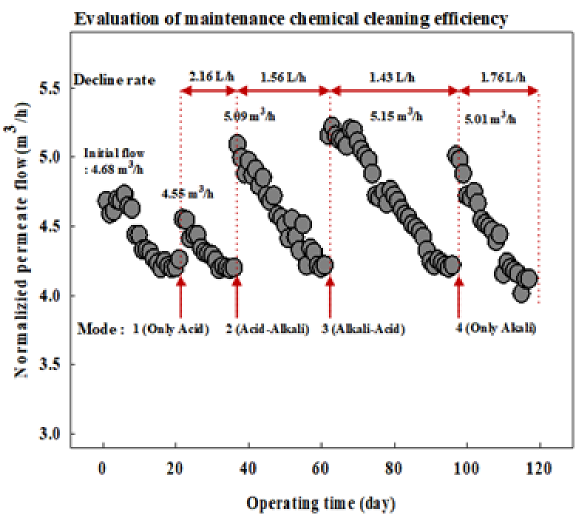

Fig. 6. Operating results of pilot plant for each MCC mode.

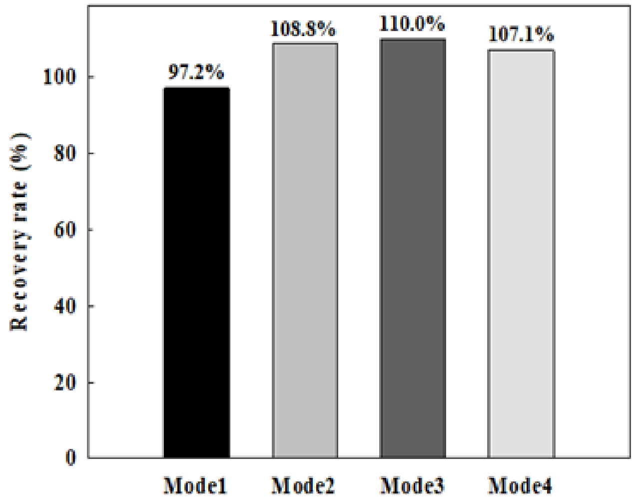

Fig. 7. Efficiency evaluation of MCC for each MCC mode.

surface and foulants (related to the decomposition of foulant molecules) due to alkali cleaning because mass transfer of cleaning agents is improved with swelling of foulant layers and membranes under alkali conditions. From literature, it appears that a predominance of hydrophobic natural organic matter (NOM) favors alkali followed by acid, whilst predominantly inorganic scaling or metal hydroxide precipitates favor acid–alkali. In this desalination pilot plant, alkali-acid cleaning showed the highest efficiency, making it possible to estimate that organic fouling was dominant. Moreover, recovery rate was increased by more than 100% if the process included alkali cleaning sequence. These results are similar to those of a previous report showed that membrane surface will become hydrophilic by NaOH (low contact angle), thus substantially increasing the recovery rate. Removal characteristics of foulants such as organic substances and cations were then examined by analyzing cleaning wastewater after each MCC. Concentrations of

Table 4
Measurement results of cation concentrations in cleaning wastewater for each MCC mode

Item	Concentration (mg/L)									
	Al	Ba	Ca	Cu	Fe	Mg	Mn	Zn	K	Si
Mode 1 (Only acid)	0.09	0.03	1,024	0.02	0.01	N.D.*	0.09	0.69	321	0.03
Mode 2 (Acid-Alkali)	0.08	0.02	724	N.D.*	0.01	N.D.*	0.04	0.1	282	N.D.*
Mode 3 (Alkali-Acid)	0.05	0.01	882	N.D.*	0.01	N.D.*	0.05	0.11	299	N.D.*
Mode 4 (Only Alkali)	0.07	0.01	608	N.D.*	N.D.*	N.D.*	N.D.*	0.08	274	N.D.*

N.D.* : Not detected

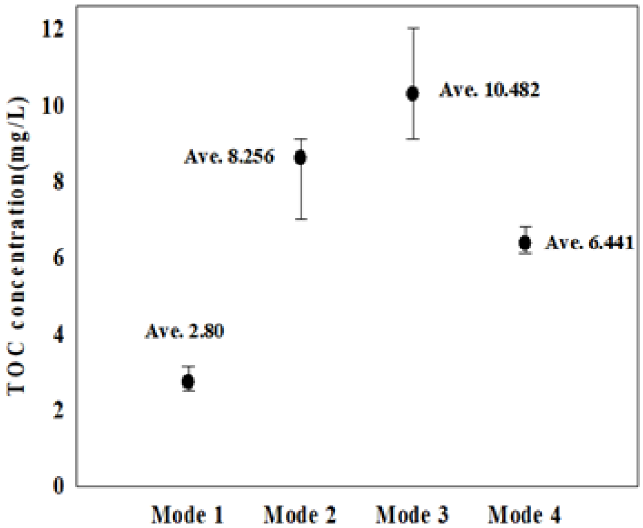

Fig. 8. Analysis results of TOC in cleaning wastewater for each MCC mode.

cation and organic matter were analyzed by ICP and TOC analyzer. Results are shown in Table 4 and Fig. 8. MCC efficiency was proportional to TOC concentration in cleaning wastewater. Based on results obtained from this pilot plant, organic fouling was considered a major cause.

