Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25851

194 (2020) 52–58
August

A simplified method for the quantification of fouling on reverse osmosis membranes: implication for the selection of effective cleaning chemicals

Naomi Orbaum[a], Linor Serlin[a], Anat Lakretz-Mashiah[b], Semion Brover[c], Eyal Sahar-Hadar[b], Yaal Lester[a,*]

[a]*Environmental Technologies, Department of Advanced Materials, Azrieli College of Engineering, Jerusalem 9103501, Israel, emails: yaalle@jce.ac.il (Y. Lester), nomi.orbaum@gmail.com (N. Orbaum), linor.serlin@gmail.com (L. Serlin)*
[b]*Mekorot-Israel Water Works, 9 Lincoln Street, Tel-Aviv 61201, Israel, emails: alakretz@mekorot.co.il (A. Lakretz-Mashiah), esahar@mekorot.co.il (E. Sahar-Hadar)*
[c]*ADO-Ashdod Desalination Operation, Ashdod 7712602, Israel, email: sbrover@mekorot.co.il (S. Brover)*

Received 6 December 2019; Accepted 20 March 2020

ABSTRACT

Reverse osmosis (RO) is the most popular technology for seawater desalination. A critical RO disadvantage is membrane fouling, which increases the operational cost of treatment and entails frequent chemical cleaning. Quantifying membrane fouling can be used as a tool for the selection of cleaning chemicals, development of cleaning procedures, and more, but it is challenging to perform. This study presents a simple method for fouling quantification at the lab scale. It employs an optical microscope to magnify and photograph fouled membrane coupons. The photomicrographs are then analyzed with optimized ImageJ software (an image-analysis software) to quantify fouling coverage through differences in surface toning. The method developed was successfully applied to quantifying membrane fouling before and after cleaning with 13 different chemicals, and to identify the most effective among them. Lab results were further validated at the pilot-scale, emphasizing the potential of this method as an effective tool for full-scale RO facilities and desalination researchers.

Keywords: Reverse osmosis; Seawater; Fouling; Image-analysis; Cleaning chemicals

1. Introduction

Reverse osmosis (RO) desalination is a leading technology for the production of potable water from seawater and brackish water. Global water production by desalination has tripled over the past two decades, with RO representing by far the most popular technology [1,2]. Notably, desalination is widespread in arid regions such as the Middle East, where seawater is an important source of drinking water [1]. In Israel, for example, seawater desalination provides more than 70% of the overall supply of drinking water, with certain areas of the country receiving more than 90% desalinated water (www.water.gov.il).

One of the main challenges in RO desalination is membrane fouling, generally defined as deposition of suspended or dissolved material on the membrane surface [3]. Fouling increases RO operational costs through (i) reduction in permeate flux and increase in energy demand, (ii) forcing frequent cleaning of membrane, and (iii) reduction in membrane lifetime; this was presented previously in a large number publications [3,4]. For example, Ruiz-García [5] observed a gradual decrease in the performance of a brackish water RO desalination plant over 80,000 h of operation, mainly due to membrane fouling. The main symptoms were increase in feed pressure (of up to 70%) and specific energy consumption; and more frequent chemical cleaning (which was ineffective in the final 10,000 h of operation).

* Corresponding author.

Furthermore, operators had to replace cleaning materials several times in the search for more effective chemicals. Other studies focused on the development of models to predict fouling of membranes at full-scale, in an attempt to optimize membrane cleaning intervals and timing of replacement [6,7].

Different mechanisms and constituents are responsible for membrane fouling, depending on the type and quality of the water source. Important foulants include natural organic matter, inorganic salts (scaling), and microbial attachment and growth (biofouling) [8–10]. Membrane fouling at full-scale is typically controlled through pretreatment and membrane chemical cleaning in place (CIP) [11,12]. Pretreatment aims at improving quality parameters related to the fouling potential of the water, such as the silt density index (SDI), turbidity, and particle count [13]. Chemical CIP involves circulating different cleaning agents through the membranes, with the goal of restoring their performance after fouling.

