Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.780724

51 (2013) 6172–6178
September

Taylor & Francis
Taylor & Francis Group

Evaluation of chemical cleaning efficiency of organic-fouled SWRO membrane by analyzing filtration resistance

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Received 30 November 2012; Accepted 30 January 2013

ABSTRACT

Membrane fouling is an unavoidable phenomenon in the operation of seawater reverse osmosis and a major obstacle to economic and efficient operation. In particular, membrane fouling by organic matter negatively affects productivity, product quality, and process cost. Therefore, a chemical cleaning process is essential to prevent interruptions for an effective RO membrane filtration process. Firstly, this study focused on the proper chemical cleaning condition for commercial polyamide RO membranes purchased from two companies. The flux decline rate of SWC5+ membrane was higher than that of SW39HRLE400 membrane regardless of organic foulants because the initial zeta potential of SWC5+ membrane (−21.17 mV) was lower than that of SW30HRLE400 membrane (−30.11 mV) and the repulsive force between membrane surface and foulants was also lower. In addition, we attempted to evaluate cleaning efficiency according to the chemical cleaning conditions and investigate the cause of fouling by analyzing membrane resistance fraction after cleaning the organic-fouled membrane. As a result of cleaning in place (CIP), as the concentration and cleaning time increased when NaOH, trisodium phosphate 12, sodium tripolyphosphate, and ethylenediaminetetraacetic acid-4Na were used without sodium dodecylsulfate, cleaning efficiency increased significantly. Subsequently, in the condition of CIP using NaOH at pH 11 for 60 min, the cleaning efficiency of membrane fouled by humic acid was higher that of membrane fouled by sodium alginate (SA) due to the strong interaction between hydrophobic membrane and hydrophobic foulants in the case of both membranes. To find the fouling rate and fouling cause, total resistance (R_t) was fractionated by the initial membrane resistance (R_m), resistance removed by flushing (R_c), resistance removed by CIP (R_a), and irreversible resistance (R_i). R_c and R_a in both membranes showed a similar proportion in $R_{t.}$ The cause of fouling of the membrane fouled by SA was mainly the absorption of

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Presented at The Fifth Desalination Workshop (IDW 2012), October 28–31, 2012, Jeju, Korea

membrane surface, and that of membrane fouled by HA was the absorption of membrane surface and pore blocking by cake layer.

Keywords: Chemical cleaning; Cleaning in place (CIP); Fouling; Reverse osmosis; Resistance

1. Introduction

Reverse osmosis (RO) is a pressure driven membrane process and has been largely applied in desalination processes as a promising technology [1,2]. It is well known that, as with other membrane separation processes, membrane fouling using the Seawater Reverse Osmosis (SWRO) desalination technique is the most serious problem affecting RO system performance [3–7].

Besides the 96.5% of pure water, seawater is composed of about 30 species of elements, including the major components of Cl^-, Na^+, SO_4^{2-}, Mg^{2+}, and Ca^{2+}, in order of the amount, accounting for 99.9% of all elements. The concentration of organic material is only 2–4 mg/L and the degree is negligible in comparison with minerals present. However, it is known that the organic material causes more than 50% of fouling, and significantly affects the SWRO desalination plant [8].

To revert to the original product permeation rate, cleaning in place (CIP) with chemicals is most widely used to remove foulants and maintain the membrane performance [4,5,9–11]. In particular, the fouling rate of RO membrane in the desalination plant depends on the characteristics of regional and seasonal seawater, although it is applied under the same operating conditions. Chemical cleaning removes foulants by using chemicals which can weaken the adhesion between the membrane and the foulants. Different chemical agents are used during CIP according to the cause of fouling. In general, there are five categories of cleaning agents: alkaline solutions, acids, metal chelating agents, surfactants, and enzymes [12,13]. However, most commercial cleaning products are often mixtures of many compounds and the actual composition is unknown. For this reason, many researchers have not been able to provide useful information to illuminate the mechanisms of chemical cleaning.

