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Abstract

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**Effect of heat treatment on fouling resistance and the rejection
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Abstract

The effect of heat treatment on membrane fouling resistance and the rejection of small and neutral solutes by reverse osmosis (RO) membranes were elucidated for water recycling applications. RO membrane modification by heat treatment reduced fouling and considerably improved boron rejection. However, heat treatment also caused a decrease in the water permeability of RO membranes. Significant improvement on fouling resistance by heat treatment was observed when RO concentrate was used to simulate a feed solution with high fouling propensity. The improved fouling resistance is likely to be due to changes in the hydrophobic interaction between the membrane surface and foulants. Boron rejection by the ESPA2 membrane was enhanced by heat treatment from 26 to 68% (when evaluated at the permeate flux of 20 L/m²h). Positron annihilation lifetime spectroscopy revealed that heat treatment did not significantly influence the free-volume hole-radius of the membrane active skin layer. The results reported in this study suggested that changes in the other membrane properties such as porosity and thickness may be the main cause improving boron rejection.

Keywords: Boron; membrane fouling; modification; reverse osmosis (RO); water reuse.

33 Introduction

34 Water recycling is an important strategy in arid regions to ensure a secured supply of water
35 for municipal use (Shannon *et al.* 2008). In a typical water recycling scheme, wastewater is
36 first treated to the secondary or tertiary effluent standard. The effluent is reclaimed and
37 further purified by a series of advanced treatment processes and then used to replenish
38 drinking water reservoirs or underground aquifers. Where necessary, this recycled water can
39 be extracted and distributed to the population for potable use. Advanced treatment processes
40 used for water recycling include microfiltration (MF) or ultrafiltration (UF), reverse osmosis
41 (RO) filtration, and advanced oxidation. Among treatment processes, RO filtration is a key
42 barrier against pathogenic agents, dissolved salts and trace organic chemicals. Given the high
43 organic content of reclaimed effluent, the RO can be prone to membrane fouling, which leads
44 to a decrease in membrane permeability and changes in separation performance (Xu *et al.*
45 2010). Membrane fouling in RO filtration systems involves a higher energy consumption and
46 more frequent chemical cleaning, thus ultimately reducing the sustainable value of water
47 recycling.

48 Membrane fouling depends on the interaction between the physicochemical characteristics of
49 the RO membrane surface and foulants. A recent study by Fujioka and Nghiem (2013)
50 demonstrated that the fouling resistance of commercially available polyamide low pressure
51 reverse osmosis (LPRO) membranes can also be improved by heat treatment. This
52 modification was performed by soaking commercial RO membranes into hot water (e.g. 70
53 °C) for a certain period of time. As a result of heat treatment, the progress of membrane
54 fouling was retarded by over 50% when sand-filtered wastewater was used for filtration
55 (Fujioka & Nghiem 2013). Nevertheless, no previous studies have investigated the effects of
56 heat treatment using actual treated wastewater with high fouling propensity – RO feed
57 solutions and RO concentrates.

58 Heat treatment performed during or immediately after the interfacial polymerisation process
59 can also improve salt rejection (Shintani *et al.* 2009). In addition to salts, the removal of
60 specific contaminants such as boron and trace organic chemicals is also important when the
61 recycled water is used for irrigation, industry or potable purposes. Boron is toxic to many
62 plant species (e.g. citrus, onion, wheat, barley) at concentrations as low as 0.3 mg/L (Tu *et al.*

2010). In some cases, when recycled water is used in thermal power plants and subsequently irrigation, due to evaporation in the cooling towers, the concentration of boron in recycled water must be reduced to 0.15 mg/L or lower. Due to its neutral and low molecular weight properties, the rejection of boron by LPRO membranes that are generally used for water recycling applications at the environmental pH (e.g. pH 6-8) has been reported to be typically less than 60% (Tu *et al.* 2010). Boron concentration in the RO feed can very high in places where wastewater is affected by seawater intrusion; thus, the removal of boron in these locations is of great concern. Similarly, the occurrence of trace organic chemicals such as N-nitrosodimethylamine (NDMA) in reclaimed effluent is of great concern to human health. In Australia, the United States, and several other countries, the NDMA concentration limit in recycled water intended for potable water reuse has been regulated at 10 ng/ L. The analysis of NDMA at a concentration of several ng/L is challenging. However, recent research has shown a strong correlation between boron and NDMA rejections by RO membranes (Tu *et al.* 2013). Thus, in this study, boron is selected as a model small and neutral solute of concern in water recycling applications.

The aim of this study was to elucidate the effects of heat treatment on fouling resistance and the rejection of small and neutral solutes. Untreated and heat-treated RO membranes were characterised by examining surface properties, permeability, and boron separation performance. The impact of the heat treatment on membrane fouling was examined using actual RO feed and RO concentrates.

Materials and methods

Membranes and Membrane filtration system

Two RO membranes, commercially known as ESPA2 and TFC-HR, were supplied by Hydranautics (Oceanside, CA, USA) and Koch Membrane Systems (Wilmington, MA, USA), respectively. They are composite polyamide RO membranes that comprise a thin polyamide active skin layer on the top of porous supporting layers. A laboratory-scale cross-flow RO filtration system used in this investigation is depicted in Supplementary Material Figure S1.

