Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986 © 2010 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2010.1666

15 (2010) 48–53
March

Behaviors of commercialized seawater reverse osmosis membranes under harsh organic fouling conditions

Phan Vu Xuan Hung, Seung-Hee Cho, Jung-Je Woo, Seung-Hyeon Moon*

Department of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST),
Gwangju, 500-712, Korea
Tel. +82 (62) 970-2435; Fax +82 (62) 970-2434; email: shmoon@gist.ac.kr

Received 12 November 2009: Accepted in revised form 25 December 2009

ABSTRACT

Reverse osmosis performance is often limited by membrane fouling, which reduces the permeate flux and membrane life-span, requires costly pretreatment, higher operating pressure, and frequent chemical cleaning; results in increased water cost. Organic fouling is inevitable in seawater reverse osmosis (SWRO) desalination plants because certain amount of humic substances — organic foulants — naturally exists in seawater. In this study, the effect of harsh organic fouling condition on performance of four commercialized SWRO membranes was compared. The performance here was defined as flux, salt rejection and boron rejection. The performance variation pattern was similar for all tested membranes. Contact angles of clean and fouled membranes were measured and analyzed to gain insight into the fouling mechanism. The results provided the clue to investigate the interaction of humic acid and membrane surfaces, how important are membrane surface properties in the interaction.

Keywords: Organic fouling; Reverse osmosis membranes; Desalination; Surface properties; Flux decline

1. Introduction

In recent years, reverse osmosis (RO) technology has been widely applied to desalinate seawater as well as brackish waters from saline aquifers and rivers [1]. However, fouling remains as one of the major challenges in plant operation and maintenance [2,3]. Membrane fouling reduces the permeate flux and membrane life-span, requires costly pretreatment, higher operating pressure, and frequent chemical cleaning; results in increased water cost [2,4–6]. Organic fouling, which is caused by the accumulation organic foulants (mostly known as natural organic matter — NOM) on the membrane surface, is inevitable in seawater reverse osmosis (SWRO) desalination plants because certain amount of NOM naturally exists in seawater [2,5]. Understanding the fouling behaviors of different types of RO membranes helps a researcher and engineer to choose the proper membrane in particular conditions. However, there is a limited number of studies on organic fouling for RO membranes which are also significantly fouled by NOM as mentioned above [2]. Most of the existing organic fouling studies have emphasized ultrafiltration (UF) and nanofiltration (NF) because they are often used to remove NOM from surface water [4,7]. Previous studies have used humic acid (representative of organic foulants) at a low concentration resembling NOM concentration in seawater (< 5 mg/l) [2,8]. In this study, the effect of harsh organic fouling condition (high concentra-

---

* Corresponding author.

Presented at SeaHERO Academic Workshop on Development and Optimization of SWRO Desalination Systems
Korea University, Seoul, Korea, November 13–14, 2009

tion of humic acid — 10 mg/l) on the performance of four commercialized SWRO membranes was compared. The performance here was defined as flux, salt rejection and boron rejection. Contact angles were also investigated to elucidate the effect of organic foulants on hydrophobicity of membrane surfaces.

2. Materials and methods

All chemicals used are pure grade chemicals. NaCl was provided by DC Chemicals (Korea); Boric acid and humic acid (HA) were provided by Sigma-Aldrich (USA). Four tested commercialized polyamide thin-film composite SWRO membranes from different companies in different countries were named A, B, C, and D. More specifications are given in Table 1. The flat-sheet membranes received were stored in vacuum-sealed plastic bags containing storage solution. Before operation, membranes were washed with deionized (DI) water and then soaked in DI water for 24 h.

A lab-scale plate-frame type membrane unit (SEPA CF II, Osmonics) was used for all organic fouling tests. The membrane is flat-sheet type with an effective area 0.0125 m^2. The operating pressure 800 psi, temperature 25°C and cross-flow velocity around 10 cm/s were maintained in all stages of each experiment. Before carrying out the real organic fouling test, membranes was precompacted and stabilized [2]. The precompaction step was conducted for 10 h with DI water as feed solution in order to compact the membrane tightly between two stainless steel sheets. The system was then proceeded to stabilization step for 20 h with the solution containing NaCl 32,000 mg/l, [B] 5 mg/l (concentration of all boron species converted to boron). Once the performances of the membranes, in terms of permeate flux and conductivity rejection, were stable, their variation later can be convincingly attributed to foulants. The permeate flux, salt rejection and boron rejection at the end of the stabilization step were named stabilized flux, stabilized salt rejection and stabilized boron rejection. The fouling test was initiated by spiking HA stock solution to feed solution of the stabilizing step to obtain 10 mg/l HA. During a three-day operation time, the conductivity of the feed solution and permeate solution as well as permeate flowrate were monitored periodically. The permeate samples also were taken to analyze boron concentration by inductively coupled plasma — optical emission spectrometry (ICP-OES) method.

