Impact of heat modification conditions on the removal of *N*-nitrosodimethylamine by polyamide reverse osmosis membranes

Takahiro Fujioka [1,*], Miyu Osako [2], Kaoru Oda [1],
Takuji Shintani [3], Hitoshi Kodamatani [4]

[1]Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

[2]School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, Japan

[3]Division of Advanced Membrane Science and Technology, Graduate School of Science, Technology and Innovation, Kobe University, 1-1 Rokkodai-cho, Kobe 657-8501, Japan

[4]Division of Earth and Environmental Science, Graduate School of Science and Engineering, Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-0065, Japan

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* Corresponding author: Takahiro Fujioka, Email: tfujioka@nagasaki-u.ac.jp, Ph +81 095 819 2695

Abstract

Advanced wastewater treatment using a reverse osmosis (RO) membrane is a key separation process for ensuring the removal of chemical hazards so that treated wastewater can be used for potable purposes. This study systematically assesses the effects of heat modification conditions of three commercial RO membranes on the removal of a challenging chemical of emerging concern–*N*-nitrosodimethylamine (NDMA). The RO membranes were modified in pure water at the heat treatment temperature between 70 and 100 °C; 90–100 °C achieved the highest NDMA rejection during separation tests. A lower pH during heat treatment generally resulted in higher NDMA rejection, however a solution pH lower than four can reduce NDMA rejection depending on the presence of a protective layer on the RO membrane surface. Overall, a linear tradeoff between NDMA rejection and water permeance was commonly observed among the heat-treated RO membranes. The stability of a heat-modified membrane in water permeability and NDMA rejection was demonstrated over a week-long test using treated wastewater. The enhanced removal of NDMA by heat-treated RO membranes was speculated to occur due to the shrinking of the passage of solutes–free-volume holes. This study demonstrates the importance of heat modification conditions on RO membranes to achieve a high NDMA rejection.

Keywords: NDMA, RO membrane, polyamide, potable water reuse, CECs.

1 Introduction

Assurance of recycled water quality, for potable reuse, can be enhanced by providing robust wastewater treatment and stringent water quality control for the removal of pathogenic and chemical hazards. In potable water reuse, chemical control is particularly focused on attenuating contaminants of emerging contaminants (CECs) in wastewater. Among CECs, *N*-nitrosodimethylamine (NDMA; $C_2H_6N_2O$), a probable carcinogenic chemical [1], has attracted considerable interest as a challenging chemical for a typical configuration of advanced wastewater treatment train including microfiltration (MF), reverse osmosis (RO) membrane, and ultraviolet (UV)-based advanced oxidation process (AOP) [2]. NDMA, a small and uncharged chemical, may be present in wastewater and forms during chloramination disinfection performed prior to RO process [3]. NDMA is only partially removed (e.g., < 50%) by low-pressure RO membranes that have been used for water recycling; thus, NDMA concentrations in the RO permeate are often found at concentrations higher than its guideline value (e.g., 10 ng/L) [4]. The following AOP is the only reliable barrier which complies with the regulated NDMA concentration [5]. Therefore, RO membranes with high and reliable NDMA removal can help enhance the safety of recycled water.

The key criteria for RO membranes to achieve high removal of NDMA remain unclear. Almost all commercial polyamide-based RO membranes have been designed for high removal of salts and high water permeability and are not capable of achieving high removal of small CECs, particularly NDMA [6-9]. These small chemicals diffuse through free-volume holes composed of small networks and large aggregate holes in the skin layer of the RO membrane [10, 11]; therefore, their transport is likely to be influenced by the dimension of clearance between chemicals and holes [12, 13]. Several recent studies [14-16] addressed the modification of commercial RO membranes using a “plugging” method to achieve high rejection of small and uncharged boric acid (molecular weight of 63 g/mol) by reducing the clearance. This method is based on plugging sub-nanometer scale pores (free-volume holes) or large defects in the polyamide skin layer. Improved selectivity of RO membranes from the plugging method has suggested an important role for the clearance between the small solute (i.e., boric acid) and sub-nanometer scale pores to achieve high rejection.

Other facile membrane modification techniques that have been demonstrated with commercial RO membranes include heat treatment. This is generally applied to RO membranes immediately after interfacial polymerization as part of its manufacturing process [17, 18]. Heat treatment can also be applied to commercial polyamide-based RO membranes by simply submerging them in a solution at high temperature; this has demonstrated the enhanced removal of NDMA and mitigated membrane fouling propensity in exchange for water permeance [19]. Increasing the removal of NDMA by the heat-treated RO membrane can possibly lead to a reduction in energy consumption of UV in current AOP, and enhance the reliability of NDMA removal through two barriers (i.e., RO and AOP). Previous studies focusing on heat treatment [19, 20] simply applied specific heat treatment temperatures (e.g., 70 or 80 °C). Moreover, mechanisms underlying the improved NDMA rejection remain undefined even after analyzing the membrane free-volume hole radius, membrane surface area, and skin layer thickness [21]. Systematically assessing the impact of heat treatment conditions can assist in further enhancing the rejection of NDMA and understanding its mechanisms.

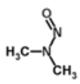
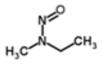
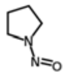
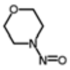
This study assesses the effects of heat treatment conditions on the performance of three commercial RO membranes for NDMA removal. The varied heat treatment conditions were treatment time, temperature, and pH. The stability of the heat treatment effect on NDMA removal and water permeability was also demonstrated on treated wastewater. Lastly, the mechanisms underlying the improved NDMA rejection were explored based on the empirical results.