90 *Chemicals*

91 Analytical grade NaCl, CaCl₂, NaHCO₃ and boric acid were supplied by Ajax Finechem
92 (Taren Point, NSW, Australia). RO feed and concentrates were collected from an RO system
93 which is from a water recycling plant in Australia. RO feed and concentrate samples from the
94 1st, 2nd and 3rd stage (Supplementary Material Table S2) were used to evaluate the fouling
95 propensity.

96 *Experimental protocols*

97 The membrane samples were rinsed with Milli-Q water to remove preservative materials
98 from the membrane surface. They were then immersed in Milli-Q water at 80 ± 0.1 °C for 4
99 hours. The water temperature was regulated using a temperature-controlled water bath
100 (TWB-12D, Thermoline Scientific, Australia).

101 Each rejection experiment started with a compaction step where the permeate flux of
102 membrane sample was stabilised at 1,800 kPa using Milli-Q feed water. During the
103 experiments the cross flow velocity and feed temperature were maintained at 0.42 m/s and
104 20.0 ± 0.1 °C, respectively. Following the compaction step, the feed solution was conditioned
105 at 20 mM NaCl, 1 mM CaCl₂, 1 mM NaHCO₃, and 5.0 mg/L boron. The permeate flux was
106 then adjusted to 20 L/m²h.

107 The membrane fouling experiments also started with the compaction step described above.
108 Feed solution was then replaced with the RO feed, or the 1st, 2nd or 3rd stage RO concentrate.
109 Thereafter, the filtration system was operated for 15 hours or until flux decline reached 50%
110 at a feed pressure of 700 kPa (untreated membrane) and 1,000 kPa (heat-treated membrane)
111 both of which correspond to approximately 30 L/m²h permeate flux. The permeate flux was
112 about 1.5 times higher than typically used for water recycling applications and thus
113 membrane fouling could be accelerated.

114 *Membrane characterisation and analytical techniques*

115 Atomic force microscope

116 Membrane surface roughness and surface area were determined using a Bio-XE atomic force
117 microscope (AFM) instrument (Park Systems, Korea). The imaging was performed in air

using tapping mode with Nanosensor PPP-FMR silicon cantilevers (spring constant of ~2.8 N/m). The scanning area was 10 µm × 10 µm and three samples were analysed to obtain the average value.

Contact angle

The hydrophobicity of membranes was evaluated using contact angle measurements. The contact angle of the membrane surface was analysed using a Rame-Hart Goniometer (Model 250, Rame-Hart, Netcong, NJ). Contact angles at ten different locations were used to obtain the average value.

Positron annihilation lifetime spectroscopy (PALS)

The free-volume hole-radius of the RO membranes were determined using PALS with a slow positron beam as previously described by Fujioka et al. (2013). The analysis was conducted at the National Institute of Advanced Industrial Science and Technology (AIST) in Tsukuba, Japan. When positrons are injected into a solid sample, the positrons annihilate with electrons of the solid sample and emit gamma-rays. Before the annihilation, some of the positrons may form ortho-positronium (*o*-Ps), the spin parallel positron-electron bound state, or para-positronium (*p*-Ps), the spin antiparallel positron-electron bound state. The lifetime of *o*-Ps (τ_{o-Ps}) can be used for the determination of the free-volume hole-size (r) using the Tao-Eldrup model (equation 1).

$$\tau_{o-Ps} = 0.5 \left[1 - \frac{r}{r + 0.166} + \frac{1}{2\pi} \sin\left(\frac{2\pi r}{r + 0.166}\right) \right]^{-1} \quad (1)$$

where r (≤ 1 nm) is the radius of the free-volume hole approximated as a spherical shape. The analysis was carried out under vacuum at 10^{-5} Pa. The positron incident energy was set at 1.0 keV to analyse free-volume hole-radii at a mean depth of around 40 nm of the sample. The positron lifetime spectrum of each sample was obtained from the collection of about 2×10^6 positron annihilation events and analysed to deduce τ_{o-Ps} by using a non-linear least-squares fitting program. The relative measurement uncertainty of τ_{o-Ps} was less than 5%.

Size exclusion chromatography analysis

The dissolved organic carbon (DOC) compositions of the RO permeate were investigated. These samples were characterised with a size exclusion chromatography technique described previously (Henderson *et al.* 2010).

Results and Discussion

Membrane surface properties

Heat treatment did not substantially change the morphology of the ESPA2 membrane. Scanning electron microscope (SEM) images of the untreated and heat-treated membranes revealed no discernible difference in visual appearance (Supplementary Material Figure S3). Membrane surface morphology evaluated by AFM analysis, which is a complementary technique to SEM for surface investigations, also revealed no significant changes after heat treatment (Supplementary Material Figure S4). Nevertheless, heat treatment caused a slight increase in membrane surface roughness and membrane surface area of the ESPA2 membrane from 79 to 101 nm and from 220 to 233 μm^2 , respectively (Table 1). These values are representative of images taken from three different membrane samples. Thus, the changes in surface roughness reported here can be within the natural variation among different membrane samples. Heat treatment also rendered the surface of the ESPA2 membrane more hydrophilic (contact angle decreased from 48 to 35°) (Table 1). The mean free-volume hole-radius of the untreated and heat-treated ESPA2 membrane analysed by the PALS were determined to be nearly identical (0.267 and 0.266 nm, respectively), indicating that heat treatment did not have any significant impact on free-volume hole-radii (Table 1). Heat treatment performed to the TFC-HR membrane caused a discernible increase in free-volume hole-radius (from 0.267 and 0.287 nm).