Table 1
Membrane specification provided by the vendors

Membrane	Area[1] (m^2)	Flowrate[2] (m^3/d)	Salt rejection[2] (%)	Boron rejection[3] (%)
A	34.4	22.7	99.75	92
B	37	24.6	99.8	93
C	37	24.6	99.75	93
D	35	22.7	99.7	—

[1] Element with 8-inch outer diameter and 40-inch long
[2] Performance at standard test condition for 8″ spiral-would SWRO membrane: 800 psi, 32,000 mg/l NaCl
[3] At pH 8 and 5mg/l boron feed with the standard test condition

Contact angles of the clean and fouled membranes were measured to evaluate the relative hydrophobicity before and after fouling tests. The measurement was conducted using a goniometer (model 100, Ramé-Hart, Montrian Lakes, USA) by a sessile drop method whose images were captured and interpreted by DROPImage Advanced software [9]. The clean membranes was treated by washing with DI water then soaked in DI for 24 h (similar to the treatment before the fouling test) and finally dried in atmosphere for 4 days before the measurement. For the fouled membranes, the membranes collected after fouling tests were gently washed with DI water then dried in atmosphere for 4 days before measuring. The measurement of each membrane type was replicated more than 10 times to calculate average contact angles and theirs standard errors.

3. Results and discussion

3.1. Surface behavior of clean and fouled membranes

The images of clean and fouled membranes after organic fouling test are presented in Fig. 1. It is obvious that there is a dark-brownish humic acid layer deposited on the membrane surfaces (hereinafter referred as a foulant layer). That layer was not evenly distributed due to the feed spacer; the deposited foulants were mitigated at spacer filaments. The layer is considered thicker in the case of membrane C based on the darkness.

Impacts of the foulant layer on membrane hydrophobicity were elucidated by contact angle measurement presented in Table 2. As shown in the table, there is no statistical correlation of contact angles between clean and fouled membranes (Pearson correlation coefficient $r^2 = 0.05$). However, the fact was that all membrane hydrophobicity significantly increased after the fouling test, especially membranes A and C. This is deduced that mainly hydrophobic HA deposited on the membrane surfaces. The results were important in understanding the fouling mechanism. Initially, the interaction of hydrophilic membrane surface and hydrophobic HA is likely to mitigate fouling phenomena. The first deposited layer then changed the membrane surface to hydrophobic and promoted hydrophobic-hydrophobic interaction that enhanced the fouling phenomenon. Standard errors of contact angles of fouled membranes were much higher than those of clean membranes because of unevenly distributed foulant layer aforementioned.