2 Materials and methods

2.1 *Chemicals*

Four analytical grade *N*-nitrosamines – NDMA, *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), and *N*-nitrosomorpholine (NMOR) **(Table 1)** – were obtained from Ultra Scientific (Kingstown, RI, USA). All are hydrophilic with a Log *D* value of < 2.0 [22] and uncharged at the tested pH of 8.0. Analytical grade NaCl, $CaCl_2$, $NaHCO_3$, HCl, and NaOH were obtained from Wako Pure Chemical Industries (Tokyo, Japan).

Table 1 – Physicochemical properties of the *N*-nitrosamines.

Compound	Structure	Molecular formula	Molecular weight [Da]	Log *D* at pH 8[a]	pK$_a$[a]
NDMA		$C_2H_6N_2O$	74.1	0.04	3.5
NMEA		$C_2H_8N_2O$	88.1	0.40	3.4
NPYR		$C_4H_8N_2O$	100.1	0.44	3.3
NMOR		$C_4H_8N_2O_2$	116.1	-0.18	3.1

[a] Chemicalize (http://www.chemicalize.org).

2.2 *Membranes and membrane treatment systems*

Three commercial flat-sheet RO membranes—ESPA2, ESPAB, and LFC3—were obtained from Nitto/Hydranautics (Osaka, Japan). These are thin-film composite polyamide RO membranes designed for brackish water treatment (including water recycling applications). Each membrane coupon, with a diameter of 1 inch (2.54 cm), was installed in a stainless steel membrane cell. The effective membrane surface area in the membrane cell was 3.35 cm^2. The bench-scale RO treatment system contained two cross-flow membrane cells, a high-pressure pump (Q30, Tacmina, Osaka, Japan), 500-mL glass reservoir, pressure regulating valve, digital flow meter, cooling unit (NCB-500, Tokyo Rikakikai, Tokyo, Japan), and heating circulator (AS ONE, Osaka, Japan) **(Fig. S1)**.

2.3 Experimental protocols

Prior to heat treatment, all RO membrane coupons were rinsed with ultrapure water. Thereafter, each RO membrane coupon was submerged in a 100 mL beaker filled with 100 mL pure water. When evaluating the impact of solution pH during heat treatment, 100 mL clean water matrix solution containing 10 mM NaCl, 1 mM $CaCl_2$, and 1 mM $NaHCO_3$ was used. Solution pH was adjusted with 0.1 M HCl or NaOH solution. Each beaker was placed in a temperature-controlled water bath (SWB-11A, AS ONE, Osaka, Japan). Prior to the heat treatment, water in the water bath was pre-heated to reach a target temperature of 70–100 °C. Water temperature during the heat treatment was maintained for 1–4 h. Following the heat treatment, the treated RO membrane samples were rinsed with ultrapure water, and were stored at 4 °C in the dark.

Each untreated and heat-treated RO membrane sample underwent a pure water permeability test at a transmembrane pressure (TMP) of 0.9 MPa and feed temperature of 20 °C for 1 h. Their separation performance was evaluated using a solution containing 20 mM NaCl, 1 mM $CaCl_2$, 1 mM $NaHCO_3$, and *N*-nitrosamine concentration of approximately 500 ng/L. The RO system was operated at a permeate flux of 20 L/m^2h, cross-flow velocity of 1.2 cm/s, and feed temperature of 20 °C. The RO concentrate and permeate were recirculated in the system during the tests. The water permeance of each RO membrane was determined based on the TMP and permeate flux during the separation test and was expressed in units of L/m^2hbar. After 1 h of operation, the RO feed and permeate samples were collected in 1.5 mL amber vials from the feed reservoir and permeate outlet, respectively. Their concentrations were used to calculate the rejection of *N*-nitrosamines and salts. Triplicated separation tests were conducted for each condition. The data obtained using non-treated RO membranes were presented as “Control”.

The stability of the modification effect on the separation performance was evaluated for a total of six days. This evaluation was conducted using the ESPAB RO membrane. The feed solution was a membrane bioreactor (MBR) effluent, collected at a pilot-scale wastewater treatment plant in Japan that intakes municipal wastewater. Prior to the test, *N*-nitrosamine stock solutions were dosed in the RO feed at each chemical concentration of 500 ng/L. The test was started at a permeate flux of 20 L/m^{2}h and feed temperature of 20 °C, and the required TMP was maintained for six days. The RO concentrate and permeate were recirculated in the system during the tests. RO feed and permeate samples were periodically collected in 1.5 mL amber vials, and their concentrations were used to calculate *N*-nitrosamine rejection. The data obtained using non-treated RO membranes were presented as "Control".

2.4 Analytical techniques

Concentrations of *N*-nitrosamines were determined by high-performance liquid chromatography-photochemical reaction-chemiluminescence (HPLC-PR-CL). Details of this technique are provided elsewhere [23]. The analysis was performed with an eluent of 1 mM phosphate buffer and methanol (95:5 v/v); sample injection volume was 200 μL.

3 Results and discussion

3.1 Heat treatment time

In general, heat modification of the ESPAB RO membranes caused a reduction in the water permeance, but an increase in NDMA rejection over a heat treatment period ranging from 0 to 4 h **(Fig. 1)**. Considerable changes in the NDMA rejection (55 to 72%) occurred during the first hour. In contrast, the water permeance, which represents the permeate flow produced at a given pressure and membrane area, reduced from 2.5 to 1.8 L/m^{2}hbar. Extended heat treatment time further reduced water permeance but increased NDMA rejection; impacts were, however, insignificant. After 4 h of heat treatment, the water permeance and NDMA rejection of the ESPAB membrane reached 1.5 L/m^{2}hbar and 80%, respectively. Similar trends (i.e., reduced water permeance and increased NDMA rejection according to heat treatment time) were observed for the LFC3 RO membrane **(Fig. S2)**. These results indicate that heat treatment between 1 and 4 h can considerably improve NDMA rejection; thus, the standard heat treatment time applied in the following tests was 4 h.