Heat treatment caused a substantial decrease in the permeability of the ESPA2 and TFC-HR membranes from 5.0 to 3.2 L/m²hbar and 3.1 to 1.9 L/m²hbar, respectively. In the pore-flow model (Kiso *et al.* 2011), the permeability of RO membranes can be governed by the physicochemical characteristics of their active skin layer, as described in the following equation:

$$L_p = \frac{r_p^2 A_k}{8\eta\Delta x}. \quad (2)$$

where L_p is water permeability, r_p is effective free-volume hole-radius of the active skin layer, A_k is the porosity, η is the viscosity of solution in a free-volume hole, and Δx is the length of the free-volume hole through membrane which is correlated with the active skin layer thickness. Among the physicochemical characteristics of their active skin layer, the mean free-volume hole-radius of the ESPA2 membrane analysed by PALS revealed no discernible changes after heat treatment. Thus, the other properties (i.e. porosity and thickness) can be the important factors influencing the changes in permeability. However, it was not possible in this study to accurately measure the porosity and thickness of the membrane active skin layer. There are currently no analytical techniques available to accurately determine active skin layer porosity. In addition, it is not generally possible to measure the effective thickness of the active layer of these membranes due to artefacts being introduced during sample preparation. Very recently, the overall thickness of the active skin layer of RO membranes including cavities and valleys that are present in the layers has been measured by high resolution transmission electron microscopy (TEM) (Kurihara & Hanakawa 2013). This required special sample preparation that was not readily available and was therefore beyond the scope of the present study. It will be the subject of further investigations.

[Table 1]

Resistance to Membrane Fouling

The impact of heat treatment on membrane fouling was evaluated using the RO feed and two different RO concentrates. A negligible difference in fouling development between the untreated and heat-treated was observed when the RO feed was used (Figure 1a). The fouling behaviour differed remarkably when RO concentrates were used as the feed solution (Figure 1b-d). For example, the permeate flux decline of the untreated membrane using the 1st stage RO concentrate reached 17% with 15 hours filtration, while the heat-treated membrane exhibited only a marginal decrease (6%) (Figure 1b). The extended period of filtration (50 hours) using the 1st stage RO concentrate caused a larger difference in permeate flux decline between the untreated membrane (39%) and heat-treated membrane (21%) (data not shown). The heat-treated membrane exhibited a slower flux decline than untreated membranes when the 2nd and 3rd stage RO concentrates were used (Figure 1c and d). Nevertheless, both heat-treated and untreated membranes exhibited a significant drop in permeate flux (over 50%). The heavy fouling observed using the 2nd and 3rd stage RO concentrates was due probably to

the high foulant concentration. In fact, TOC of the 3rd stage RO concentrate was as high as 50 mg/L (Supplementary Material Table S1). Overall, the results obtained here indicate that heat treatment could improve fouling resistance for RO concentrates. An increase in hydrophilicity of the RO membrane by heat treatment (Table 1) is one potential cause for the enhanced fouling resistance. Hydrophilic modification of RO membrane surfaces has been reported to reduce the organic fouling of membranes (Zou *et al.* 2011). A hydrophilised membrane surface can lead to a decrease in the hydrophobic interaction between membrane surface and foulants.

[Figure 1]

Solute Rejection

Boric acid is hydrophilic and most boron exists in the uncharged form of boric acid (B(OH)_3) at the tested pH of 7.9 (Tu *et al.* 2013). Heat treatment led to a considerable increase in the rejection of boric acid under a range of permeate flux (Figure 2). For example, heat treatment applied to the ESPA2 membrane increased boron rejection from 26 to 68% under 20 L/m²h permeate flux (Figure 2a). By increasing permeate flux to 40 L/m²h permeate flux, boron rejection by the heat-treated ESPA2 membrane reached as much as 78%. A similar improvement on boron rejection was observed for the TFC-HR membrane (Figure 2b). The results reported here indicate that heat treatment is an effective method to improve the rejection of small and neutral solute (i.e. boric acid).

The molecular volume of boric acid (0.071 nm³) is smaller than the free-volume hole-space of the virgin RO membrane (0.080 nm³), thus the degree of boron rejection can be potentially affected by free-volume hole-radii within the active skin layer of RO membranes. A previous study (Henmi *et al.* 2010) reported that the rejection of boron increased with decreasing free-volume hole-radius. Nevertheless, no apparent difference in free-volume hole-radius before and after heat treatment was observed in this study (Table 1). On the other hand, a strong correlation between permeability and boron rejection was observed (Figure 3). As described earlier, the porosity and thickness of the active skin layer are also important factors affecting permeability (Equation 2). Thus, the improvement of solute rejection by heat treatment may be attributed to these two active skin layer properties.

