Plugging nonporous polyamide membranes for enhanced rejection of small contaminants during advanced wastewater treatment

Takahiro Fujioka [1,*], Miyu Osako [2], Shuji Tanabe [1],

Hitoshi Kodamatani [3], Takuji Shintani [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 Earth and Environmental Science, Graduate School of Science and Engineering, Kagoshima University, 1-21-35 Korimoto, Kagoshima 890-0065, Japan*

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

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

Abstract

Removing *N*-nitrosodimethylamine (NDMA), a regulated carcinogenic chemical, with a reverse osmosis (RO) membrane is a key challenge for enhancing the safety of reused potable water. This study aimed to achieve high rejection of NDMA and salts by plugging the nanopores in an RO membrane with linear-chain amines, amides, and epoxides. Plugging with amines or epoxides generally led to a reduction in water permeance and an increase in conductivity rejection. NDMA rejection increased linearly with the size of amines. The RO membrane plugged with dodecylamine exhibited an NDMA rejection of 87% when treating the effluent from a membrane bioreactor, and this performance was maintained for 8 d. In contrast, amide or epoxide plugs resulted in only minor improvements in NDMA rejection. We speculate that the amine plugs remain in the nanopores through electrostatic attractions, whereas amides and epoxides become readily detached from the nanopores because they are only bound through weaker hydrogen-bonding interactions. This study provides an understanding of the plugging mechanism that enhances NDMA rejection and demonstrated high NDMA rejection using treated wastewater.

Keywords: RO membrane, NDMA removal, membrane modification, water reuse, micropollutants.

1 Introduction

Potable water reuse is being increasingly adopted in many regions in the US, Australia, and Singapore to augment drinking water supplies [1]. Such water reuse is based on the purification of secondary wastewater effluents through an advanced wastewater treatment train (e.g., microfiltration, reverse osmosis, and advanced oxidation) [2, 3]. The removal of contaminants of emerging concern (CECs) during this process is important to ensure public safety and to maintain health [4, 5]. Although most CECs in wastewater are typically removed by reverse osmosis (RO) membranes [6, 7], *N*-nitrosodimethylamine (NDMA; $C_2H_6N_2O$), a regulated carcinogenic chemical [8], is insufficiently removed (typically < 50% rejection) [9] and can be found in RO permeates at concentrations higher than regulated values (e.g., 10 ng/L) [10].

There is a clear need for the development of an RO membrane capable of achieving the highly efficient removal of CECs, particularly NDMA [11]. Salt removal is a typical criterion of an RO membrane, and a significant amount of previous research has aimed to develop a variety of surface-modification and interfacial-polymerization methods for rejecting boron at high levels by RO membranes in seawater desalination [12-16]. In addition, polyamide-based RO membranes designed to highly reject boron are also commercially available. However, no commercial polyamide-based RO membranes have been designed to reject CECs that include NDMA [17]. Likewise, some research using graphene oxide surface-modification [18] and heat-modification [19] techniques have been reported for enhancing NDMA rejection.

The removal of small and uncharged constituents, including NDMA, is challenging for RO membranes that have sub-nanometer-scale free-volume holes (or nanopores) in their separation layers [20, 21]. The permeation of these small molecules through an RO membrane is dependent on the clearance between the solute and the sub-nanometer-scale pores located in the active polyamide skin layer [22-24]. The minimal projection area (MPA), which is a two-

58 dimensional projected area of the molecule, has been introduced as an important molecular-
59 size parameter that correlates with chemical rejection [21]. The MPA of NDMA is 19.4 $Å^2$,
60 whereas the mean cross-sectional area of the pores in commercial polyamide RO membranes
61 determined by positron annihilation lifetime spectroscopy (PALS) is approximately 24 $Å^2$ [25].
62 Therefore, reducing the mean cross-sectional nanopore area is critical in order to reduce
63 clearance and, consequently, achieve high NDMA rejection.

64 "Plugging" is a modification technique intended to narrow sub-nanometer-scale pores, and has
65 been demonstrated to enhance the removal of boric acid [16, 26]. It should be noted that boric
66 acid is rejected in a similar manner to NDMA [27, 28]. The plugging method is designed to
67 narrow the nanopores of RO membranes by plugging them with small hydrophobic molecules
68 such that less of the target solute can permeate through. A previous study by Shultz et al. [22]
69 successfully improved boron (molecular weight = 63 g/mol) rejection by plugging an RO
70 membrane with relatively large aliphatic amines, such as decylamine and dodecylamine
71 (molecular weights of 157 and 185 g/mol, respectively). The hydrophobic properties of the
72 molecular plugs appear to be the key to successfully modifying the membrane for enhanced
73 boron rejection, as the plugs need to be immobilized within the nanopores of the RO membrane.
74 In fact, hydrophobic molecules (e.g., with octanol-water coefficients ($\log D$) ≥ 4) are readily
75 adsorbed on the surfaces of RO membranes [20, 29, 30]; however, the detailed mechanism
76 critical for successful plugging has not been clarified.