A wide variety of chemicals is used for cleaning, depending on the type and composition of fouling. Acids are commonly employed for treating inorganic scaling, while bases are used for removing organic fouling and biofouling. Other popular chemicals include surfactants (e.g., sodium dodecyl sulfate – SDS), chelating agents (e.g., ethylenediaminetetraacetic acid – EDTA), and mixtures of various compounds [3,14,15]. Numerous studies evaluated different cleaning procedures, testing parameters such as the combination of diverse chemicals (e.g. only acid, acid-alkali, only alkali, alkali-oxidants), cleaning duration, and more. Park et al. [16] for example, found that alkali-acid cleaning was most effective when organics were the dominant foulants; whereas, Wang et al. [17] showed that using $KMnO_4$ + NaOH, followed by $NaHSO_3$, allowed not only effective cleaning but also the recycling of membrane after their use.

It is therefore clear that selecting suitable and effective cleaning chemicals for full-scale applications is imperative for a reliable RO operation. However, this task is highly challenging for RO operators and engineers, since testing new chemicals at full-scale is impractical, and pilot systems are not always available.

Evaluating the effectiveness of cleaning chemicals in the laboratory is typically performed using a high-pressure bench-scale crossflow test unit, where changes in flux or differences in pressure (Δp) are used to determine fouling removal by a tested chemical [18]. Other methods include low-pressure systems or stirred vessels, with fouled membrane coupons, and quantification of fouling before and after treatment. At full-scale fouling is typically characterized and quantified by performing membrane autopsy [19], which includes cutting the membrane module, detaching the membrane leaves and sending fouled pieces for analysis by, for example, atomic force microscopy [20], colony-forming units, scanning electron microscopy, energy-dispersive X-ray spectroscopy, epifluorescence microscopy, and confocal laser scanning microscopy [4,11,21–23].

The goal of this study was to develop a simple (laboratory) method for quantification of RO membrane fouling, which can be used as a tool for selecting effective cleaning chemicals, developing optimal cleaning procedures, and more. The method employs an optical microscope and image-analysis software and was applied to test and compare the efficacy of 13 different cleaning chemicals on fouled membrane coupons from the Ashdod seawater desalination facility. Image analysis indicated a high potential for online membrane monitoring and the early detection of fouling formation [24,25]; however, previous studies employed complicated software developed especially for their needs. We propose to use a simple, open-access software. In addition, this is the first time image analysis is applied in the context of identifying effective cleaning chemicals.

The Ashdod facility is one of five large RO desalination plants in Israel (capacity of 100 million m^3/y), which altogether provide most of the country's supply of drinking water. Since its construction in 2015, the plant has suffered extensive membrane fouling, resulting in intensive use of cleaning chemicals, and the ongoing need for new and effective chemicals. The results of our lab tests were successfully validated in the plant's pilot-scale system and will be further used for chemical selection for full-scale membrane cleaning.

2. Experimental setup

2.1. Cleaning chemicals examined

The study tested and compared 13 different cleaning chemicals, from different classes and manufacturers (Table 1). Most are commercially available; some are still in development. The detailed composition of the chemicals is proprietary and cannot be published.

2.2. Laboratory cleaning procedure

Examined membranes (polyamide composite spiral wound; Toray TM820R-400) were taken from the first stage of the desalination process. Membranes were in service since the initiation of the Ashdod facility in 2015, operating under typical seawater desalination conditions: feed pressure of approximately 70 bar and 45% recovery. The facility employs a CIP procedure, using acidic and alkali/biocide chemicals alternately, at intervals of several weeks to several months (depending on the need).

Fouled membrane elements were transported in a cooled container (4°C) to the Environmental Technologies Laboratory (Azrieli College of Engineering, Jerusalem) for testing. In a typical cleaning test, membranes were cut as uniformly as possible into 10 squares, each measuring 5 mm × 5 mm, and glued onto a glass microscope slide. The solution of each cleaning chemical was prepared in a 100 mL vessel. 10 membrane squares were submerged in each vessel. The vessel was shaken for 45 min, then soaked for 45 min with no shaking, and finally shaken again for an additional 30 min. The temperature was kept constant at 25°C throughout. This cleaning procedure was not designed for maximal cleaning, but rather to differentiate between the efficacies of the tested chemicals.