[Figure 2]

[Figure 3]

The rejection of organic matter by the untreated and heat-treated membranes was also evaluated using the 1st stage RO concentrate. Permeate samples were collected shortly after the start of the filtration tests. As a result, TOC rejection by heat-treated membrane (99.64%) was equivalent to that by the untreated membrane (99.60%). Further investigation was carried out by analysing organic size fractions in the permeate solutions using LC-OCD analysis. Overall, there was negligible difference between organic size fractions detected in the permeate of untreated and heat-treated membranes (Figure 4) and therefore ratios of each organic fraction (e.g. building blocks, LMW neutrals, LMW acids) present in the respective permeates were almost equivalent (Supplementary Material Table S5). Nevertheless, a peak of low molecular weight (LMW) neutrals observed in the permeate of the untreated membrane (between 85 and 95 min retention time) was not detected in the permeate of the heat-treated membrane (Figure 4). The results indicate that the heat-treated membrane can enhance the rejection of small organic matter in comparison to the untreated membrane.

[Figure 4]

Conclusions

Modification of the RO membranes through heat treatment resulted in an improvement on fouling resistance and boron separation performance. However, heat treatment reduced the pure water permeability of the RO membranes. The improved fouling resistance by heat treatment was observed for different RO concentrate solutions (i.e. 1st, 2nd and 3rd stage RO concentrates). The improved fouling resistance of the heat-treated membrane was due possibly to the decreased hydrophobic interaction between the modified RO membrane surface and foulants. Heat treatment improved boron rejection significantly. Heat treatment resulted in an increase in boron rejection by the ESPA2 membrane from 26% (without heat treatment) to 68% (after heat-treatment). PALS revealed that heat treatment did not significantly influence the free-volume hole-radius of the membrane active skin layer. The study suggested that other active skin layer properties such as porosity and thickness may be the critical factors improving the rejection of boron. Further research focusing on membrane characterisation of the untreated and heat-treated membranes is necessary to clarify the mechanism of the improved effects of heat treatment.

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306 **Table 1:** Membrane properties of untreated and heat-treated ESPA2 and TFC-HR membranes.

Category	Method	Parameter	ESPA2		TFC-HR	
			Untreated	Heat-treated	Untreated	Heat-treated
Permeability	Filtration system	Pure water permeability ^a [L/m ² hbar]	5.0±0.1	3.2±0.1	3.1±0.1	1.9±0.1
Topography	AFM	Surface roughness ^a [nm]	79±6	101±11	n.a.	n.a.
	AFM	Surface area ^b [μm ²]	220±3	233±7	n.a.	n.a.
Hydrophobicity	Goniometer	Contact angle [°]	48±3	35±3	n.a.	n.a.
Free-volume hole-size	PALS	τ_{o-ps} [ns]	1.83	1.82	1.83	2.04
		Mean free-volume hole-radius, r_p [nm]	0.267	0.266	0.267	0.287

307 ^a Determined with Milli-Q water at 1000 kPa and 20 °C feed temperature.

308 ^b Surface area was determined by the scanning area of 100 μm².

309 n.a.: data not available.

LIST OF FIGURES

Figure 1: Fouling development on untreated and heat-treated ESPA2 membranes using the (a) RO feed, and (b) 1st stage, (c) 2nd stage, and (d) 3rd stage RO concentrates (cross flow velocity 40.2 cm/s, feed temperature 20.0 °C, feed pressure for heat-treated membranes 1,000 kPa and untreated membranes 700 kPa). Each filtration experiment started with approximately 30 L/m²h permeate flux and operated under the constant pressure.

Figure 2: Effect of heat treatment on boron rejection by the (a) ESPA2 and (b) TFC-HR membranes as a function of permeate flux (20 mM NaCl, 1mM NaHCO₃, 1 mM CaCl₂, cross flow velocity 40.2 cm/s, feed pH 7.9, feed temperature 20.0 °C).

Figure 3: Boron rejection as a function of pure water permeability by the untreated and heat-treated membranes (permeate flux 20 L/m²h). Results were obtained from Table 1 and Figure 2.

Figure 4: LC-OCD chromatograms of the RO permeate treated by the (a) untreated and (b) heat-treated ESPA2 membranes. OCD and UVD represent organic carbon detection and UV detection at 254 nm, respectively.