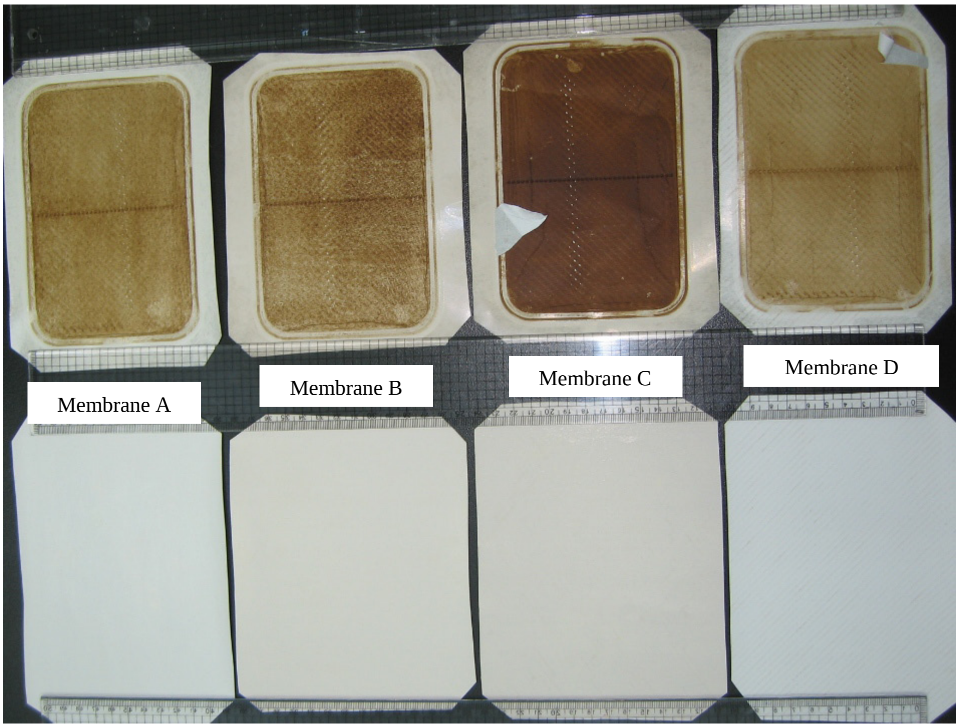

Fig. 1. Images of membranes before (below images) and after (upper images) the fouling test.

Table 2
Contact angles and membrane performances before and after fouling tests

Membrane	Contact angles[1]		Stabilized flux (m/d)	Flux decline (%)	Salt rejection (%)		Boron rejection (%)	
	Clean	Fouled			Stabilized	End of fouling test	Stabilized	End of fouling test
A	32.9±1.5	76.0±3.3	0.73	23.5	98.3	98.5	72.6	67.2
B	40.4±1.1	61.2±5.1	0.62	21.8	98.1	98.6	80.2	79.4
C	34.9±1.1	73.6±6.0	0.83	28.6	97.4	98.6	83.4	82.1
D	30.1±2.5	61.7±4.4	0.57	19.2	97.3	99.0	83.1	84.0

[1] The values were given by average ± standard error (f = 6–19, p = 0.05 – confident level 95%)

The correlation between contact angles and flux declines of four membranes are graphically presented in Fig. 2. It can be seen that there is no correlation between the contact angles of clean membranes and flux declines. This observation was consistent with a previous study [10]. It is noted that the contact angles of all tested clean SWRO membranes were in highly hydrophilic range (30.1°–40.4°). Consequently, it was suggested that the slight change in hydrophilicity does not affect membrane fouling in terms of flux decline. The data in Fig. 2 demonstrate that the contact angles of fouled membranes somehow correlate with flux decline, even though the trend was not obviously observed. Membranes A and C with higher flux declines (23.5 and 28.6, respectively) showed higher contact angles (fouled ones). Both higher contact angles and flux declines might be caused by more foulants deposited on the membrane surfaces.

3.2. *Performance variation during the fouling test*

The summary of contact angles, flux declines, salt rejection and boron rejection is presented in Table 2. The variation of normalized fluxes during operation time of four membranes is demonstrated in Fig. 3. Though the absolute stabilized fluxes of four membranes were different (Table 2), the decline pattern of normalized flux was almost similar. The slope of normalized flux was analyzed to see how severely the flux declined during the operation time. Almost all slopes were negative indicating that flux was decreasing (hereinafter ‘slope’

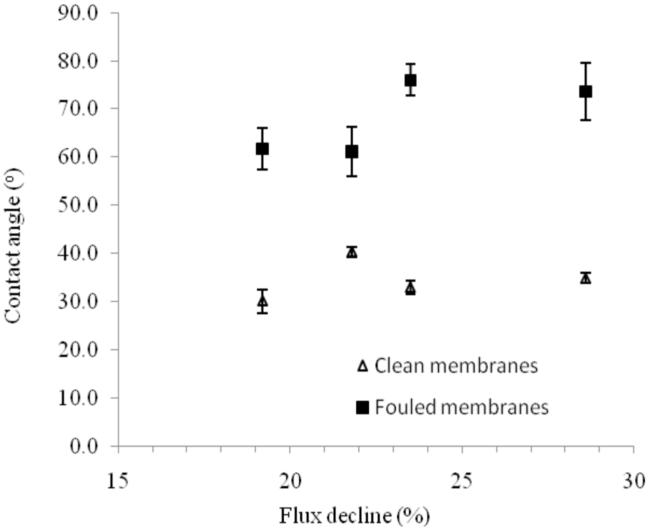

Fig. 2. Correlation between flux declines and contact angles.