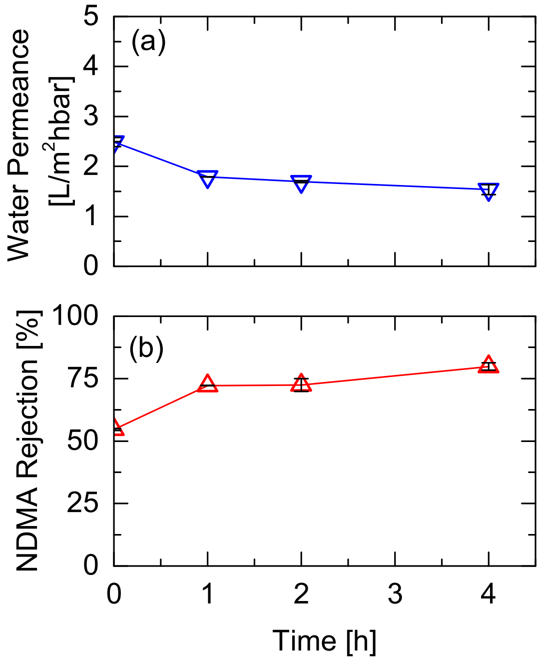


Fig. 1 – Effect of heat treatment time on (a) water permeance and (b) *N*-nitrosodimethylamine (NDMA) rejection of the ESPAB reverse osmosis (RO) membranes. The symbols and error bars represent the average and range, respectively, of the triplicated separation results.

3.2 Treatment temperature

The effect of heat treatment temperature on NDMA rejection was evaluated by changing the treatment temperature between 70 and 100 °C. For the ESPA2 RO membrane, an increase in the heat treatment temperature from 70 to 100 °C resulted in a consistent increase in NDMA rejection from 36 to 53% **(Fig. 2a)**. The water permeance did not show a similar trend, varying between 3.1 and 4.0 L/m^{2}hbar. Similarly, the ESPAB RO membrane showed an increase in NDMA rejection from 69 to 80% as temperature increased from 70 to 100 °C; water permeance varied between 1.3 and 1.9 L/m^{2}hbar **(Fig. 2b)**. The LFC3 RO membrane showed a consistent increase in NDMA rejection and a decrease in water permeance from 66 to 76% and 3.0 to 2.4 L/m^{2}hbar, respectively, as temperature increased **(Fig. 2c)**. Overall, the performance of the RO membranes for NDMA rejection improved as heat treatment temperature increased; 90–100 °C achieved the highest NDMA rejection. Heat treatment could increase NDMA rejection by up to approximately 20%, regardless of membrane type. The enhanced separation performance from 70 to 100 °C was similar to a previous study focusing on salt rejection, in which heat treatment was applied immediately after the interfacial polymerization during membrane synthesis [18]. They [18] suggested that high temperatures induced higher cross-linking of polyamide within the skin layer. However, their fundamental heat treatment approach (i.e., heat treatment immediately after membrane synthesis) differs from this study (i.e., heat treatment of commercial RO membranes). Further mechanisms associated with improved separation capacity by heat treatment are discussed in **Section 3.4**.

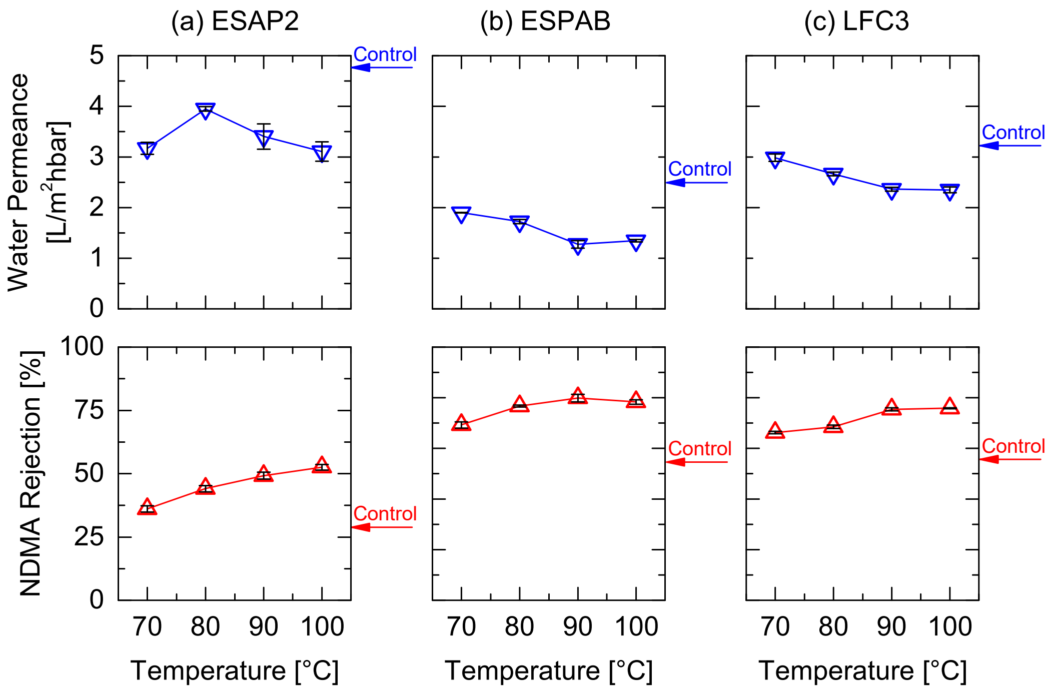


Fig. 2 – Effect of heat treatment temperature on water permeance and *N*-nitrosodimethylamine (NDMA) rejection of (a) ESPA2, (b) ESPAB, and (c) LFC3 reverse osmosis (RO) membranes. The symbols and error bars represent the average and range, respectively, of the triplicated separation tests. "Control" indicates the values obtained using non-treated RO membranes.