The typical chemical cleaning frequency is 1 to 2 times annually, although this can be increased according to operation conditions. Also, in CIP, a down time for frequent RO operation stoppage is required, resulting in low effectiveness of production and creating environmental issues related to waste chemical disposal. Also, inappropriate CIPs shorten the membrane lifetime and increase the cost of maintenance. Therefore, the derivation of an efficient chemical cleaning condition is essential to prevent interruptions for the effective SWRO membrane process.

Ang et al. [9] studied the role of physical and chemical interactions in the cleaning of organic-fouled membranes. They attempted to find the optimal physical (time, cross-flow velocity, and temperature) and chemical (dose and pH) conditions using various chemical agents and to evaluate cleaning efficiency by measuring the interfacial force between membrane and foulants. Li et al. [14] and Vrijenhoek et al. [15] also evaluated cleaning efficiency by using atomic force microscopy. On the other hand, Park et al. [16] evaluated cleaning efficiency by analyzing the fluorescence excitation-emission matrix (FEEM) between feed water and cleaning wastewater after chemical cleaning. Also, from the result of FEEM analysis, chemical agents could be chosen considering the organic characteristics of seawater and the combined structure of organic foulants.

In this study, we attempted to evaluate cleaning efficiency according to the CIP conditions (i.e. various chemical agents, concentration, contact time) and investigate the cause of fouling by analysis of the membrane resistance fraction, which is one of the methods analyzing the fouling applied in the low-pressure membrane, after cleaning organic-fouled membrane.

2. Methods and materials

2.1. Organic foulant

Humic acid (HA) and sodium alginate (SA) were used as organic membrane foulants in this study. HA, a typical hydrophobic organic, has a molecular weight (MW) between 1.5 and 2.5 kDa, while SA, a representative polysaccharide, has a MW between 12 and 80 kDa. Powdered forms of HA and SA were used and were purchased from Sigma-Aldrich (St. Louis, MO). Each foulant was dissolved in deionized water (DI) and passed through a 0.45 μm filter to make stock solutions.

2.2. RO membrane

This study adopted the SW3OHRLE400 SWRO membrane manufactured by the Dow chemical company and the SWC5+ SWRO membrane manufac-

Table 1
Specification of SWRO membrane

Model	Material (surface charge)	Permeate flow rate (m^3/day)	Stabilized salt rejection (%)	Max. operating pressure (MPa)	Test condition
SW30HRLE400	PA (negative)	28	99.80	8.5	32,000 ppm NaCl, 5.5 MPa, 25 ℃ pH 8 8% recovery
SWC5+	PA (negative)	34.1	99.7	8.27	32,000 ppm NaCl, 5.5 MPa, 25 ℃ pH 6.5–7.0 10% recovery

Table 2
Characteristics of membrane surface

Model	Roughness (nm)	Dynamic contact angle (˚)	Static contact angle (˚)	Zeta potential at pH 7 (mV)
SW30HRLE400	78.09	56.49	22.51	−30.11
SWC5+	100.70	66.07	55.13	−21.17

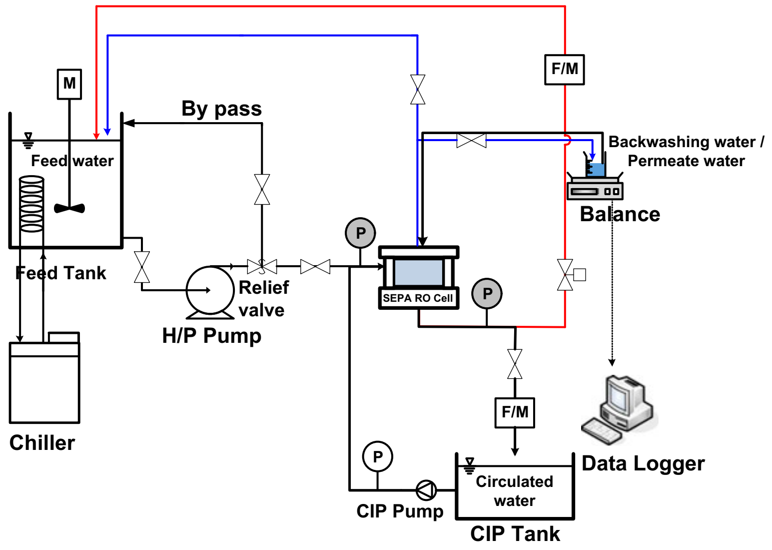

Fig. 1. Schematic description of the cross-flow RO membrane test unit.