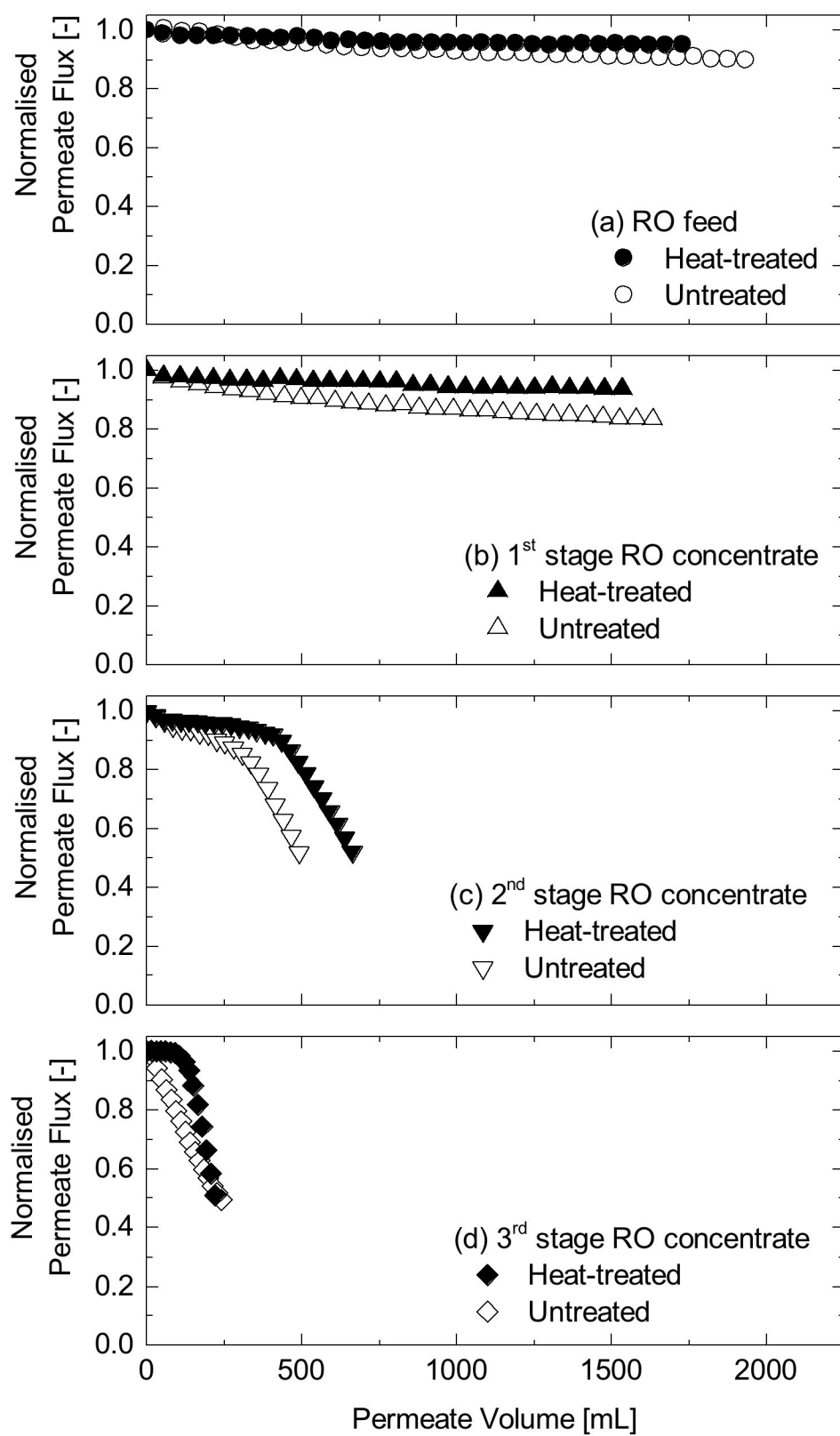
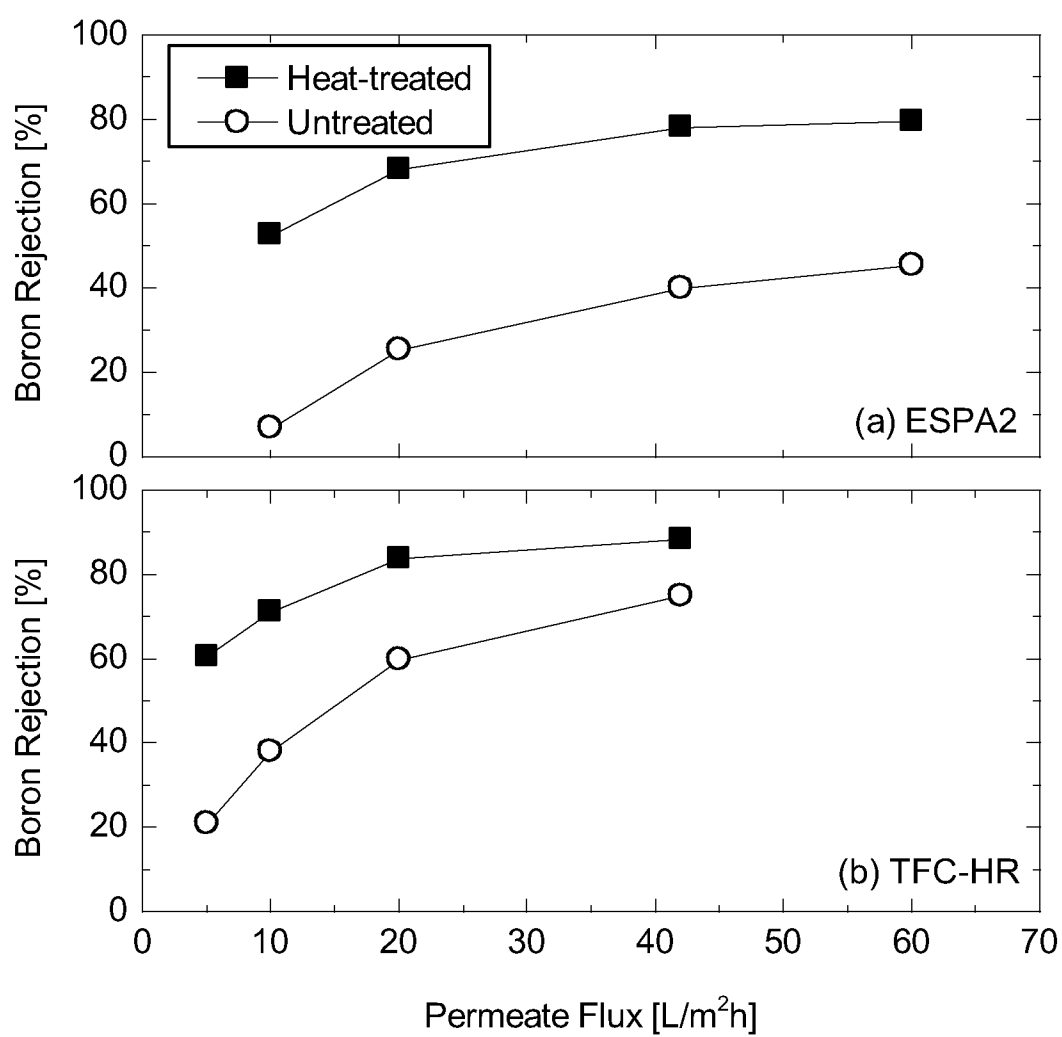