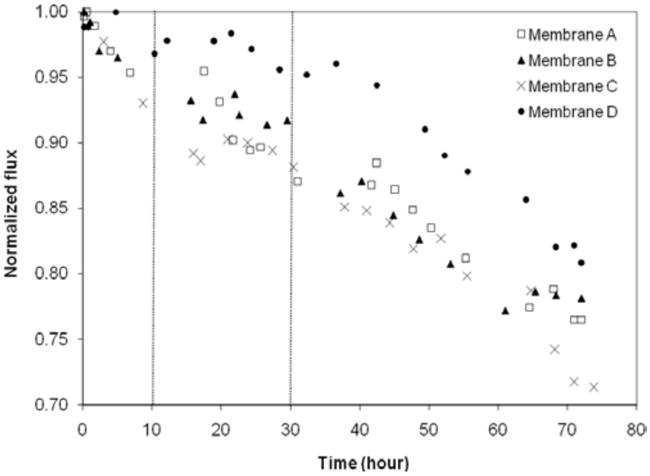

Fig. 3. Normalized flux variation during the fouling tests.

was referred to as 'slope magnitude', regardless of the sign). The higher slope, the more severe flux declined. According to the slope analysis, 72 h operation time was fundamentally divided into three stages: 0–10 h; 10–30 h and 30–72 h; and slopes of each stages are given in Table 3. For almost all cases, the magnitude of the slope was similar at each stage and varied similarly from stage 1 to stage 3. Consequently, the decline characteristics varied through stages. In the first 10 h, the slope was the highest (except membrane D) due to the initial blocking of diffusive routes by HA molecules [2,11]. The exceptional slope of membrane D in this stage (positive slope) was not well understood. It might be attributed to the highest potential of fouling resistance of membrane D, revealing in its much higher normalized flux compared to the remaining membranes. The second stage had the lowest slope (except membrane A) owing to the hydrophilic–hydrophobic interaction of the membrane surface and foulants causing slow deposit of foulants on the membrane surface. The high slope of A in this stage could be due to the sudden increase of pressure at the time of flowrate measurement. After a foulant layer was formed, the flux decline was enhanced in the last stage of the experiments (4–10 times enhancement of the slope accordingly). The variation trend of the second and last stages was consistent with the fouling mechanism rationalized by contact angle measurement in the previous section.

Table 3
Slopes of normalized flux in different stages of the fouling test

	A	B	C	D
Stage 1 (0–10 h)	–0.0070	–0.0073	–0.0083	0.0026
Stage 2 (10 h–30 h)	–0.0059	–0.0009	–0.0003	–0.0006
Stage 3 (30 h–72 h)	–0.0038	–0.0032	–0.0039	–0.0039

In this study, it was found that the stabilized flux correlated with flux decline, shown in Fig. 4. The higher water flux causes the higher convective flux of foulants toward membrane surfaces, resulting in more foulants deposited on the membranes surfaces.

Salt rejection of four membranes also varied similarly although their stabilized salt rejections were different (Fig. 5). For all four membranes, salt rejections increased sharply during the first 1–2 h, then they were constant in the next 30 h and gradually declined after that. It was suggested that in the beginning of the fouling test, humic acid instantly blocked the diffusive routes of solutes causing the increase of salt rejection [2,11]. The next stable stage of salt rejection was supposedly attributed to the foulant layer growth on the membrane surfaces, which did not

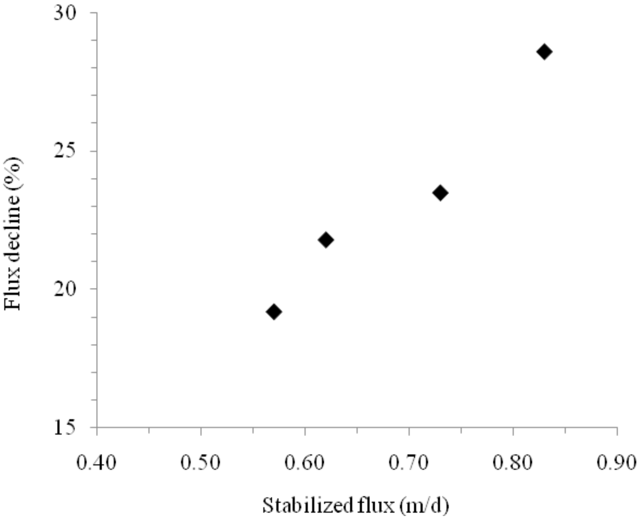

Fig. 4. Correlation between stabilized fluxes and flux declines of four membranes.