tured by the Hydranautics company. To apply the membranes to continuous lab-scale RO equipment, a common 8 inch spiral module of the membrane was cut out to a plate shape and the properties of the membrane are shown in Tables 1 and 2. This membrane material is a polyamide, which has weaknesses including chemical resistance of Cl^- and propagation of microorganisms. While the membrane was stored, a conservative solution was used with a mixture of 20% propylene glycol and 1% sodium bisulfate. The effective membrane area was 0.0126 m^2 and a spacer was placed the raw water side of the membrane due to the reduction of the general membrane fouling.

2.3. Membrane system

The lab-scale equipment of RO was the SEPA cell of General Electric, and was linked with a high pressure pump, impeller, temperature controller, digital press meter, and flow meter (Fig. 1). The equipment comprised an all-in-one system and could operate automatically and continuously. Also, the high pressure pump is made of SUS-316 stainless steel, which is not decayed by seawater. For motor control, a phase inverter was installed and the operation pressure was adjusted between 1 and 5 MPa. Temperature control was provided by a heat exchanger and a coiled stainless steel tube which was immersed in the feed tank with circulating cooling water at 25 ℃. For measurement of cross-flow velocity, a flow meter was configured and installed in the concentrated flow line. Fig. 1 shows the feed water flowing into the SEPA unit by the high pressure pump, and the permeate water is filtrated by the RO membrane in the SEPA unit and brought into balance to measure the flux. To ensure proper flux measurement, the permeate was fed into a collection vessel held by a balance. Balance measurements were sent to the computer through an Rskey signal.

2.4. Methods

The chemical cleaning efficiency was compared based on different fouling characteristics according to the properties of the organic materials. The artificial feed water with 35 g/L of total dissolved solids (TDS) was made by injecting NaCl into DI water. In addition, HA and SA were injected at a concentration of 50 mg/L, respectively. The operating pressure was 4.0 MPa and a circulating flow (cross-flow velocity) was 1 L/min. When the flux decline rate (FDR) reached 30%, the chemical cleaning was implemented for 1 h using various chemicals, concentrations and contact times. CIP was carried out by selecting five chemicals (NaOH, sodium tripolyphosphate [STP], trisodium phosphate 12 water [TSP], ethylenediaminetetraacetic acid [EDTA–4Na], and sodium dodecylsulfate [SDS]) mainly used for organic fouling under different concentrations and cleaning times in Table 3. However, temperature and cross-flow velocity were 25 ℃ and 1 L/min kept constant during CIP, respectively. These chemical agents were chosen by the guideline of manufacturers of RO membrane and CIP conditions were determined by the previous study of Park et al. [16].

Table 3
The condition of chemical cleaning

Chemicals	Contact time (min)	pH/concentration
NaOH	30, 60	pH 10, 11, 12
STP	30, 60	0.1, 0.5, 1.0%
TSP	30, 60	0.1, 0.5, 1.0%
EDTA–4Na	30, 60	0.1, 0.5, 1.0%
SDS	30, 60	0.05, 0.1, 0.5%