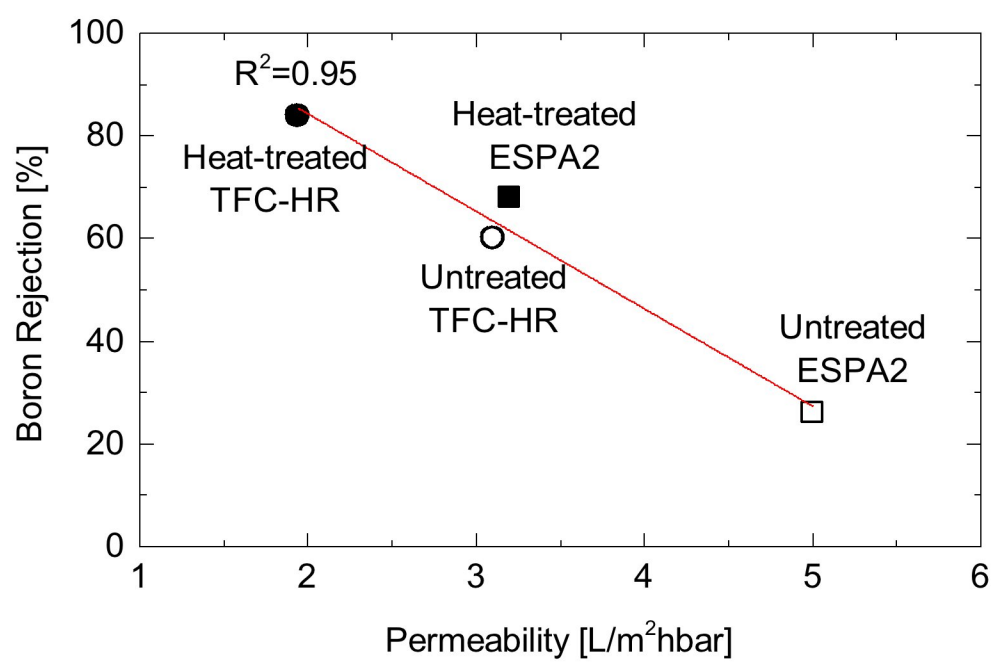