2.3. Fouling analysis and quantification

Fouling on the membrane squares was quantified before and after cleaning, to assess the efficacy of the 13

Table 1
Cleaning chemicals tested

Class	Chemical	Main active substances	Concentration applied (%wt.)*
Surfactants	*A*	Sodium dodecyl benzene sulfonate	1
	B	EDTA; NaOH	2
	D	Sodium tripolyphosphate; NaOH, proprietary surfactant	4
	E	$Na_2H_3CO_6$; EDTA; NaOH	2
	F	5-chloro-2-methyl-2H-isothiazol-3-one; 2-methyl-2H-isothiazol-3-one (3:1); $Mg(NO_3)_2$	2
	G	Ethoxylated alcohol; sodium citrate	4
Acidic	*C*	Unknown	4
	M	Trisodium hydroxyethyl-EDTA (HEDTA); hydroxyacetic acid; nitrilotriacetic acid; trisodium salt; methoxyacetic acid	0.5
Basic	*K*	$Na_2H_3CO_6$; EDTA; NaOH	1.5
	L	$Na_2H_3CO_6$; NaOH	1.5
	H	2,2-Dibromo-2-cyanoacetamide; $NaBO_3{\cdot}H_2O$; EDTA; NaOH; tetrasodium pyrophosphate	0.25
Alkaline surfactant	*I*	HEDTA; triethanolamine; ethanolamine; diethanolamine; trisodium nitrilotriacetate	2.5
	J	Trisodium HEDTA; 9-octadecenoic acid; sulfonated, potassium salts; trisodium nitrilotriacetate; NaOH; K_2CO_3	1.5

*According to manufacturer's recommendations

chemicals tested. Each square was first photographed through a Nikon SMZ800N optical microscope (×40; Morrell Instruments Co. Inc., New York) using a DeltaPix 200 camera. Microscope working distance and camera contrast/brightness were kept constant throughout for consistent image processing. Surface coverage of the fouling was then analyzed and quantified using ImageJ software (v1.52p) – an open-access NIH Java-based image-processing program, which measures multiple pixels and calculates area based on user-defined selections. In this instance, fouling was identified according to differences in color tone, with each pixel brighter than a defined level-designated as fouling. The most appropriate brightness threshold was carefully selected using ten random micrographs.

2.4. Pilot-scale experiments

The Ashdod plant's pilot system comprises a 400 L feed tank, a high-pressure pump (9 m^3/h) and two serially connected pressure vessels, each containing four membrane elements (Fig. 1).

The system was operated at 44% recovery, using either flow-through mode during stabilization or full-recycle for membrane cleaning. Prior to cleaning, eight fouled membrane elements were taken from the desalination plant and placed in the pilot vessels. Seawater was then pumped through the system for 24 h to stabilize all parameters (e.g., pressure), and membranes were then backwashed using permeate water. Cleaning tests were designed to simulate the full-scale procedure. First, the tested cleaning chemical was mixed in the feed tank and circulated through the membranes for 2 min. Next, a sequence of soaking (no flow), chemical circulation and repeat soaking was applied (45 min for each phase). Finally, membranes were backwashed to remove chemical residues, and seawater was reintroduced for 24 h at flow-through mode.

2.5. Statistical analysis

Removal degree (%) of fouling by the different chemicals is presented as mean and standard errors of eight 5 mm × 5 mm squares. The two extreme values from each test were omitted. One-way analysis of variance (ANOVA) was performed at a 95% confidence level, followed by the Tukey HSD post hoc test, to determine statistical significance.

3. Results and discussion

3.1. Fouling quantification

Photomicrograph examples of membrane squares, taken by the DeltaPix 200 camera before and after cleaning, are presented in Fig. 2. The image analysis process is shown in Fig. 3.

Photomicrographs were uploaded to the ImageJ software for analysis. The software was calibrated by setting a clean white membrane as background and optimizing pixel brightness and contrast (from 48 to 210 arbitrary units).

Black and white detection threshold were set at 56.2%, with all pixels darker than this threshold designated as fouling. Based on these parameters, uploaded images were made binary by the software (each pixel stored as a single bit — i.e., black or white). The software then measured the fouling and the total membrane surfaces. Eq. (1) was used