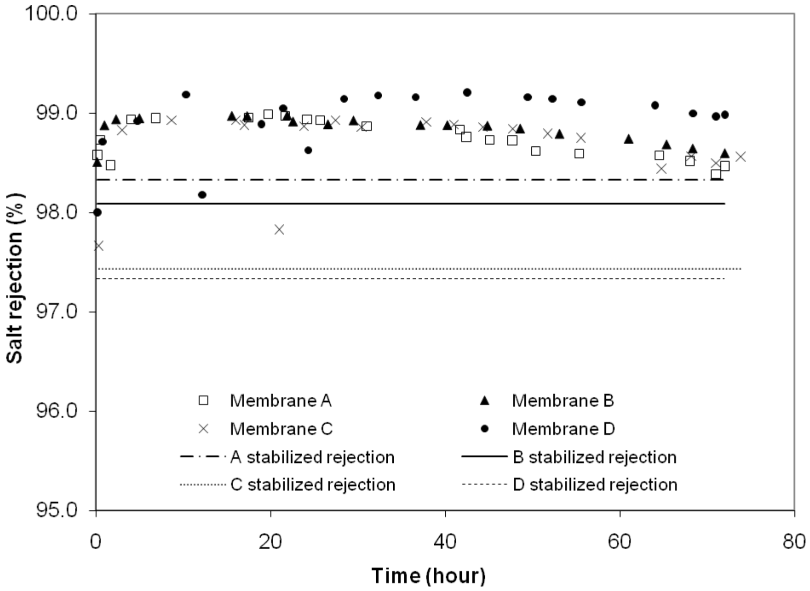

Fig. 5. Salt rejection variation during the fouling tests.

affect salt rejection. Once a compact foulant layer was formed, it significantly modified the membrane surface properties, including the change from hydrophilic to hydrophobic as mentioned above. The hydrophobic surface reduces charge repulsion, one important mechanism of salt rejection. That might result in the gradual decrease of salt rejection in the last 40 h. In addition to a similar variation trend, absolute salt rejections of membranes A, B and C during the fouling test were very close despite the fact that their stabilized salt rejections (without HA in the feed solution) were different (98.3, 98.1 and 97.4% respectively). In the case of membrane D, its stabilized salt rejection was the lowest (97.3%) but its salt rejection was the highest after around one day. That was again because of a high potential of fouling resistance of membrane D. Those observations indicate that once membranes induce organic fouling, the foulant layer contributes noticeably in modifying the membrane surface properties.

Another parameter considered was boron rejection. It is demonstrated in Fig. 6 that boron rejection of four

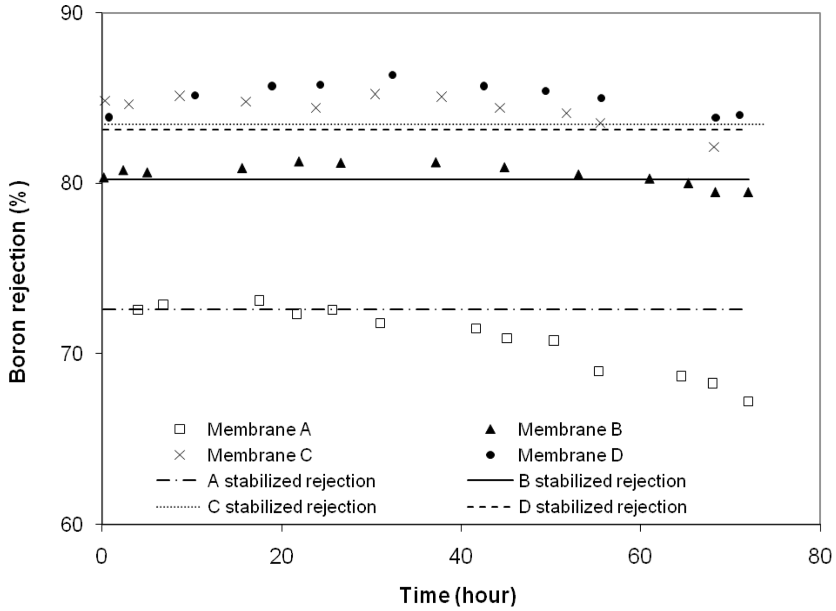

Fig. 6. Boron rejection variation during the fouling tests.