Figure 1



327
328 **Figure 2**



329

330 **Figure 3**

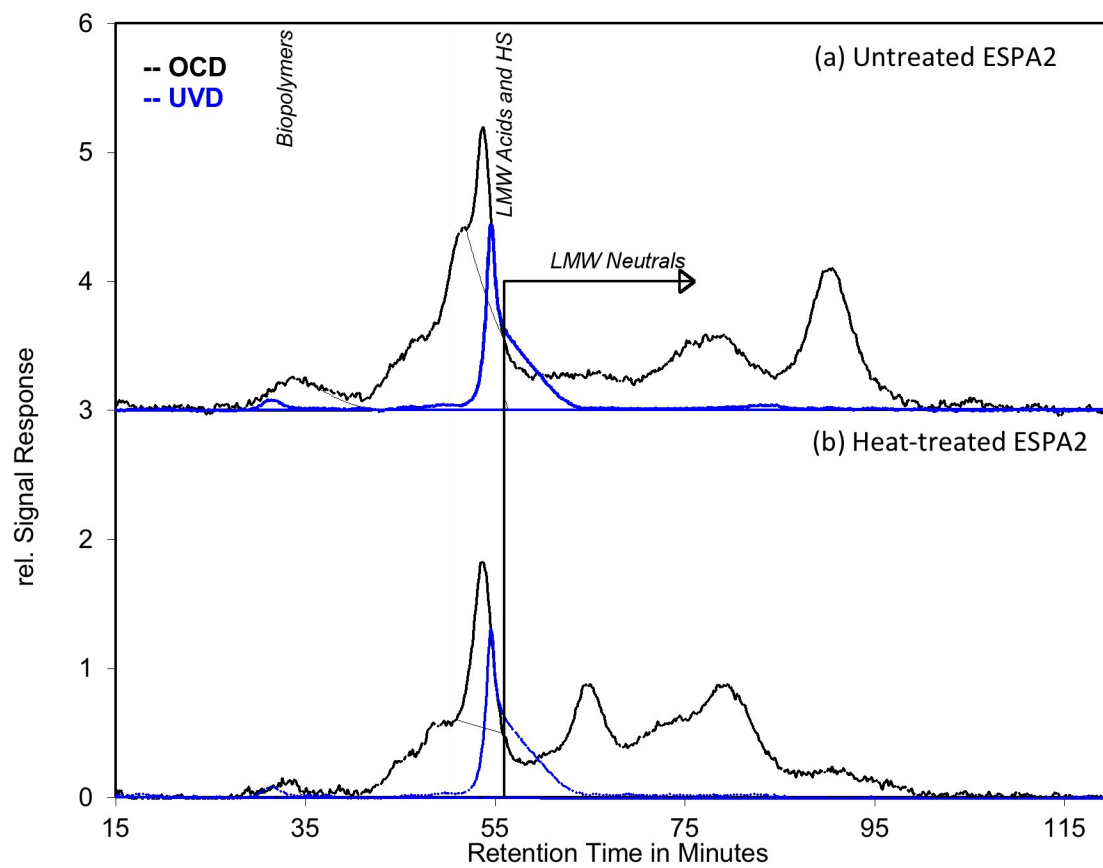


Figure 4

Effect of heat treatment on fouling resistance and the rejection of small and neutral solutes by reverse osmosis membranes

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SUPPLEMENTARY MATERIAL

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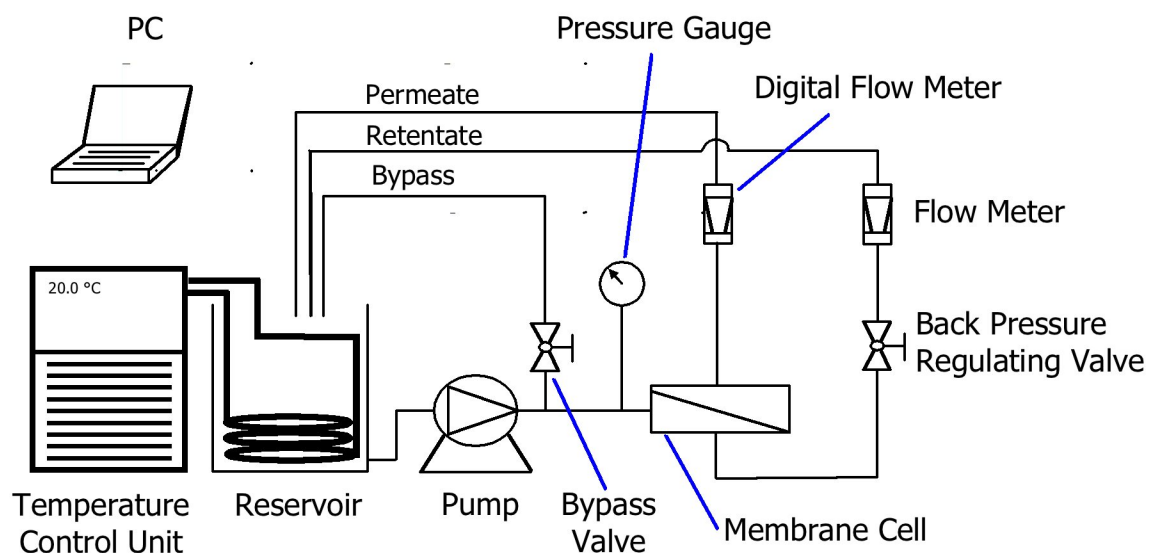


Figure S1: Schematic diagram of the cross flow RO filtration system.

RO filtration system

The membrane cell had a channel height of 2 mm and holds an effective area of 40 cm² (4 cm × 10 cm) membrane sheet. The pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN, USA) delivered the feed solution from the feed reservoir to the membrane cell. The permeate flow rate was monitored using a digital flow meter (FlowCal, GJC Instruments Ltd, Cheshire, UK) and recorded by a personal computer. The feed solution temperature in the feed reservoir was maintained at 20 °C using stainless steel heat exchanging pipes which was connected to a temperature control unit (Neslab RTE 7, Thermo Scientific Inc., Waltham, MA, USA).

Table S1: Water quality of the RO feed and concentrates.

Parameter	RO feed	1 st stage concentrate	2 nd stage concentrate	3 rd stage concentrate
TOC [mg/L]	9	19	38	50
pH [-]	6.9	7.2	7.4	7.7
Conductivity [mS/cm]	1.0	2.0	4.1	6.0
Ions [mg/L]				
Boron	0.11	0.15	0.21	0.26
Na ⁺	135	283	604	865
Mg ²⁺	12	26	57	83
K ⁺	23	48	103	149
Ca ²⁺	29	62	134	194
Cl ⁻	201	510	950	1361
NO ₃ ⁻	57	120	225	373
SO ₄ ²⁻	45	92	188	277

Water quality analysis

Conductivity, pH and temperature of solutions were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo scientific, USA). Total organic carbon (TOC) concentrations were determined using a TOC-V CSH analyser (Shimadzu, Japan). Cation and boron concentrations were analysed using an inductively coupled plasma – mass spectrometer (7500CS, Agilent Technologies, Wilmington, DE, USA). Anion concentrations were determined using an ion chromatography system (Shimadzu, Tokyo, Japan).