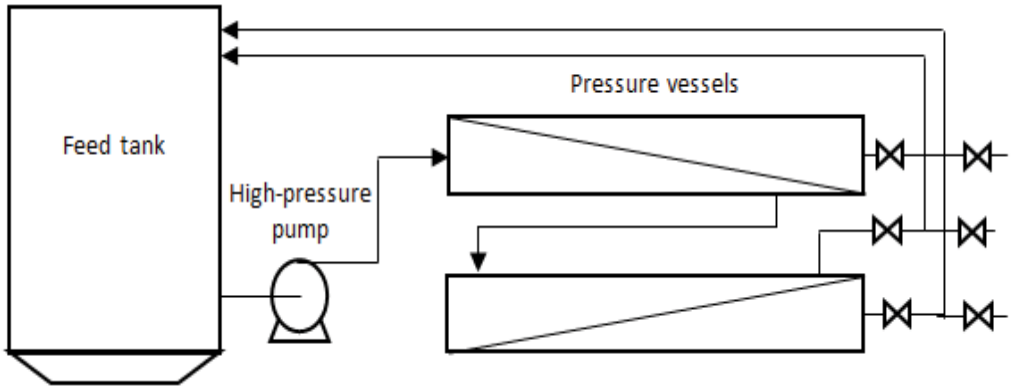

Fig. 1. Schematic diagram of the pilot system.

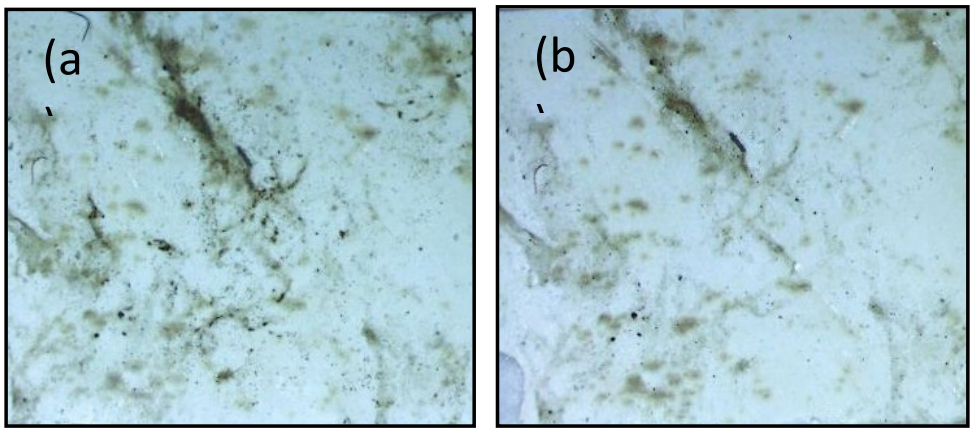

Fig. 2. Photomicrographs of a 5 mm × 5 mm membrane square (a) before and (b) after chemical cleaning, taken by the DeltaPix 200 camera.