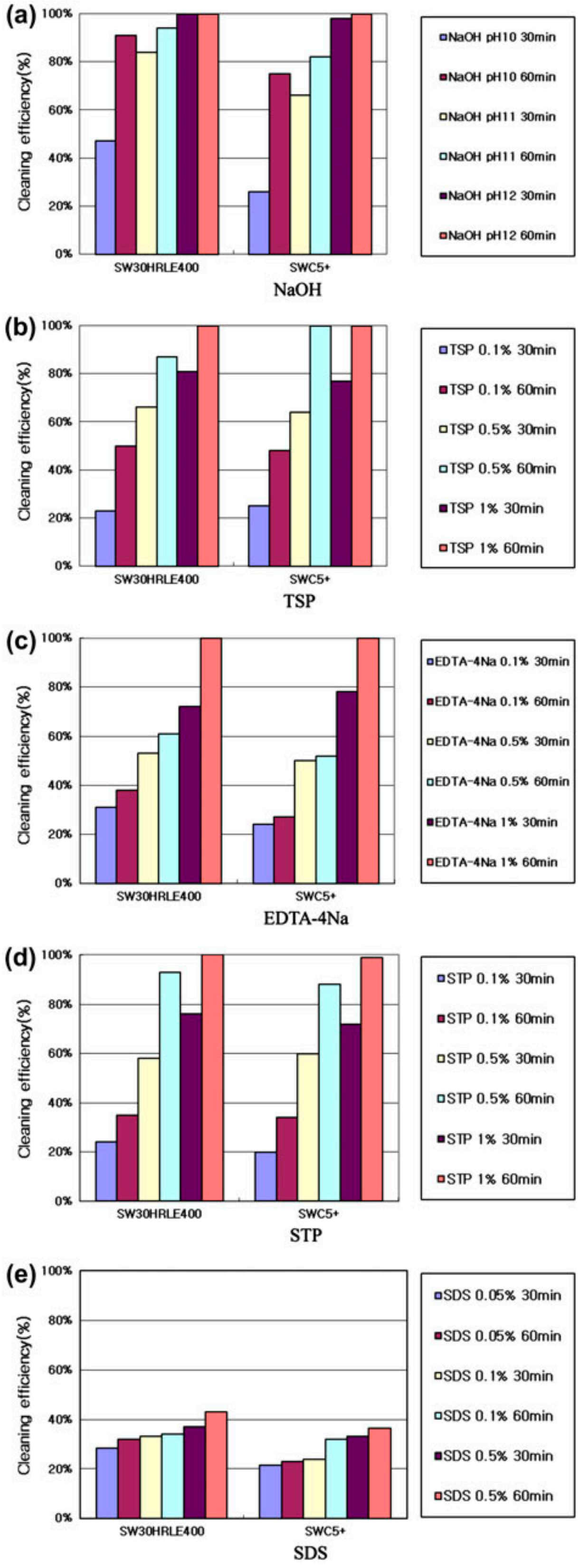

Fig. 2. Cleaning efficiencies by various chemical agents ((a) NaOH, (b) TSP, (c) EDTA–4Na, (d) STP, and (e) SDS).

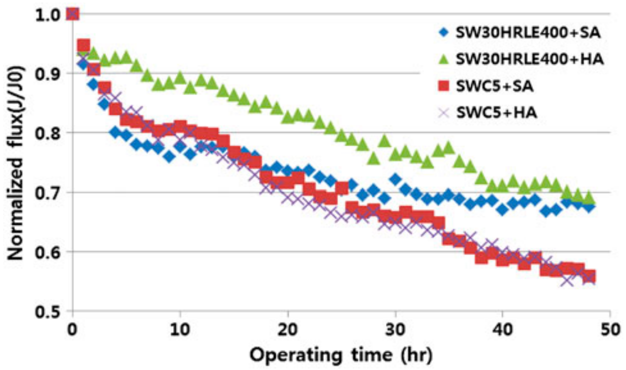

Fig. 3. Flux decline rate according to the organic foulants.

The cleaning efficiency can be calculated as follows for confirmation of the flux recovery after osmotic backwashing:

$$\text{Cleaning efficiency (CE)} = \frac{(f_c - f_f)}{(f_i - f_f)} \times 100\ (\%) \qquad (1)$$

where f_i: initial flux, f_f: declined flux by fouling, and f_c: recovered flux after cleaning.

RO and nano filtration membranes can be described by the well established osmotic-resistance filtration model of total filtration resistance. In this study, total resistance was fractionated by each resistance using Eq. (1) (assuming $M_f = 1$), and the fouling cause was found by analyzing resistances.

$$J = \frac{\Delta P - M_f \Delta\pi}{\mu(R_t)} = \frac{\Delta P - M_f \Delta\pi}{\mu(R_m + R_c + R_a + R_i)} \qquad (2)$$

where J = flux (L/m^{2}h), R_t = total filtration resistance, R_m = initial membrane resistance, R_c = resistance removed by flushing, R_a = resistance removed by CIP, and R_i = irreversible resistance. R_t was obtained by measuring the flux of organic-fouled membrane, R_c was obtained by measuring flux after flushing, and R_a was obtained by measuring flux after CIP. Cleaning efficiency and each resistance were measured at three times and showed as the mean value.