tests varied similarly: it remained constant in the first 50 h and slightly decreased after that. This variation pattern is similar to the salt rejection variation which is elucidated above, except the first 2 h during which the boron rejection was not monitored. Unlike salt rejection, stabilized boron rejection and boron rejection during the fouling test were correlative. It is well known that boron existing in natural pH (feed pH in this study) almost as boric acid which is very small and uncharged. Boric acid molecules might pass through the fouling layer easily and interact with the membrane surface and become similar as boric acid interacts with virgin membranes. Borate, its conjugated base existing at high pH, however, is negatively charged and has a hydrated layer so it is rejected higher by SWRO membranes [12]. Therefore, the investigation on boron rejection during organic fouling at high pH should be conducted further.

4. Conclusions

Although four membranes were provided from four different companies, they are all thin-film composite polyamide membranes. Therefore, their similar variation pattern of normalized flux, salt rejection and boron rejection aforementioned suggested that a slight difference in membrane surface properties does not affect the organic fouling behavior. In the highly hydrophilic range, there is no correlation between contact angles of clean membranes and flux decline. However, it seems that the higher flux decline, the higher contact angles of fouled membranes. The magnitude of flux decline is found to be in linear relationship with the stabilized flux. It is also inferred from the results of salt rejection that as long as membranes induce fouling, foulant–permeant interaction plays in important role in determining the permeant rejection.

Acknowledgements

This research was supported by a grant (07seaheroB02-01-01) from the Plant Technology Advancement Program funded by the Ministry of Land, Transport and Maritime Affairs of the Korean government.

References

[1] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas and A.M. Mayes, Science and technology for water purification in the coming decades. Nature, 452(7185) (2008) 301–310.

[2] C.Y. Tang, Y.-N. Kwon and J.O. Leckie, Fouling of reverse osmosis and nanofiltration membranes by humic acid — Effects of solution composition and hydrodynamic conditions. J. Membr. Sci., 290 (2007) 86–94.

[3] W.S. Ang, S. Lee and M. Elimelech, Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes. J. Membr. Sci., 272 (2006) 198–210.

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

[5] C. Fritzmann, J. Löwenberg, T. Wintgens and T. Melin, State-of-the-art of reverse osmosis desalination. Desalination, 216 (2007) 1–76.

[6] J.A. Redondo and I. Lomax, Experiences with the pretreatment of raw water with high fouling potential for reverse osmosis plant using FILMTEC membranes. Desalination, 110 (1997) 167–182.

[7] A.I. Schäfer, A. Pihlajamäki, A.G. Fane, T.D. Waite and M. Nyström, Natural organic matter removal by nanofiltration: effects of solution chemistry on retention of low molar mass acids versus bulk organic matter. J. Membr. Sci., 242 (2004) 73–85.

[8] C.Y. Tang, Y.-N. Kwon and J.O. Leckie, The role of foulant-foulant electrostatic interaction on limiting flux for RO and NF membranes during humic acid fouling —Theoretical basis, experimental evidence, and AFM interaction force measurement. J. Membr. Sci., 326 (2009) 526–532.

[9] S. Sarp, S. Lee, X. Ren, E. Lee, K. Chon, S.H. Choi, S. Kim, I.S. Kim and J. Cho, Boron removal from seawater using NF and RO membranes, and effects of boron on HEK 293 human embryonic kidney cell with respect to toxicities. Desalination, 223 (2008) 23–30.

[10] C. Hobbs, S. Hong and J. Taylor, Effect of surface roughness on fouling of RO and NF membranes during filtration of a high organic surficial groundwater. J. Wat. Supply: Res. Technol. — AQUA, 55(7–8) (2006) 559–570.

[11] E.M. Vrijenhoek, S. Hong and M. Elimelech, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes. J. Membr. Sci., 188 (2001) 115–128.

[12] P.V.X. Hung, S.-H. Cho and S.-H. Moon, Prediction of boron transport through seawater reverse osmosis membranes using solution-diffusion model. Desalination, 247 (2009) 33–44.