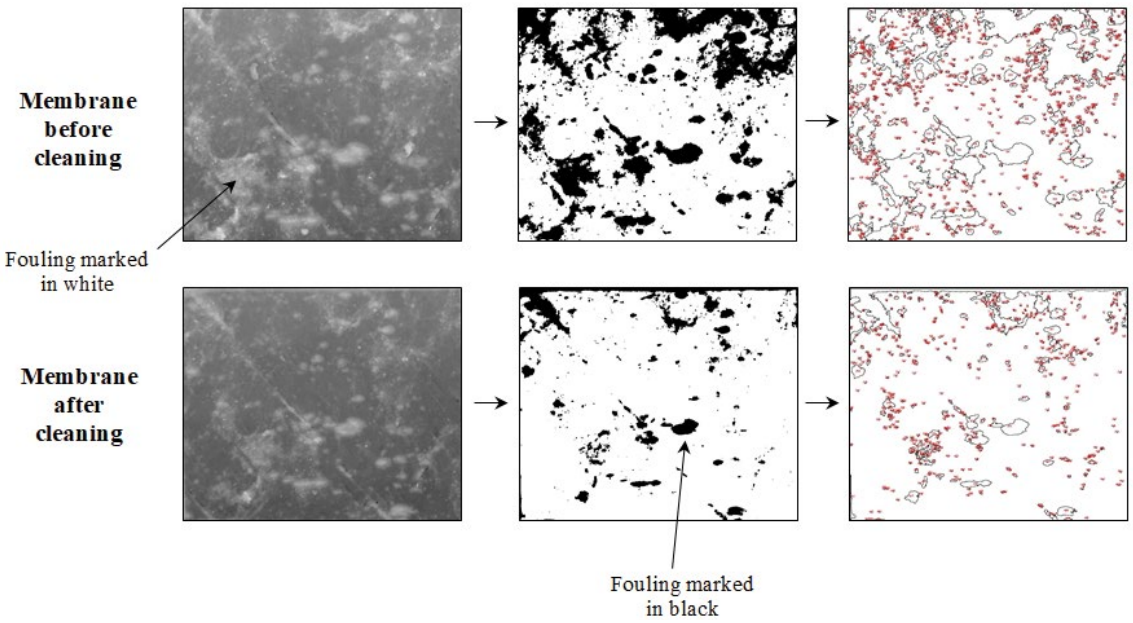

Fig. 3. ImageJ processing technique: (left) photomicrograph of the membrane, (middle) photomicrograph converted to a binary image, and (right) polygon numbering and surface coverage.

to calculate the fouling removal rate for each 5 mm × 5 mm square. An example (for chemical *A*) is presented in Table 2.

$$\%\ \text{Fouling removed} = \frac{\text{Fouling area before cleaning} - \text{Fouling area after cleaning}}{\text{Fouling area before cleaning}} \times 100 \quad (1)$$

3.2. Comparing different chemicals at lab scale

Using the method developed, fouling removal from membrane squares by the different chemicals was calculated and measured (Fig. 4). A significant difference in the degree of fouling removal ($p < 0.05$, ANOVA) was found between chemicals *E*, *H* and *D*, (*E* > *H* > *D*). Chemical *D* was not significantly better than *J* ($p > 0.05$, ANOVA), which in turn had no statistical significance with chemicals *F*, *M*, *G* and *K*. Efficiency of chemical *C* was statistically lower than *K* and equal to *A*. No difference can be seen between the efficiencies of the last four chemicals (the least efficient). Interestingly, we could not identify any correlation between fouling removal efficiency and the (known) composition of the chemicals. This implies that: (i) fouling is not homogenous, but rather composed of a mixture of organic, biological and inorganic elements and (ii) proprietary constituents in the chemicals substantially contribute to fouling removal.

Table 2
Fouling removal by chemical *A* using ImageJ software data

Membrane square *N*°	Fouling area (pixels)		Fouling removed (%)
	Before cleaning	After cleaning	
1	78,215	59,925	23.4
2[a]	181,623	180,210	0.8
3	78,373	58,241	25.7
4	106,651	82,259	22.9
5	85,500	67,295	21.3
6	61,595	37,347	39.4
7	87,818	71,860	18.2
8	98,892	62,370	36.9
9	87,196	63,500	27.2
10[a]	56,317	31,483	44.1
Average removal (%)			27.4 (±8.7)

[a]Extreme values omitted from the statistical analysis

3.3. Pilot-scale testing

As a result of the lab finding, the Ashdod desalination plant has selected two chemicals (*H* and *M*), with different efficiencies, for further testing in its onsite pilot system. The chemicals were additionally selected according to their availability and cost. The efficiency of the chemicals in the pilot system was evaluated by monitoring the specific water flux and feed pressure, before and after cleaning, while maintaining a constant flow rate. Results indicate that chemical *H* is superior to chemical *M* as a cleaning agent, increasing specific flux, and decreasing feed pressure by approximately 68% and 5% respectively (Table 3).

Specific flux (which is the water flux divided by Δp) is often used as indication of membrane fouling and the restoration of membrane productivity after chemical cleaning [26]. Changes in feed pressure are indicatives of the fouling situation of the spacer between the membrane envelopes, and a decrease in feed pressure may imply an effective spacer cleanup. The data presented in Table 3 correlate well with the laboratory findings (Fig. 4), which showed chemical *H* to be significantly more efficient than chemical *M*.