3.3 Treatment pH

In general, a lower pH was found to induce higher NDMA rejection. For example, NDMA rejection by the ESPA2 RO membrane treated at pH 4 was 55%, which was greater than those treated at pH 7 and 10 (35% and 36%, respectively) **(Fig. 3a)**. Water permeance proportionally increased from 3.3 to 4.4 L/m^{2}hbar as pH increased to 10. The ESPAB and LFC3 RO membranes showed similar trends: heat treatment at pH 4 resulted in the highest NDMA rejections of 76 and 77%, respectively **(Figs. 3b and 3c)**. The results indicate that heat treatment under acidic conditions can enhance NDMA rejection. However, a lower pH of two resulted in lower NDMA rejection. Reducing pH from four to two for the ESPAB membrane resulted in a considerable reduction in NDMA rejection (76 to 55%). In contrast, the LFC3 RO membrane showed a minor decrease with heat treatment from pH 4 (77%) to pH 2 (72%). At high temperatures, polyamides in an acidic solution (e.g., HCl) are more subject to hydrolysis:

$$R - CONH - R' \overset{H_2O}{\longleftrightarrow} RCOOH + R'NH_2. \qquad (1)$$

This reaction can separate cross-linked polyamide chains of the skin layer, which can enlarge the free-volume holes and allow more NDMA to pass through. Less cross-linking, caused by hydrolysis, can ultimately counteract the improved NDMA rejection. Thus, hydrolysis can be the cause of the low NDMA rejection by the ESPAB membrane at pH 2.0 (55%) than that at pH 4.0 (76%). In contrast to the ESPAB RO membrane, the LFC3 RO membrane showed less impact at low pH (2.0), probably because its surface has a poly(vinyl alcohol) [PVA, $(C_2H_4O)_x$] layer on top of an ESPA RO membrane sheet [24]. This indicates that the coated RO membrane is less subject to hydrolysis during heat treatment, while the low pH of two does not contribute to further enhancement of NDMA rejection. The results indicate that the best NDMA separation performance is commonly observed at a relatively low pH of four.

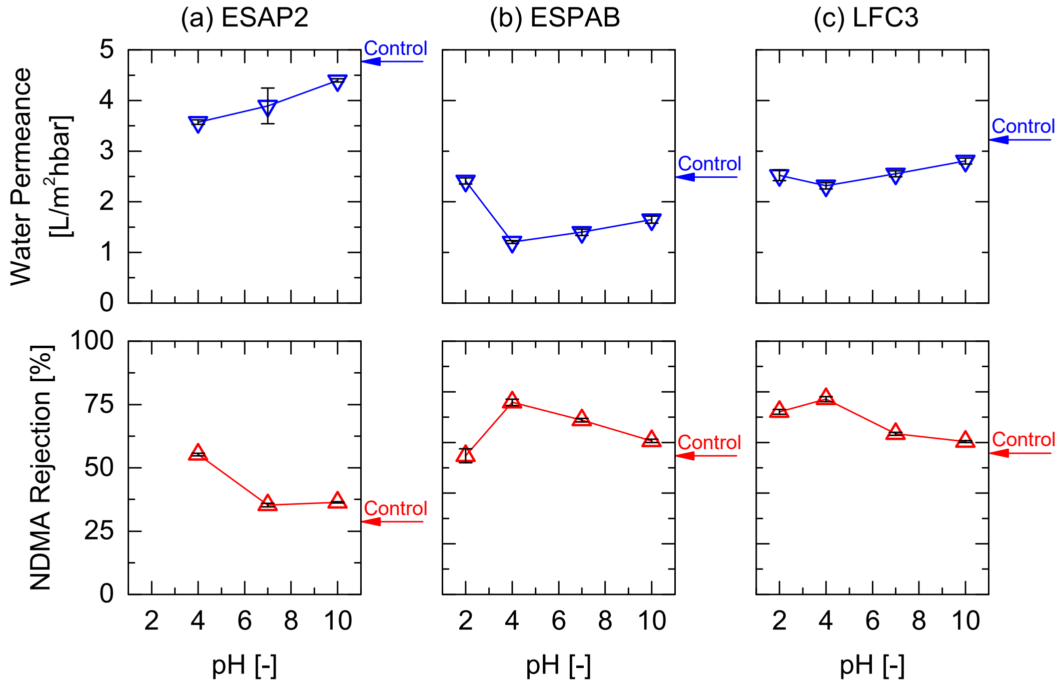


Fig. 3 – Effect of solution pH (at a heat treatment of 90 °C) on water permeance and *N*-nitrosodimethylamine (NDMA) rejection for (a) ESPA2, (b) ESPAB, and (c) LFC3 reverse osmosis (RO) membranes. The symbols and error bars represent the average and range, respectively, of the triplicated separation tests. "Control" indicates the values obtained using non-treated RO membranes.