77 The importance of the properties of the molecular plug can be clarified by understanding the
78 impact of different plugging moieties on NDMA rejection. As alternative plugs, this study
79 investigated linear-chain molecules bearing amino, amid, or epoxy functional groups. Amides
80 can be immobilized in the nanopores of a polyamide RO membrane through hydrogen bonding
81 between both sets of amide functional groups [31]. Epoxides are more hydrophobic than their

amine counterparts; hence, they are expected to be better immobilized in membrane nanopores than amines.

This study aimed to identify the properties of molecular plugs that are important for successfully plugging membrane nanopores for enhanced NDMA rejection. The plug materials used in this study include linear-chain amines, amides, and epoxides that have MPAs of at least 20 $Å^2$. The performance stabilities of the modified RO membranes were assessed by treating the effluent from a membrane bioreactor. The ultimate goal of this study was to establish a promising plugging approach for high NDMA rejection by understanding the key properties of the molecular plugs.

2 Experimental

2.1 Chemicals

Four *N*-nitrosamines, namely NDMA, *N*-nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), and *N*-nitrosomorpholine (NMOR) were obtained from Ultra Scientific (Kingstown, RI, USA) **(Table 1)**. Their chemical properties (MPA, log*D*, pKa, dipole moment, and charge) were calculated using commercial MarvinSketch version 18.30 software (ChemAxon; Budapest, Hungary). The MPA of a compound is a two-dimensional projected area of the molecule calculated based on the van der Waals radius **(Fig. S1)**. Log*D* is the octanol-water coefficient that determines the hydrophobicity of a molecule. Based on the log*D* (-0.2–0.4) and pKa (3.1–3.5) values of *N*-nitrosamines, they are classified as hydrophilic and uncharged compounds. The molecular plugs used in this study include linear-chain amines, amides, and epoxides that have MPAs ≥ 20 $Å^2$ **(Table 2)**; their chemical structures and hazard information are provided in **Table S1** and **Table S2**, respectively. Other chemicals (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	Molecular formula	Molecular weight [g/mol]	Minimum projection area [Å^2]
NDMA	$C_2H_6N_2O$	74.1	19.4
NMEA	$C_2H_8N_2O$	88.1	22.1
NPYR	$C_4H_8N_2O$	100.1	24.1
NMOR	$C_4H_8N_2O_2$	116.1	26.9

Table 2 – Physicochemical properties of the selected amines, amides, and epoxides.

Chemicals	Molecular plug	Molecular formula	Molecular weight [g/mol]	Minimum projection area [Å^2]	pK_a[a] [-]	Log *D* at pH 8 [-]	Dipole moment [D]
Amine	Hexylamine	$C_6H_{15}N$	101.2	20.7	10.5[b]	-0.6	0.8
	Octylamine	$C_8H_{19}N$	129.2	21.4	10.4[b]	0.3	0.8
	Decylamine	$C_{10}H_{23}N$	157.3	23.4	10.4[b]	1.2	0.8
	Dodecylamine	$C_{12}H_{27}N$	185.4	30.2	10.4[b]	2.1	0.8
Amide	Butyramide	C_4H_9NO	87.1	20.3	ni[c]	0.1	4.4
	Hexanamide	$C_6H_{13}NO$	115.2	20.5	ni[c]	1.0	4.4
	Octanamide	$C_8H_{17}NO$	143.2	25.1	ni[c]	1.9	4.4
	Decanamide	$C_{10}H_{21}NO$	171.3	28.4	ni[c]	2.8	4.4
	Dodecanamide	$C_{12}H_{25}NO$	199.3	28.0	ni[c]	3.7	4.4
Epoxide	1,2-Epoxybutane	C_4H_8O	72.1	19.5	ni[c]	0.9	2.5
	1,2-Epoxyhexane	$C_6H_{12}O$	100.2	21.8	ni[c]	1.8	2.5
	1,2-Epoxyoctane	$C_8H_{16}O$	128.2	25.0	ni[c]	2.7	2.5
	1,2-Epoxydecane	$C_{10}H_{20}O$	156.3	27.9	ni[c]	3.6	2.5
	1,2-Epoxydodecane	$C_{12}H_{24}O$	184.3	27.2	ni[c]	4.5	2.5

[a]pKa value in the 0–14 pH range.

[b]99.6% of the species are dissociated and are positively charge in a pH 8.0 solution.

[c]ni: Not ionized in the 0–14 pH range.

2.2 Membrane treatment systems

A bench-scale RO treatment system with two cross-flow stainless-steel membrane cells was used in this study **(Fig. S2)**. The system contains the two membrane cells, a high-pressure pump (Q30, Tacmina, Osaka, Japan), a 500-mL glass reservoir, a pressure regulating valve, a digital flow meter, a cooling unit (NCB-500, Tokyo Rikakikai, Tokyo, Japan), and a heating circulator (AS ONE, Osaka, Japan). Commercial polyamide low-pressure reverse osmosis (LPRO) membrane (ESPAB) coupons (Nitto/Hydranautics, Osaka, Japan) were installed in the membrane cells. Each membrane sample had an effective surface area of 3.35 cm^2. In addition to ESPAB membrane, three other RO membranes—SWC5 and HYDRApro (Nitto/Hydranautics, Osaka, Japan), and BW30 (Dupont/Filmtec, Midland, MI, USA)—were used.