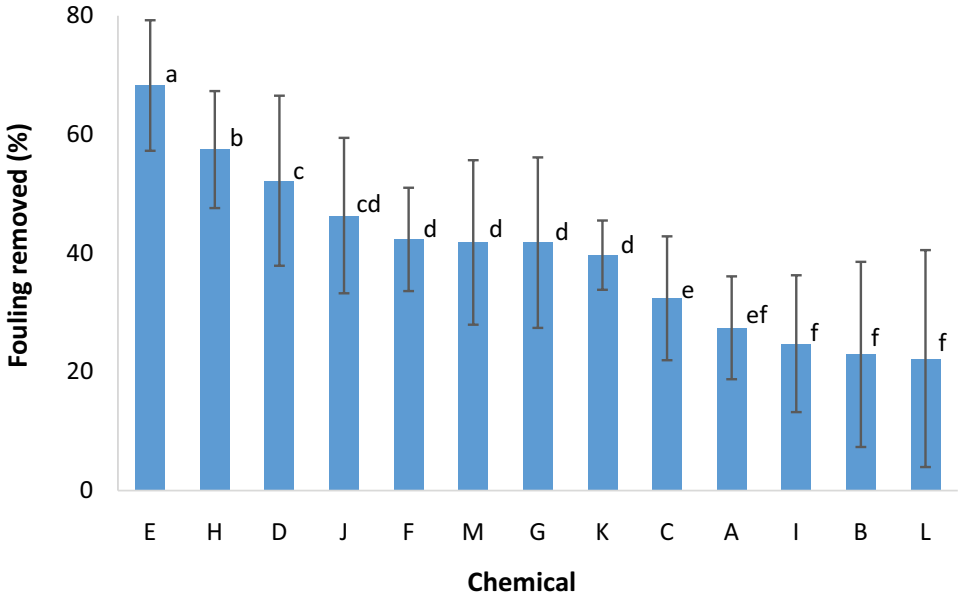

Fig. 4. Fouling removed (%) by the different chemicals presented in order of chemical efficiency. Columns topped by the same letter were not significantly different ($p > 0.05$) according to one-way ANOVA.

Table 3
Data from the experiments in the Ashdod pilot system

Chemical	Specific flux (L/m^2 h bar)		Feed pressure (bar)		Improvement (%)	
	Before cleaning	After cleaning	Before cleaning	After cleaning	Specific flux	Feed pressure
H	8.0	13.5	56.5	52.5	67.9	5
M	10.7	11.8	47.8	46.9	10.6	1.9

4. Conclusions

Membrane fouling is a major drawback of RO desalination, affecting the operational cost of full-scale facilities through, for example, increased consumption of cleaning chemicals. Quantifying membrane fouling may be highly advantageous for the selection of effective cleaning chemicals, optimization of cleaning procedures and more. This study demonstrates a simple and effective method for fouling quantification, using optical microscopy and image-analysis software. It demonstrates that the method can be used for evaluating the efficacy of different cleaning chemicals in the laboratory, and that results correlate well with fouling removal in a pilot RO system (for two of the chemicals). The method developed can be used by desalination plants as an operational tool for selecting and applying cleaning chemicals, and by desalination scientists for studying fouling formation and removal processes and mechanisms. It should be noted, however, that the method is limited to visible foulants, such as colored organics and microorganisms.

Acknowledgment

We would like to thank the Ashdod desalination technical staff (Mor Gindin and Rafael Ochaion) for assisting with the pilot operation.