4. Conclusion

This paper evaluated operating characteristics and efficiency of MCC in SWRO pilot plant using hot wastewater generated from power plant as feed water. Variation in water temperature caused by characteristics of hot wastewater from the power plant directly affected membrane fouling. Analysis results of MCC and cleaning wastewater showed that organic fouling was dominant. With increasing water temperature, protein structure was unfolded and its surface charge was converted to positive charge. Protein converted to positively charged will form insoluble aggregates through mutual bonding with negative charge of polysaccharide. This is considered the main cause of accelerated membrane fouling. In order to control membrane fouling, MCC method was derived. It is suitable for field application. It was performed under various conditions (only acid, acid-alkali, alkali-acid, only alkali). As a result, alkali-acid cleaning was found to be an optimal protocol. The main cause of membrane fouling with water temperature change was found to be organic foulants. Therefore, it is considered that MCC can be applied as a operational strategy for organic fouling control in a seawater desalination plant using feed water with frequent temperature changes in a power plant.

Acknowledgments

This research was supported by a grant (code 17IFIP-C088924-04) from Industrial Facilities & Infrastructure Research Program funded by Ministry of Land, Infrastructure and Transport (MOLIT) of the Korea government and the Korea Agency for Infrastructure Technology Advancement (KAIA).

References

[1] S. Ebrahim, Cleaning and regeneration of membranes in desalination and wastewater applications: state-of-the-art, Desalination, 96 (1994) 225–238.
[2] A. Sagiv, R. Semiat, Backwash of spiral wound membranes, Desalination, 179 (2005) 1–9.
[3] J.P. Chen, S.L. Kim, Y.P. Ting, Optimization of membrane physical and chemical cleaning by a statistically designed approach, J. Membr. Sci., 219 (2003) 27–45.
[4] I.S. Ngene, R.G.H. Lammertink, A.J.B. Kemperman, W.J.C. Van de Ven, L.P. Wessels, M. Wessling, W.G.J. Van der Meer, CO_2 nucleation in membrane spacer channels remove biofilms and fouling deposits, Ind. Eng. Chem. Res., 49 (2010) 10034–10039.
[5] G. Ducom, C. Cabassud, Possible effects of air sparging for nano filtration of salted solutions, Desalination, 156 (2003) 267–274.
[6] C. Cabassud, S. Laborie, L. Durand-Bourlier, J.M. Laine, Air sparging in ultra filtration hollow fibers: relationship between flux enhancement, cake characteristics and hydrodinamic parameters, J. Membr. Sci., 181 (2001) 57–69.
[7] B. Liberman, I. Liberman, Replacing membrane CIP by direct osmosis cleaning, Desal. Water Reuse, 15 (2005) 28–34.
[8] D. Feng, J.S.J. van Deventer, C. Aldrich, Ultrasonic defouling of reverse osmosis membranes used to treat wastewater effluents, Separ. Purif. Technol., 50 (2006) 318–323.
[9] J.M.D. Coey, S. Cass, Magnetic water treatment, J. Magnet. Magnet. Mater., 209 (2000) 71–74.
[10] ASTM D 4516-00, Standard practice for standardizing reverse osmosis performance data, in American Society of Testing Materials, 2000.
[11] T.D. Wolfe, Membrane process optimization technology, bureau of reclamation, Desalination and Water Purification Research and Development Report No. 100, 2003.

[12] de C. Kruif, G. Tuinier, Polysaccharide protein interactions, R. Food Hydrocolloid, 15 (2001) 555–563.
[13] K.D. Martínez, C.C. Sánchez, V.P. Ruíz-Henestrosa, J.M. Rodríguez Patino, J.M. Pilosof, Effect of limited hydrolysis of soy protein on the interactions with polysaccharides at the air–water interface, A.M.R. Food Hydrocolloid, 21 (2007) 813–822.
[14] C. Schmitt, C. Sanchez, S. Desobry-Banon, Structure and technofunctional properties of protein-polysaccharide complexes: a review, Hardy, Crit. Rev. Food Sci. Nutrit., 38 (1998) 689–753.
[15] G. Tragardh, Membrane cleaning, Desalination, 71 (1989) 325–335.
[16] C. Liu, S. Caothien, J. Hayes, T. Caothuy, Membrane chemical cleaning: from art to science, in: Proc. AWWA 2000 Water Quality Technology Conference, Denver Co., 2001.
[17] A. Al-Amoudi, R.W. Lovitt, Fouling strategies and the cleaning system of NF membranes and factors affecting cleaning efficiency, J. Membr. Sci., 303 (2007) 4–28.
[19] S. Hong, M. Elimelech, Chemical and physical aspects of natural organic matter (NOM) fouling of nano filtration membranes, J. Membr. Sci., 132 (1997) 159–181.
[20] S. Muthukumaran, K. Yang, A. Seuren, S. Kentish, M. Ashokkumar, G.W. Stevens, F. Grieser, The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry, Sep. Purif. Technol., 39 (2004) 99–107.