2.3 Experimental protocols

Membrane plugging was carried by treating the RO membranes with the required plugging solution using the above-mentioned laboratory-scale RO system. Unless otherwise specified, a 2-mM solution of the molecular plug was prepared in a clean water matrix (NaCl = 40 mM, $NaHCO_3$ = 1 mM, and $CaCl_2$ = 1 mM). Prior to plugging treatment, each RO membrane was stabilized using pure water at a transmembrane pressure of 1 MPa, a cross-flow velocity of 1.2 cm/s, and a feed temperature of 20 °C, and the water permeance (L/m^2hbar) of each RO membrane coupon was recorded. The pure water was then replaced with the plugging solution, and the RO system was operated at a transmembrane pressure of 1 MPa and a feed temperature of 30 °C for 15 h, after which the RO system was operated using pure water to flush out detached residual chemicals from the membrane surface. Water permeance was recorded following this treatment using the same procedure described above.

The performance of each modified RO membrane was evaluated using clean water matrix (NaCl = 40 mM, $NaHCO_3$ = 1 mM, and $CaCl_2$ = 1 mM, and NDMA = 500 ng/L). The RO system was operated at a specific permeate flux of 15 L/m^2h and feed temperature of 20 °C for 1 h, with RO feed and permeate samples collected from the feed reservoir and permeate exit, respectively. The separation performance of each modified RO membrane was also assessed using membrane-bioreactor-treated (MBR-treated) wastewater, which was collected from a municipal wastewater treatment plant in Japan. The MBR-treated wastewater was dosed with 500 ng/L of each *N*-nitrosamine (i.e., NDMA, NMEA, NPYR, and NMOR), and the system was operated at a permeate flux of 15 L/m^2h, with RO feed and permeate samples periodically collected from the feed reservoir and permeate exit, respectively. After the analysis of these feed and permeate samples, observed rejections of each *N*-nitrosamines and conductivity were calculated.

2.4 Analytical techniques

Concentrations of *N*-nitrosamines were determined by high-performance liquid chromatography–photochemical reaction chemiluminescence (HPLC-PR-CL). Full details of this analytical method has been provided in a previous study [32]. Fourier transform infrared spectroscopy (FTIR) (Nicolet iS5, Thermo Fisher Scientific, Waltham, MA, USA) in attenuated total reflection (ATR) mode was used to obtain the spectrum of each membrane surface. Prior to analysis, the RO membrane samples were pre-treated by freeze drying (FD-1000, Tokyo Rikakikai, Tokyo, Japan) for 24 h.

3 Results and discussion

3.1 Effectiveness of plugging chemicals

3.1.1 Amines

Plugging with amines generally resulted in a remarkable reduction in water permeance but in increases in conductivity rejection and NDMA rejection **(Fig. 1)**. Water permeance was found to be inversely related to the size of the molecular plug, which was observed to decrease from 2.8 to 1.2 L/m^{2}hbar with increasing chain length **(Fig. 1a)**. Conductivity rejection (98.4–99.6%) was consistent and did not depend on the amine plug; however, all conductivity rejections were higher than that of the pristine (without plugging) membrane (97.5%) **(Fig. 1b)**. NDMA rejection was observed to increase linearly as the number of carbon atoms was increased from six to twelve, with the RO membrane plugged with the largest amine (dodecylamine, $C_{12}H_{27}N$) exhibiting an NDMA rejection of 82%, which is almost twice that of the pristine membrane (42%) **(Fig. 1c)**. It should be noted that the data presented for the largest amine (dodecylamine) were obtained at an amine concentration of 0.75 mM, as plugging at a concentration of 2 mM, which was the standard concentration used in the remaining experiments, resulted in almost no water permeance following treatment, presumably due to

complete nanopore blockage. All dodecylamine concentrations were found to affect water permeance and NDMA rejection **(Fig. S3)**, which is in agreement with the findings reported in a previous study that focused on boron removal by plugged seawater RO membranes [22]. Overall, the results indicate that amines as molecular plugs effectively enhance NDMA rejection by an LPRO membrane in exchange for water permeance, with larger plug molecules having a greater impact.