3. Results and discussion

3.1. Cleaning efficiency depending on chemical agents

CIP was conducted to determine the cleaning efficiency according to the chemical agents. Fig. 2 shows the cleaning efficiency of various chemical agents under different concentrations and contact times. When NaOH, TSP, STP, and EDTA–4Na were used without SDS, as the concentration and cleaning time increased, cleaning efficiency increased significantly. The concentrations of NaOH were adjusted at pH 10, 11, and 12. The cleaning efficiency of both membranes was 100% at pH 12 for longer than 30 min. The concentration of TSP increased to 0.1, 0.5, and 1.0%. When applied at 0.5 and 1.0% for 60 min, the cleaning efficiency was more than 80%. Also, the concentrations of EDTA–4Na and STP were changed to 0.1, 0.5, and 1.0%. When applied at only 1.0% for 60 min, the cleaning efficiency was 100%. Finally, the concentration of SDS increased to 0.05, 0.1, and 0.5%; however, in the case of both membranes, the cleaning efficiency was low at 20–40%. In addition, the cleaning efficiency by SDS, which is an anion surfactant, and that by flushing were compared. As a result, there was no significant difference between the two. Thus, it was suggested that chemical cleaning was not effective when only SDS was used and SDS should be used in a mixture with other agents for removing organic foulants.

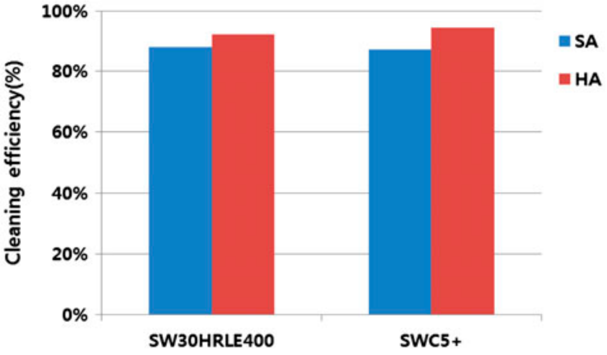

Fig. 4. Cleaning efficiency by NaOH at pH 11.

3.2. Investigation of cause of fouling by analyzing resistances

Fig. 3 shows the flux decline of membrane fouled by organic matters in the conditions of TDS 35 g/L, 5 MPa, and pH 7. The FDR of SWC5+ membrane was higher than that of SW39HRLE400 membrane regardless of organic foulants. Because the initial zetapotential of SWC5+ membrane (–21.17 mV) was lower than that of SW30HRLE400 membrane (−30.11 mV) and the repulsive force between membrane surface and foulants was lower, SWC5+ membrane was fouled relatively more than SW30HRLE400. Also, the hydrophobic interaction and FDR of membrane fouled by HA were lower than those of membrane fouled by SA because HA had lower MW and higher carboxylic acidity than SA [17].

CIP was conducted to investigate the cause of fouling by using NaOH at pH 11 for 60 min, which was one of the effective cleaning conditions. Fig. 4 shows cleaning efficiency according to organic foulants. In the case of both membranes, the cleaning efficiency of membrane fouled by HA was higher than that of membrane fouled by SA because of the high interaction between hydrophobic membrane and hydrophobic foulants.