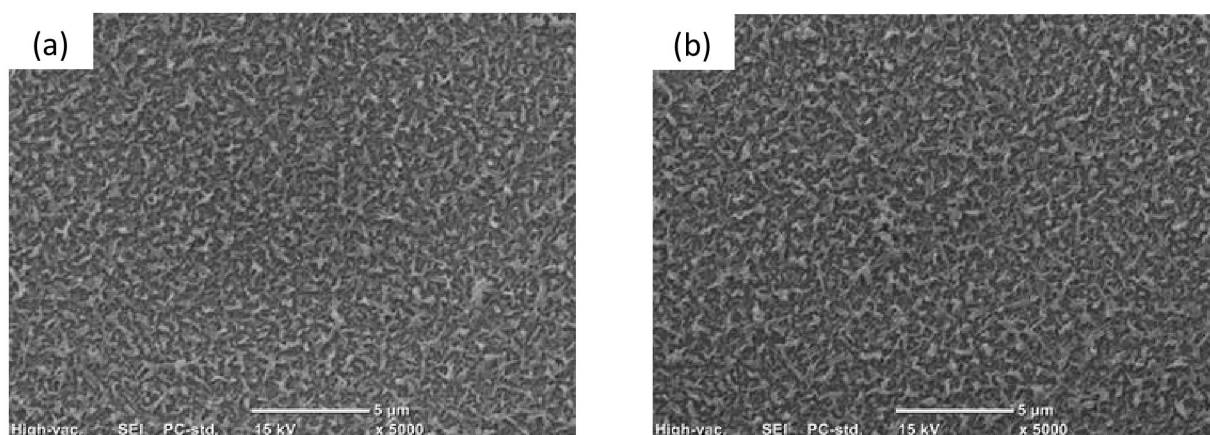


Figure S3: SEM images of the (a) untreated and (b) heat-treated ESPA2 membranes.

Scanning electron microscope

The untreated and heat-treated membranes were examined using a JCM-6000 scanning electron microscope (SEM) instrument (JEOL Japan). Prior to analysis, each membrane sample was air dried and coated with gold using a gold sputter. Images of the membrane surface were taken at 15 kV and a working distance of 12 mm.

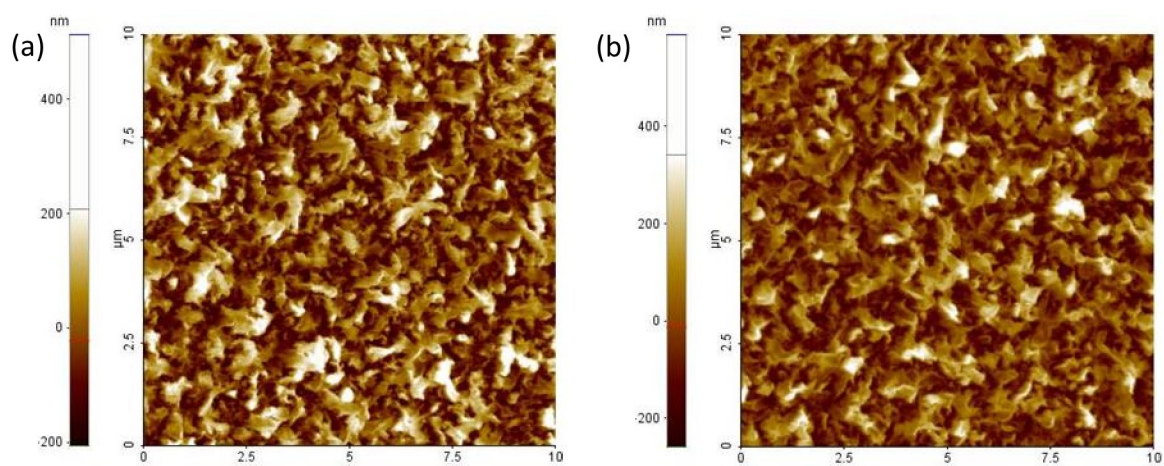


Figure S4: AFM images of the (a) untreated and (b) heat-treated ESPA2 membranes. The size of the images is approximately $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$.

Table S5: Organic matter fractions in each solution.

Parameter	Molecular weight [kg/mol]	Permeate – Untreated [%]	Permeate – Modified [%]	Feed [%]
Bio-polymers [%]	>20	2.6	0.6	15.4
Humics [%]	12-80	n.q.	n.q.	8.6
Building blocks [%]	0.3-0.5	14.7	10.2	3.8
LMW neutrals [%]	< 0.35	25.3	30.2	52.2
LMW acids [%]	n.a.	3.2	4.8	n.q.

n.a.: Not available.

n.q.: Not quantifiable.

Size exclusion chromatography analysis

A Liquid Chromatography - Organic Carbon Detection (LC-OCD) Model 8 system (DOC-LABOR, Karlsruhe, Germany) was used in which the sample is passed through a Toyopearl[®] TSK HW-50S column (Tosoh Bioscience, Tokyo, Japan) to a UV-detector (254 nm), organic carbon detector and nitrogen detector. The mobile phase prepared was phosphate buffer at pH 6.37, 2.5 g/L KH₂PO₄ and 1.5 g/L Na₂HPO₄·H₂O. The flow rate of the mobile phase was set at 1.1 mL/min. The injected sample volume into the instrument was 4 mL.