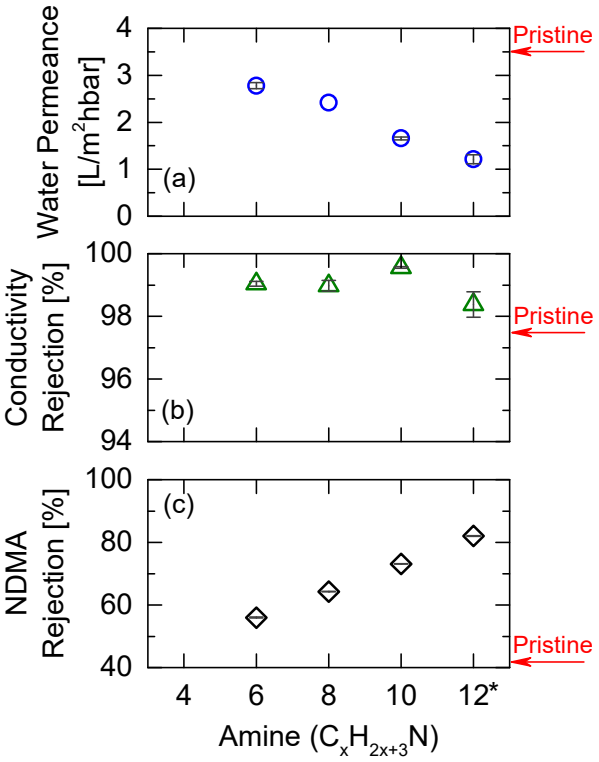

Fig. 1 – (a) Water permeance, (b) conductivity rejection, and (c) NDMA rejection by ESPAB reverse osmosis (RO) membranes modified with amines (permeate flux = 15 L/m^{2}h). Dodecylamine ($C_{12}H_{27}N$) modifications highlighted with an asterisk (*) were carried out at 0.75 mM; other modifications were carried out at 2.0 mM. The symbols and error bars represent averages and ranges, respectively of duplicated separation results.

3.1.2 Amides

In contrast to amines as plugs, amides were observed to have little effect on water permeance, conductivity rejection, and NDMA rejection. The five amides commonly exhibited higher NDMA rejections (52–64%) than the pristine membrane (42%) **(Fig. 2)**, and plugging with the largest amide (dodecanamide, $C_{12}H_{25}NO$) resulted in the highest NDMA rejection (64%),

whereas the conductivity rejection of the plugged membrane (95.5%) was considerably lower than that of the pristine membrane (97.5%). These results indicate that high molecular weight amides reduce conductivity and increase NDMA rejection; however they are not as effective as amines of comparable size.

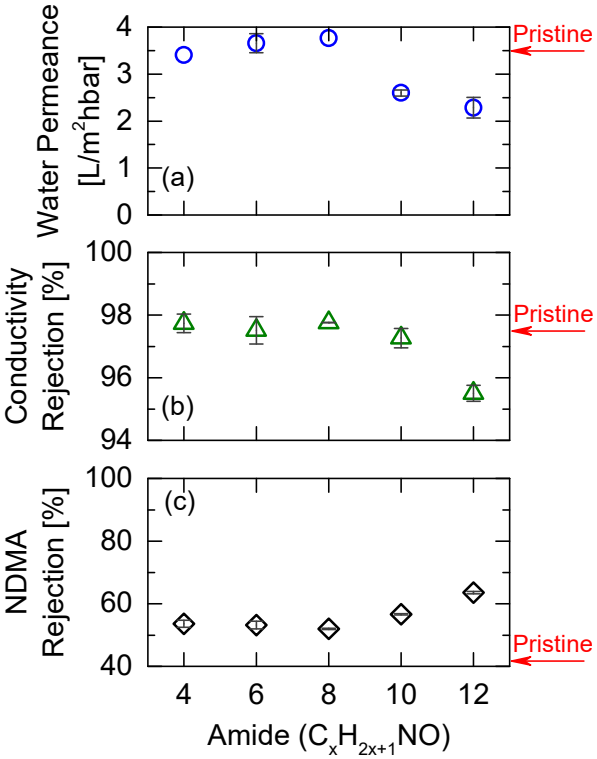

Fig. 2 – (a) Water permeance, (b) conductivity rejection, and (c) NDMA rejection by ESPAB reverse osmosis (RO) membranes modified with amides (permeate flux = 15 L/m^{2}h). The symbols and error bars represent averages and ranges, respectively, of duplicated separation results.

3.1.3 Epoxides

Unlike amines and amides, plugging with epoxides did not show a clear molecular-size dependence, with the plugged membranes commonly showing higher NDMA rejections (53–60%) than the pristine membrane (41%) **(Fig. 3)**. Unlike amides, water permeance did not decrease in exchange for increased NDMA rejection. However, the highest NDMA rejection achieved with an epoxide plug was only 60%; consequently, a plugging method that uses epoxides for enhanced NDMA rejection is unlikely to be feasible.