The enhanced removal of NDMA by polyamide membranes after exposure to an acidic solution agrees with previous studies that focused on CEC removal after chemical cleaning (e.g., pH = 3–4) [25, 26]. The surface of polyamide RO membranes, including the ESPA series, have an isoelectric point of approximately pH 4 [25], at which the charge of the skin layer is neutral. In other words, electrostatic repulsion among residual (i.e., unreacted) carboxylic acid functional groups (–COOH) or amine functional groups (–NH_2) can occur at pH values higher or lower than the isoelectric point, respectively. Therefore, adjusting the solution pH at the isoelectric point (i.e., pH = 4) can reduce the electrostatic repulsion among the polymers of the free-volume hole and potentially reduce the free-volume hole size [26-28]. Reduced free-volume hole size can reduce the clearance between solutes and free-volume holes, leading to increased NDMA rejection and decreased water permeance. The solution pH during the NDMA rejection tests (i.e., after heat treatment) was commonly adjusted to eight, which has the potential to harmonize the properties of RO membranes treated at various pHs. However, varying NDMA rejections were observed among these RO membranes; thus, membrane property changes during heat treatment at different pH values can be irreversible.

3.4 Performance and stability

The efficacy of heat-modified RO membranes can be evaluated based on membrane performance (i.e., NDMA rejection and water permeance) and stability. Firstly, NDMA rejection values of the RO membranes treated at various temperatures, solution pH, and time were evaluated based on their water permeance **(Fig. 4)**. Overall, NDMA rejection (29–80%) was inversely proportional to water permeance (1.2–4.8 L/m^{2}hbar); NDMA rejection increased by heat treatment in exchange for reduced water permeance. Such a tradeoff can be typically observed among differently fabricated polyamide RO membranes [29-32], in which the passage of both solutes and solution in the skin layer (e.g., free-volume holes) can be reduced. This indicates that the heat treatment applied in this study followed a classical tradeoff between membrane selectivity and water permeance. Despite the observed tradeoff, heat treatment can be considered as a modification option that can help achieve an NDMA rejection as high as 80%.

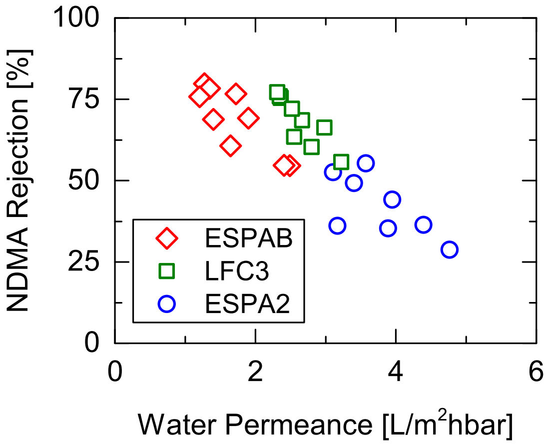


Fig. 4 – *N*-nitrosodimethylamine (NDMA) rejection by ESPA2, ESPAB, and LFC3 reverse osmosis (RO) membranes as a function of their water permeance at various heat treatment temperatures, pH, and time.

Performance stability of heat-modified RO membranes is important for full-scale applications. A long-term stability test was conducted using the MBR-treated wastewater and the heat-treated ESPAB RO membrane, which was prepared at a heat treatment temperature of 90 °C, solution pH of four, and treatment time of 4 h. In addition to the main target chemical, NDMA, three other *N*-nitrosamines (i.e., NMEA, NPYR, and NMOR) were used. Over the course of the six day test, both water permeance and *N*-nitrosamine rejection slightly increased **(Fig. 5a and 5b)**. The water permeance increased from 2.0 to 2.1 L/m^{2}hbar during the first day before stabilizing at 2.2 L/m^{2}hbar; it did not return to the control value (i.e., before heat treatment). NDMA rejection increased from 74 to 78% during the first day, remaining constant until the 5th day (120 h), and eventually reaching a rejection of 86% despite the stable water permeance and stable rejection of the other three *N*-nitrosamines. NDMA concentration in the RO feed continuously decreased from approximately 500 ng/L after 48 h, reaching 59 ng/L at 144 h **(Fig. S3)**. Because the RO concentrate and permeate were recirculated during the test, NDMA may have degraded due to biological activities in a similar manner to conventional wastewater treatment [33]. Although the impact of NDMA concentration on its rejection is minor in the RO feed [34], the data showing increased NDMA rejection at 144 h may not be reliable. The rejection of other *N*-nitrosamines also remained constant at 92–94% (NMEA), 96–97% (NPYR), and 98–99% (NMOR). During the six day test, conductivity rejection remained stable at 99.1–99.2% **(Fig. 5c)**. Similarly, the heat-treated EPSA2 RO membrane also showed stable NDMA rejection of 48–51% in a clean water matrix solution over the course of the six day test **(Fig. S4)**. The results indicate that the stability of the heat-treated RO membranes for the rejection of *N*-nitrosamines is relatively high. Considering that RO membrane elements are typically used for over five years, it is important to conduct further long-term studies.