References

[1] IDA, Desalination Yearbook 2016–2017, International Desalination Association, Topsfield, MA 01983, USA, 2016, pp. 1–30.
[2] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res., 43 (2009) 2317–2348.
[3] S.X. Jiang, Y.N. Li, B.P. Ladewig, A review of reverse osmosis membrane fouling and control strategies, Sci. Total Environ., 595 (2017) 567–583.
[4] A. Al Ashhab, A. Sweity, B. Bayramoglu, M. Herzberg, O. Gillor, Biofouling of reverse osmosis membranes: effects of cleaning on biofilm microbial communities, membrane performance, and adherence of extracellular polymeric substances, Biofouling, 33 (2017) 397–409.
[5] A. Ruiz-garcía, E. Ruiz-Saavedra, 80,000 h operational experience and performance analysis of a brackish water reverse osmosis desalination plant. Assessment of membrane replacement cost, Desalination, 375 (2015) 81–88.
[6] A. Ruiz-García, I. Nuez, Long-term performance decline in a brackish water reverse osmosis desalination plant. Predictive model for the water permeability coefficient, Desalination, 397 (2016) 101–107.
[7] S.J. Lim, Y.M. Kim, H. Park, S.J. Ki, K.H. Jeong, J.W. Seo, S.H. Chae, J.H. Kim, Enhancing accuracy of membrane fouling prediction using hybrid machine learning models, Desal. Water Treat., 146 (2019) 22–28.
[8] S.P. Chesters, Innovations in the inhibition and cleaning of reverse osmosis membrane scaling and fouling, Desalination, 238 (2009) 22–29.
[9] 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.
[10] T. Tong, A.F. Wallace, S. Zhao, Z. Wang, Mineral scaling in membrane desalination: mechanisms, mitigation strategies, and feasibility of scaling-resistant membranes, J. Membr. Sci., 579 (2019) 52–69.
[11] C. Whittaker, H. Ridgway, B.H. Olson, Evaluation of cleaning strategies for removal of biofilms from reverse-osmosis membranes, Appl. Environ. Microbiol., 48 (1984) 395–403.
[12] P.S. Goh, W.J. Lau, M.H.D. Othman, A.F. Ismail, Membrane fouling in desalination and its mitigation strategies, Desalination, 425 (2018) 130–155.
[13] A. Matin, Z. Khan, S.M.J. Zaidi, M.C. Boyce, Biofouling in reverse osmosis membranes for seawater desalination: phenomena and prevention, Desalination, 281 (2011) 1–16.
[14] K.-B. Park, C.K. Choi, H.-W. Yu, S.-R. Chae, I.S. Kim, Optimization of chemical cleaning for reverse osmosis membranes with organic fouling using statistical design tools, Environ. Eng. Res., 23 (2018) 474–484.
[15] J.M. Arnal, B. García-Fayos, M. Sancho, Chapter 3: Membrane Cleaning, R.Y. Ning, Ed., Expanding Issues in Desalination, IntechOpen Limited, London UK, 2011, pp. 63–84.
[16] K.T. Park, J.Y. Park, M.J. Kim, H.S. Kim, P.R. Kim, J.-H. Kim, Evaluation of maintenance chemical cleaning in seawater reverse osmosis pilot plant using hot wastewater from power plant, Desal. Water Treat., 141 (2019) 1–7.
[17] M. Wang, Z.J. Yu, Y. Zhang, X.F. Zhou, H.Q. Chu, Cleaning and regeneration of irreversibly fouled and discarded reverse osmosis membranes: method and mechanism, Desal. Water Treat., 137 (2019) 1–10.
[18] A. Sweity, Y. Oren, Z. Ronen, M. Herzberg, The influence of antiscalants on biofouling of RO membranes in seawater desalination, Water Res., 47 (2013) 3389–3398.
[19] A. Ruiz-garcía, N. Melián-Martel, V. Mena, Fouling characterization of RO membranes after 11 years of operation in a brackish water desalination plant, Desalination, 430 (2018) 180–185.
[20] Q.L. Li, M. Elimelech, Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms, Environ. Sci. Technol., 38 (2004) 4683–4693.
[21] T. Nguyen, F.A. Roddick, L. Fan, Biofouling of water treatment membranes: a review of the underlying causes, monitoring techniques and control measures, Membranes (Basel), 2 (2012) 804–840.
[22] F. Beyer, J. Laurinonyte, A. Zwijnenburg, A. Stams, C.M. Plugge, Membrane fouling and chemical cleaning in three full-scale reverse osmosis plants producing demineralized water, J. Eng. (United States), 2017 (2017) 1–14, doi: 10.1155/2017/6356751.
[23] L. Weinrich, C.N. Haas, M.W. LeChevallier, Recent advances in measuring and modeling reverse osmosis membrane fouling in seawater desalination: a review, J. Water Reuse Desal., 3 (2013) 85–101.
[24] M. Uchymiak, A.R. Bartman, N. Daltrophe, M. Weissman, J. Gilron, P.D. Christofides, W.J. Kaiser, Y. Cohen, Brackish water reverse osmosis (BWRO) operation in feed flow reversal

mode using an ex situ scale observation detector (EXSOD), J. Membr. Sci., 341 (2009) 60–66.
[25] A.R. Bartman, E. Lyster, R. Rallo, P.D. Christo, Y. Cohen, Mineral scale monitoring for reverse osmosis desalination via real-time membrane surface image analysis, Desalination, 273 (2011) 64–71.
[26] L.N. Sim, T.H. Chong, A.H. Taheri, S.T.V. Sim, L. Lai, W.B. Krantz, A.G. Fane, A review of fouling indices and monitoring techniques for reverse osmosis, Desalination, 434 (2018) 169–188.