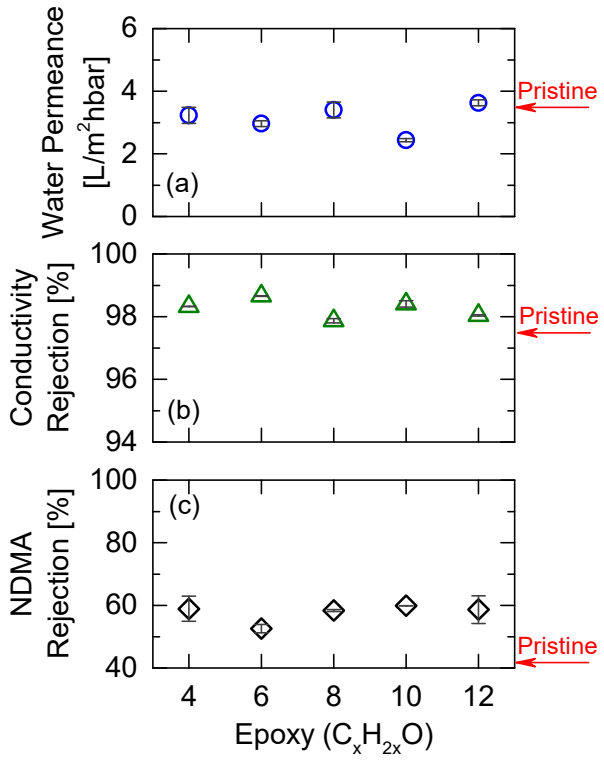

Fig. 3 – (a) Water permeance, (b) conductivity rejection, and (c) NDMA rejection by ESPAB reverse osmosis (RO) membranes modified by epoxides (permeate flux = 15 L/m^{2}h). The symbols and error bars represent averages and ranges, respectively, of duplicated separation results.

3.1.4 Trade-off

The effects of the various plugs (amines, amides, and epoxies) on key membrane transport parameters, namely water permeance and separation performance (i.e., conductivity and NDMA rejection), are summarized in **Fig. 4**. Plugging with amides resulted in a reduction in both water permeance and conductivity rejection **(Fig. 4a)**. In contrast, plugging with amines or epoxides generally led to a reduction in water permeance and an increase in conductivity rejection; this trade-off between water permeance and selectivity is typical for RO membranes [33-35]. The impact of plugging on NDMA rejection varied among the various molecular plugs **(Fig. 4b)**. RO membranes plugged with epoxides commonly showed NDMA rejections of approximately 60%, regardless of the level of water permeance, while RO membranes plugged with amides showed an inverse correlation (trade-off) between water permeance and NDMA rejection. However, both amides and epoxides did not necessarily reduce water permeance. In

contrast, the amine plugs exhibited a high inverse correlation (trade-off) between water permeance and NDMA rejection, which highlights the potential of plugging RO membrane nanopores in order to restrict the passage of both water and NDMA. The mechanism responsible for this trade-off is discussed in Section 3.3.

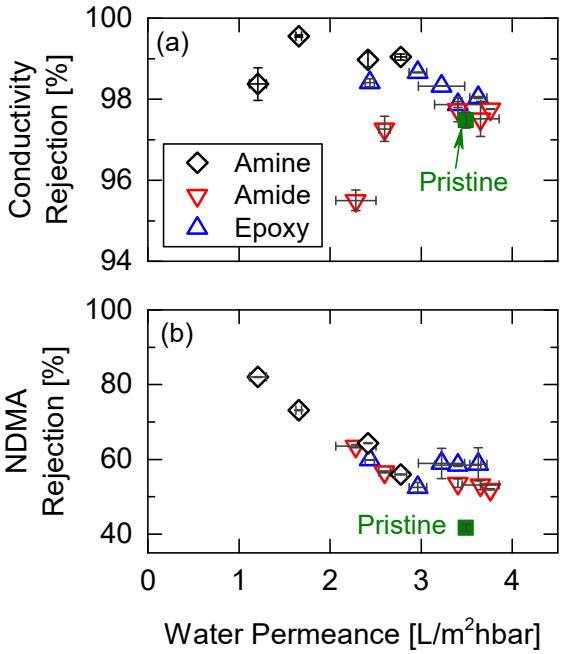

Fig. 4 – (a) Conductivity rejection and (b) NDMA rejection as functions of water permeance of pristine and modified ESPAB reverse osmosis (RO) membranes.

3.2 Practicability

3.2.1 Comparison with commercial RO membranes

The practicability of the RO membrane plugged with dodecylamine ($C_{12}H_{27}N$) was assessed by comparing its key membrane transport properties (i.e., water permeance and the rejection of salts and NDMA) against those of commercial RO membranes. RO membranes with high water permeances and high NDMA rejections are suitable for use in water-reuse applications. Conductivity rejection by the docecylamine-plugged RO membrane (98.4%) was lower than that of the SWC5 seawater RO membrane (99.0%) **(Fig. 5a)**. Although the plugged RO membrane did not show the highest conductivity rejection, its salt removal (> 98%) is sufficient

for recycling wastewater, which is less saline than seawater. Among the tested RO membranes, the plugged RO membrane showed the highest NDMA rejection **(Fig. 5b)**. Despite its low water permeance, the results suggest that the plugged RO membrane can achieve NDMA rejections in excess of 80%, and can potentially be used for potable water reuse.