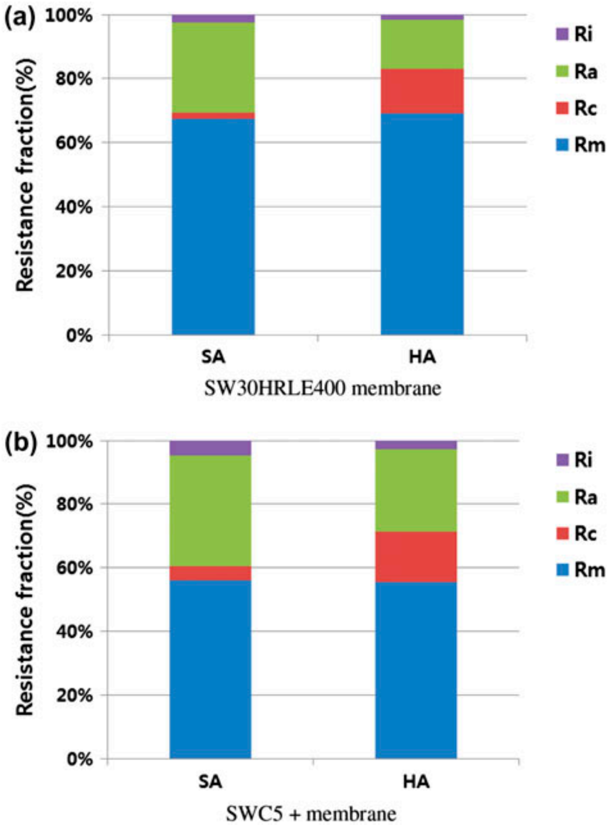

Fig. 5. Resistance fraction of organic-fouled membrane.

To find the fouling rate and fouling cause, total resistance R_t was fractionated by R_m, R_c, R_a, and R_i. Fig. 5 shows that R_c and R_a in both membranes have similar proportions of R_t. As shown in Fig. 5, R_c and R_a in SW30HRLE400 membrane and SWC5+ membrane fouled by SA were 1.87 and 27.96%, and 4.49 and 34.76%, respectively. Also, Fig. 5 shows that R_c and R_a in SW30HRLE400 membrane and SWC5 + membrane fouled by HA were 13.84 and 15.24%, and 15.92 and 25.83%, respectively. From these results, the cause of fouling of membrane fouled by SA was mainly the absorption of membrane surface and that of membrane fouled by HA was the absorption of membrane surface and pore blocking by cake layer.

4. Conclusions

In this study, we selected two commercial membranes which were cleaned using five agents after fouling by organic matters. We then attempted to evaluate cleaning efficiency according to the CIP conditions and investigate the cause of fouling by analyzing membrane resistance fraction after cleaning the organic-fouled membrane.

(1) As a result of CIP, when NaOH, TSP, STP, and EDTA–4Na were used without SDS, as the concentration and cleaning time increased, the cleaning efficiency increased significantly.

(2) The FDR of SWC5+ membrane was higher than that of SW39HRLE400 membrane regardless of organic foulants. In general, as the contact angle and the roughness is larger, interaction force between the membrane and hydrophobic organics is larger [15]. Also, because the initial zeta potential (−21.17 mV) of SWC5+ membrane was lower than that (−30.11 mV) of SW30HRLE400 membrane and the repulsive force between membrane surface and foulants was lower, SWC5+ membrane was fouled relatively more than SW30HRLE400.
As shown in Fig. 2, in the case of both membranes during CIP using NaOH at pH 11 for 60 min, the cleaning efficiency of membrane fouled by HA was higher than that of membrane fouled by SA because of the high interaction between hydrophobic membrane and hydrophobic foulants.

(3) The cause of fouling of membrane fouled by SA was mainly the absorption of membrane surface and that of membrane fouled by HA was the absorption of membrane surface and pore blocking by cake layer. Some researchers reported similarly that SA fouling is more severe than the

one caused by humic acids [9,14,17]. On the contrary, since SA fouling has weak interaction between the membrane surface and the foulant, only physical cleaning (i.e. backwashing, increase of cross-flow velocity, etc.) reduces the fouling.

In general, the resistance fraction analysis is applied to analyze the fouling in the low-pressure membrane. In this study, this method was applied to RO membrane which was operated at high pressure. Therefore, it is suggested that resistance fractions analysis can be used as a tool to evaluate chemical cleaning efficiency and to investigate the cause of fouling.

In future, we would investigate how various conditions (i.e. operating pressure, cross-flow velocity, temperature, characteristic of the membrane and foulants) affect the membrane fouling through resistance fraction analysis.

Acknowledgement

This research was supported by a grant (CTI C-01) from Construction Technology Innovation Program funded by Ministry of Land, Transport and Maritime Affairs of Korean government.

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