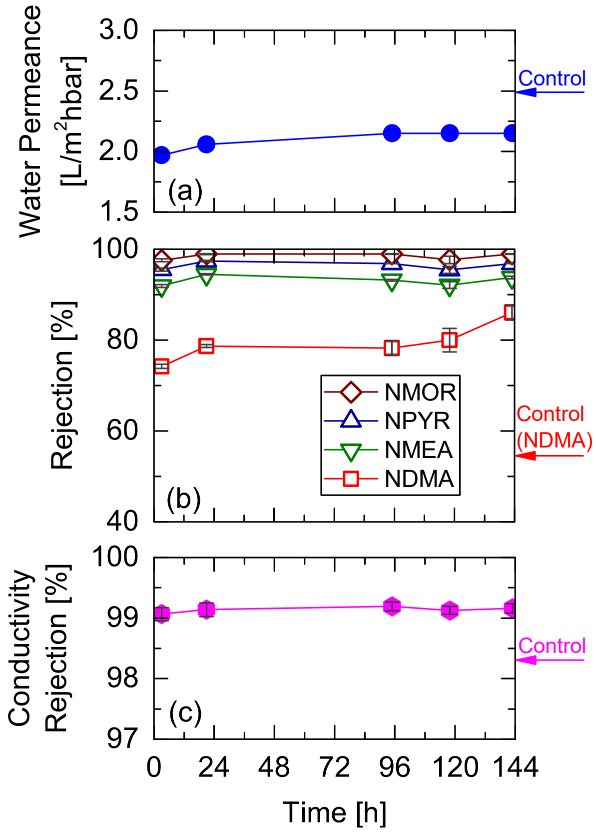


Fig. 5 – Stability of (a) water permeance, (b) *N*-nitrosamine rejection, and (c) conductivity rejection with a heat-treated ESPAB reverse osmosis (RO) membrane during the treatment of the membrane bioreactor (MBR) effluent at a transmembrane pressure of 1.55 MPa. The symbols and error bars represent the average and range, respectively, of the duplicated separation tests. "Control" indicates the values obtained using non-treated RO membranes.

3.5 Underlying mechanisms

It has been suggested [12, 35, 36] that the rejection of uncharged CECs, including *N*-nitrosamines, is mainly governed by size exclusion mechanisms, in which the clearance between the solute size and free-volume hole size is likely to be a critical factor. The theory is based on empirical data using a wide range of CECs. Our previous study [37] addressed the clarification of the mechanisms by measuring the membrane property (i.e., free-volume hole size) using positron annihilation lifetime spectroscopy. However, no correlation between the solute rejection and free-volume hole size was observed, possibly due to the limitation of the analyzed holes in the skin layer, indicating challenges in correlating the size of free-volume holes with NDMA transport.

This study addressed the mechanisms using another classical indicator–molecular weight cut-off (MWCO). MWCO can be defined as the minimum molecular weight of the chemical that is 90% retained by the membrane. MWCO is a surrogate indicator that indirectly represents the size of the free-volume hole; a tighter membrane has a lower MWCO. The MWCO in this study was determined based on the rejection of *N*-nitrosamines, including NDMA **(Fig. 6a)**. As a result, the calculated MWCO of these membranes was highly correlated with NDMA rejection **(Fig. 6b)**, indicating that tighter (lower MWCO) RO membranes show higher NDMA rejection. This implies that the reduction in free-volume hole size (i.e., tightness) of RO membranes by heat treatment is likely to play an important role in enhancing NDMA rejection.

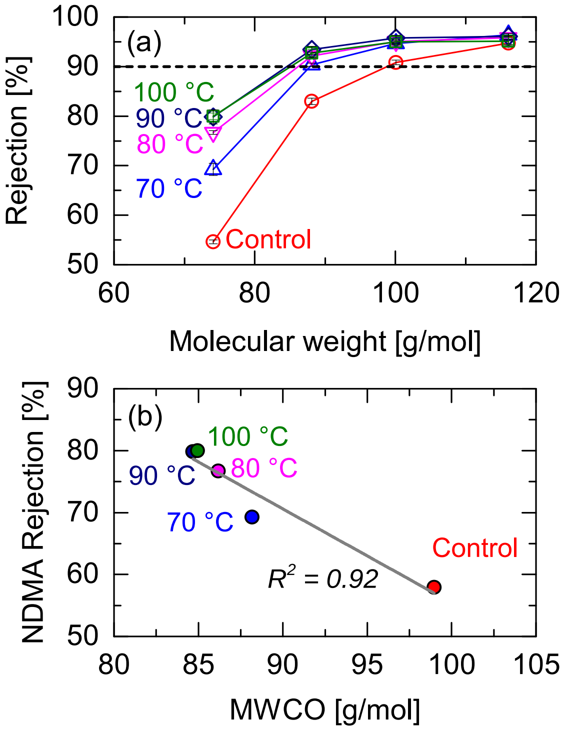


Fig. 6 – (a) *N*-nitrosamine rejection by the heat-treated ESPAB reverse osmosis (RO) membrane as a function of their molecular weight and (b) rejection of *N*-nitrosodimethylamine (NDMA) as a function of the molecular weight cut-off (MWCO). The symbols and error bars represent the average and range, respectively, of the duplicated separation tests. “Control” indicates the values obtained using non-treated RO membranes.

The potential causes of the enhanced tightness of the RO skin layer include the compression of free volume holes. A previous study [18] found that the polysulfone (PS) ultrafiltration (UF) support layer, which is located underneath the skin layer of the RO membrane, can be shrunk by heat treatment. The shrunk UF support layer can pull the RO skin layer located immediately above, with compression of the free-volume holes occurring **(Fig. 7)**. The free-volume hole size in water can be minimized when heat treatment is conducted at a high temperature of 90–100 °C and a low solution pH of approximately four, which is the isoelectric point of typical RO membranes. The polyamide (PA) skin layer can be very sensitive to hydrolysis at a low solution pH of two, whereas the PVA coating layer of the RO membrane (LFC3 RO membrane in this study) may act as a protective layer against hydrolysis. As free-volume holes are the passage of solutes (e.g., NDMA) and solution (e.g., water), heat treatment can ultimately cause enhanced NDMA rejection and reduced water permeance regardless of membrane selection and heat treatment conditions. To improve the feasibility of the high NDMA rejection RO membrane, an approach that enhances both NDMA rejection and water permeance needs to be explored in a future study.