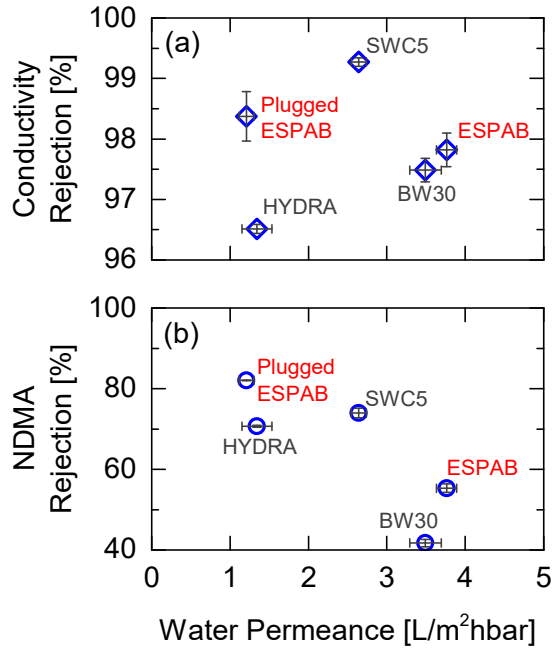

Fig. 5 – (a) Conductivities and (b) NDMA rejections of the RO membrane plugged with dodecylamine ($C_{12}H_{27}N$) and other commercial RO membranes (permeate flux of 15 L/m^{2}h).

3.2.2 Long-term operation

The practicability of the RO membrane plugged with dodecylamine ($C_{12}H_{27}N$) was assessed to ensure the persistency of the molecular plugs immobilized on or in the RO membrane skin layer by treating the effluent from a membrane bioreactor. The separation performance of the membrane during RO treatment was evaluated using four *N*-nitrosamines (i.e., NDMA, NMEA, NPYR, and NMOR). Over the course of eight days, permeate flux was maintained at a constant value of 15 L/m^{2}h at a constant transmembrane pressure of 1.25 MPa, which confirms that the molecular plugs are immobile. The plugged RO membrane showed a constant NDMA rejection of 78–81% **(Fig. 6)**. Similarly, the rejection of NMEA, NPYR, and NMOR remained high, at 93–95%, 97–98%, and 99.5–99.7%, respectively. The results show that the dodecylamine-

plugged RO membrane can stably deliver an NDMA rejection of 87%. This eight day test also demonstrated that the molecular plugs do not readily detach themselves from the RO membrane during the treatment of treated wastewater. Since molecular plugs including dodecylamine can be toxic to human health **(Table S2)**, the stability of the immobilized molecular plugs in the RO membranes needs to be further evaluated through long-term evaluations. In addition, further studies are needed to demonstrate the long-term performance and fouling propensity of this membrane.

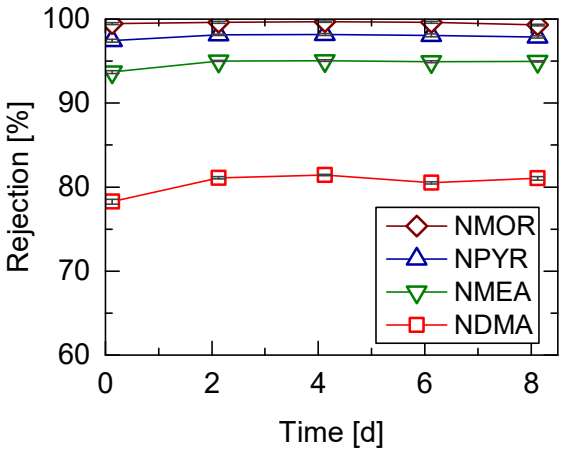

Fig. 6 – *N*-nitrosamine rejection by the dodecylamine-plugged ESPAB reverse osmosis (RO) membrane during the treatment of the effluent from a membrane bioreactor at a permeate flux of 15 L/m^{2}h and a constant transmembrane pressure of 1.25 MPa. The symbols and error bars represent averages and ranges, respectively, of duplicated separation results.

3.3 Mechanisms

The mechanism that determines how molecular-plug size impacts NDMA rejection was examined by determining the free nanopore area in the RO membrane. The pristine ESPAB RO membrane exhibited an NDMA (MPA = 19.4 Å^2) rejection of approximately 55% **(Fig. 7)**, which indicates that the pristine membrane contains many nanopores with free cross-sectional areas greater than 20 Å^2 through which NDMA molecules permeate. On the other hand, NMOR (MPA = 26.9 Å^2), the largest *N*-nitrosamine examined, was 95% rejected by this membrane; thus, we conclude that the pristine membrane contains nanopores with free cross-sectional

areas less than 27 Å^2. It should be noted that our previous PALS study [36] determined that the ESPAB RO membrane has a mean free cross-sectional nanopore area of 24 Å^2 (mean radius = 0.275 nm), which is equivalent to the observations made in this study. Overall, this study suggests that the high NDMA rejection (e.g., >95%) is likely due to the plugging of membrane nanopores with MPAs of 19–27 Å^2. In other words, molecular plugs with MPAs greater than 19 Å^2 are likely to effectively block large nanopores.

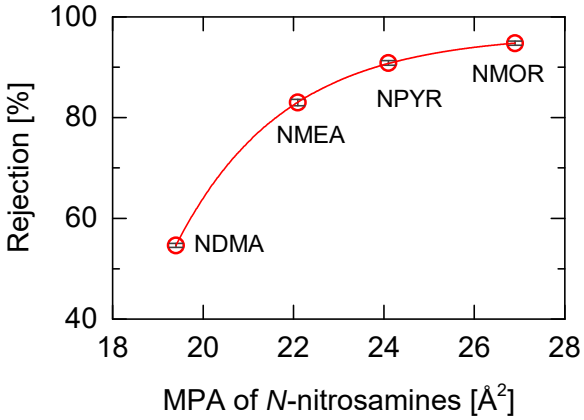

Fig. 7 – Rejections of *N*-nitrosamines by the pristine ESPAB RO membrane as a function of minimum projection area (MPA) (permeate flux of 15 L/m^{2}h).

The plugging effect observed in this study is consistent with the estimated free cross-sectional area of 19–27 Å^2. The RO membrane exhibited higher NDMA rejections when plugged with amines with MPAs greater than 20 Å^2 **(Fig. 8)**. The effect of the amine plug on NDMA rejection was greater at a higher MPA, and the highest NDMA rejection was achieved with the largest amine (dodecylamine; MPA = 30.2 Å^2). This long-chain amine has locally thinner parts with cross-sectional areas less than 30 Å^2, and the narrower regions of dodecylamine molecules may penetrate into the nanopores and enhance the plugging effect for NDMA removal. Dodecylamine (amine) contains a positively charged amino functional group at pH 8.0 **(Table 2)**. Since the membrane surface of the ESPAB RO membrane is negatively charged at pH of 8.0 **(Fig. S4)**, the membrane surface and dodecylamine can be electrostatically attracted to each

other **(Fig. 9a)**. Hence, the persistence of dodecylamine can be explained through the presence of strong electrostatic interactions.

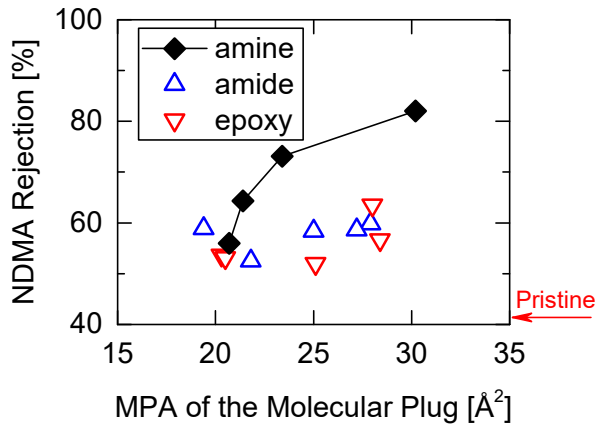

Fig. 8 – Effect of minimum projection area (MPA) of the molecular plug on NDMA rejection by the ESPAB RO membrane.

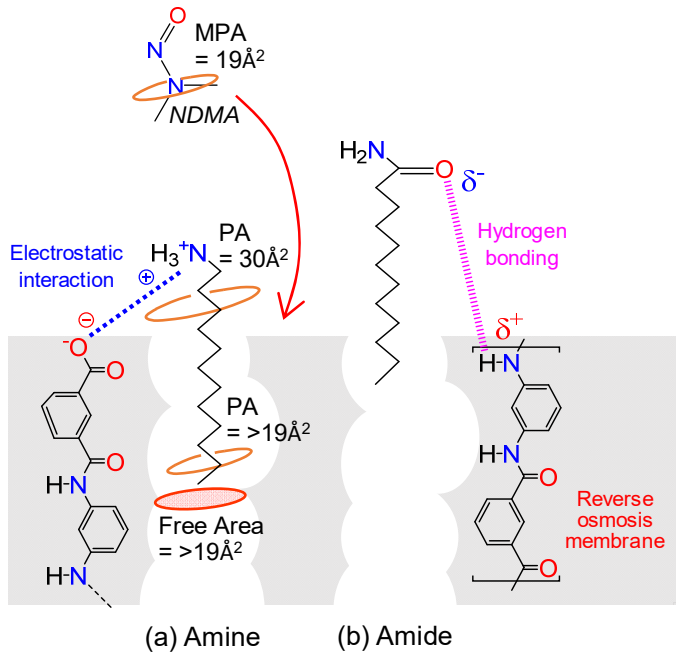

Fig. 9 – Speculative mechanisms that underpin membrane nanopores plugging with an amine (dodecylamine) and an amide (dodecanamide). PA = projection area, NDMA = *N*-nitrosodimethylamine.