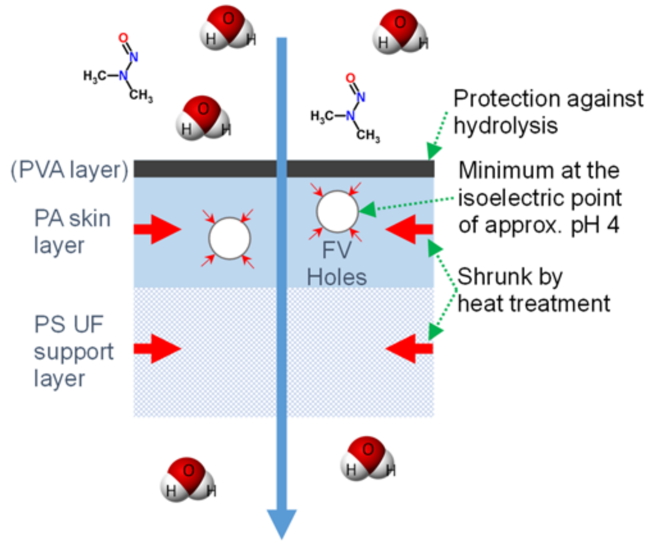


Fig. 7 – Speculated mechanisms underlying the changes in free-volume (FV) holes in the polyamide (PA) skin layer along with a polysulfone (PS) ultrafiltration (UF) support layer and polyvinyl (PVA) coating layer.

4 Conclusions

This study showed that the effect of heat treatment on *N*-nitrosodimethylamine (NDMA) rejection and water permeance varies depending on time, temperature, and solution pH. Heat treatment at a solution temperature of 90 °C and solution pH of four provided the highest NDMA rejection of three commercial reverse osmosis (RO) membranes (ESPA2, ESPAB, and LFC3). The heat-treated ESPAB RO membrane showed a maximum NDMA rejection of 80%. Heat treatment commonly resulted in a tradeoff between the selectivity (i.e., NDMA rejection) and water permeance. Despite this tradeoff, this study suggests that facile heat modification under the optimized heat treatment conditions can effectively enhance the performance of RO membranes for NDMA removal.

5 Acknowledgements

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6 References

[1] USEPA, N-Nitrosodimethylamine (CASRN 62-75-9) - Integrated risk information system (IRIS), in, U.S. Environmental Protection Agency, 1993.

[2] CSWRCB, Investigation on the feasibility of developing uniform water recycling criteria for direct potable reuse, in: California State Water Resources Control Board, Sacramento, CA, 2016.

[3] A.D. Shah, W.A. Mitch, Halonitroalkanes, Halonitriles, Haloamides, and N-Nitrosamines: A Critical Review of Nitrogenous Disinfection Byproduct Formation Pathways, Environ. Sci. Technol., 46 (2012) 119-131.

[4] NRMMC, EPHC, AHMC, Australian guidelines for water recycling: Managing health and environmental risks (Phase 2): Augmentation of drinking water supplies, Environment Protection and Heritage Council, National Health and Medical Research Council, Natural Resource Management Ministerial Council, Canberra, 2008.

[5] H.L. Leverenz, G. Tchobanoglous, T. Asano, Direct potable reuse: A future imperative, J. Water Reuse Desalination, 1 (2011) 2-10.

[6] C.Y. Tang, Z. Yang, H. Guo, J.J. Wen, L.D. Nghiem, E. Cornelissen, Potable Water Reuse through Advanced Membrane Technology, Environ. Sci. Technol., 52 (2018) 10215-10223.

[7] H. Croll, A. Soroush, M.E. Pillsbury, S. Romero-Vargas Castrillón, Graphene oxide surface modification of polyamide reverse osmosis membranes for improved N-nitrosodimethylamine (NDMA) removal, Sep. Purif. Technol., 210 (2019) 973-980.

[8] L.N. Breitner, K.J. Howe, D. Minakata, Boron Can Be Used to Predict Trace Organic Rejection through Reverse Osmosis Membranes for Potable Reuse, Environ. Sci. Technol., 52 (2018) 13871-13878.

[9] V. Albergamo, B. Blankert, E.R. Cornelissen, B. Hofs, W.-J. Knibbe, W. van der Meer, P. de Voogt, Removal of polar organic micropollutants by pilot-scale reverse osmosis drinking water treatment, Water Res., 148 (2019) 535-545.

[10] V. Kolev, V. Freger, Molecular Dynamics Investigation of Ion Sorption and Permeation in Desalination Membranes, J. Phys. Chem. B, 119 (2015) 14168-14179.

[11] V. Kolev, V. Freger, Hydration, porosity and water dynamics in the polyamide layer of reverse osmosis membranes: A molecular dynamics study, Polymer, 55 (2014) 1420-1426.

[12] T. Fujioka, S.J. Khan, Y. Poussade, J.E. Drewes, L.D. Nghiem, *N*-nitrosamine removal by reverse osmosis for indirect potable water reuse – A critical review based on observations from laboratory-, pilot- and full-scale studies, Sep. Purif. Technol., 98 (2012) 503-515.

[13] T. Fujioka, N. Oshima, R. Suzuki, S.J. Khan, A. Roux, Y. Poussade, J.E. Drewes, L.D. Nghiem, Rejection of small and uncharged chemicals of emerging concern by reverse osmosis membranes: The role of free volume space within the active skin layer, Sep. Purif. Technol., 116 (2013) 426-432.

[14] S. Shultz, M. Bass, R. Semiat, V. Freger, Modification of polyamide membranes by hydrophobic molecular plugs for improved boron rejection, J. Membr. Sci., 546 (2018) 165-172.

[15] S. Shultz, V. Freger, In situ modification of membrane elements for improved boron rejection in RO desalination, Desalination, 431 (2018) 66-72.

[16] Y. Li, S. Wang, X. Song, Y. Zhou, H. Shen, X. Cao, P. Zhang, C. Gao, High boron removal polyamide reverse osmosis membranes by swelling induced embedding of a sulfonyl molecular plug, J. Membr. Sci., (2019) 117716.

[17] M. Shi, W. Yan, C. Dong, L. Liu, S. Xie, C. Gao, Solvent activation before heat-treatment for improving reverse osmosis membrane performance, J. Membr. Sci., 595 (2020) 117565.

[18] T. Shintani, H. Matsuyama, N. Kurata, Effect of heat treatment on performance of chlorine-resistant polyamide reverse osmosis membranes, Desalination, 247 (2009) 370-377.

[19] T. Fujioka, N. Oshima, R. Suzuki, M. Higgins, W.E. Price, R.K. Henderson, L.D. Nghiem, Effect of heat treatment on fouling resistance and the rejection of small and neutral solutes by reverse osmosis membranes, Water Sci. Technol. Water Supply, 15 (2015) 510-516.

[20] T. Fujioka, L.D. Nghiem, Modification of a polyamide reverse osmosis membrane by heat treatment for an enhanced fouling resistance, Water Sci. Technol. Water Supply, 13 (2013) 1553-1559.

[21] T. Fujioka, K.P. Ishida, T. Shintani, H. Kodamatani, High rejection reverse osmosis membrane for removal of N-nitrosamines and their precursors, Water Res., 131 (2018) 45-51.

[22] B. Van der Bruggen, A. Verliefde, L. Braeken, E.R. Cornelissen, K. Moons, J.Q.J.C. Verberk, H.J.C. van Dijk, G. Amy, Assessment of a semi-quantitative method for estimation of the rejection of organic compounds in aqueous solution in nanofiltration, J. Chem. Technol. Biotechnol., 81 (2006) 1166-1176.

[23] H. Kodamatani, S.L. Roback, M.H. Plumlee, K.P. Ishida, H. Masunaga, N. Maruyama, T. Fujioka, An inline ion-exchange system in a chemiluminescence-based analyzer for direct analysis of N-nitrosamines in treated wastewater, J. Chromatogr. A, 1553 (2018) 51-56.

[24] T. Fujioka, H. Kodamatani, L.D. Nghiem, T. Shintani, Transport of N-Nitrosamines through a Reverse Osmosis Membrane: Role of Molecular Size and Nitrogen Atoms, Environ. Sci. Technol. Letters, 6 (2019) 44-48.

[25] T. Fujioka, S.J. Khan, J.A. McDonald, A. Roux, Y. Poussade, J.E. Drewes, L.D. Nghiem, *N*-nitrosamine rejection by reverse osmosis: Effects of membrane exposure to chemical cleaning reagents, Desalination, 343 (2014) 60-66.

[26] A. Simon, W.E. Price, L.D. Nghiem, Influence of formulated chemical cleaning reagents on the surface properties and separation efficiency of nanofiltration membranes, J. Membr. Sci., 432 (2013) 73-82.

[27] A.E. Childress, M. Elimelech, Relating nanofiltration membrane performance to membrane charge (electrokinetic) characteristics, Environ. Sci. Technol., 34 (2000) 3710-3716.

[28] M.S. Oak, T. Kobayashi, H.Y. Wang, T. Fukaya, N. Fujii, pH effect on molecular size exclusion of polyacrylonitrile ultrafiltration membranes having carboxylic acid groups, J. Membr. Sci., 123 (1997) 185-195.

[29] H. Zhang, G.M. Geise, Modeling the water permeability and water/salt selectivity tradeoff in polymer membranes, J. Membr. Sci., 520 (2016) 790-800.

[30] G.M. Geise, H.B. Park, A.C. Sagle, B.D. Freeman, J.E. McGrath, Water permeability and water/salt selectivity tradeoff in polymers for desalination, J. Membr. Sci., 369 (2011) 130-138.

[31] R. Bernstein, S. Belfer, V. Freger, Toward Improved Boron Removal in RO by Membrane Modification: Feasibility and Challenges, Environ. Sci. Technol., 45 (2011) 3613-3620.

[32] J.R. Werber, C.O. Osuji, M. Elimelech, Materials for next-generation desalination and water purification membranes, Nature Reviews: Materials, 1 (2016) 16018.

[33] D. Sedlak, M. Kavanaugh, Removal and destruction of NDMA and NDMA precursors during wastewater treatment, WateReuse Foundation, 2006.

[34] T. Fujioka, L.D. Nghiem, S.J. Khan, J.A. McDonald, Y. Poussade, J.E. Drewes, Effects of feed solution characteristics on the rejection of *N*-nitrosamines by reverse osmosis membranes, J. Membr. Sci., 409–410 (2012) 66-74.

[35] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment - A literature review, Water Res., 38 (2004) 2795-2809.

[36] K. Doederer, M.J. Farré, M. Pidou, H.S. Weinberg, W. Gernjak, Rejection of disinfection by-products by RO and NF membranes: Influence of solute properties and operational parameters, J. Membr. Sci., 467 (2014) 195-205.

[37] T. Fujioka, B.E. O'Rourke, K. Michishio, Y. Kobayashi, N. Oshima, H. Kodamatani, T. Shintani, L.D. Nghiem, Transport of small and neutral solutes through reverse osmosis membranes: Role of skin layer conformation of the polyamide film, J. Membr. Sci., 554 (2018) 301-308.