In contrast, amides and epoxides are uncharged species **(Table 2)**. Although amides (e.g., dodecanamide) and epoxides (e.g., epoxydodecane) contains a hydrogen acceptor, which can be attracted to a hydrogen donor of the RO membrane **(Fig. 9b)**, this hydrogen bonding is weaker than electrostatic attraction. Therefore, we speculate that hydrogen bonding is

insufficient to securely immobilize these molecules in the membrane nanopores. Overall, in addition to the size of the molecular plug, the presence of positively charged atoms in the plugging molecule is likely to control how successfully the membrane nanopores are plugged for enhanced NDMA rejection. It should be noted that linear-chain molecules bearing negatively charged functional groups were not used in this study; thus, the impact of these molecular plugs on NDMA rejection will be evaluated in a future study. Further, a future study that focuses on the plugging method will explore an approach that limits NDMA passage while allowing water molecules to pass through, such that NDMA rejection is enhanced without considerably compromising water permeance.

4 Conclusions

This study investigated the importance of the properties of the molecular plugs used to block an RO membrane in order to achieve high NDMA rejection. Plugging with selected linear-chain amides or epoxides was not sufficiently effective for NDMA-rejection purposes. In contrast, the selected linear-chain amines, which contain positively charged nitrogen atoms at pH 8 and a minimum projection area of at least 20 $Å^2$, were found to enhance NDMA rejection, whereas the water permeances of these modified membranes are inversely related to NDMA rejection. This study demonstrated that the RO membrane plugged with dodecylamine delivered a stable NDMA rejection of 87% over an 8-d period. We suggest that, in addition to the size of the molecular plug, the presence of positively charged atoms on the plugging molecule is likely to determine its ability to plug membrane nanopores for enhanced NDMA rejection.

5 Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP18H01572. We thank Nitto/Hydranautics for providing RO membrane samples for this investigation.

6 References

[1] WHO, Potable reuse: guidance for producing safe drinking-water, in, World Health Organization, Geneva, 2017.

[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] D. Gerrity, B. Pecson, R.S. Trussell, R.R. Trussell, Potable reuse treatment trains throughout the world, J. Water Supply Res Technol.-Aqua, 62 (2013) 321-338.

[4] S. Bieber, S.A. Snyder, S. Dagnino, T. Rauch-Williams, J.E. Drewes, Management strategies for trace organic chemicals in water – A review of international approaches, Chemosphere, 195 (2018) 410-426.

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

[6] 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.

[7] 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.

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

[9] 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.

[10] 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.

[11] J.R. Werber, A. Deshmukh, M. Elimelech, The Critical Need for Increased Selectivity, Not Increased Water Permeability, for Desalination Membranes, Environ. Sci. Technol. Letters, 3 (2016) 112-120.

[12] L. Liu, X. Xie, S. Qi, R. Li, X. Zhang, X. Song, C. Gao, Thin film nanocomposite reverse osmosis membrane incorporated with UiO-66 nanoparticles for enhanced boron removal, J. Membr. Sci., 580 (2019) 101-109.

[13] S. Wang, Y. Zhou, C. Gao, Novel high boron removal polyamide reverse osmosis membranes, J. Membr. Sci., 554 (2018) 244-252.

[14] Y.-H. La, J. Diep, R. Al-Rasheed, D. Miller, L. Krupp, G.M. Geise, A. Vora, B. Davis, M. Nassar, B.D. Freeman, M. McNeil, G. Dubois, Enhanced desalination performance of polyamide bi-layer membranes prepared by sequential interfacial polymerization, J. Membr. Sci., 437 (2013) 33-39.

[15] M. Di Vincenzo, M. Barboiu, A. Tiraferri, Y.M. Legrand, Polyol-functionalized thin-film composite membranes with improved transport properties and boron removal in reverse osmosis, J. Membr. Sci., 540 (2017) 71-77.

[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] 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.

[18] 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.

[19] 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.

[20] 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.

[21] 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.

[22] 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.

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

[24] 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.

[25] T. Fujioka, N. Oshima, R. Suzuki, W.E. Price, L.D. Nghiem, Probing the internal structure of reverse osmosis membranes by positron annihilation lifetime spectroscopy:

400 Gaining more insight into the transport of water and small solutes, J. Membr. Sci., 486
401 (2015) 106-118.

402 [26] S. Shultz, V. Freger, In situ modification of membrane elements for improved boron
403 rejection in RO desalination, Desalination, 431 (2018) 66-72.

404 [27] K.L. Tu, T. Fujioka, S.J. Khan, Y. Poussade, A. Roux, J.E. Drewes, A.R. Chivas, L.D.
405 Nghiem, Boron as a surrogate for N-nitrosodimethylamine rejection by reverse osmosis
406 membranes in potable water reuse applications, Environ. Sci. Technol., 47 (2013)
407 6425–6430.

408 [28] L.N. Breitner, K.J. Howe, D. Minakata, Boron Can Be Used to Predict Trace Organic
409 Rejection through Reverse Osmosis Membranes for Potable Reuse, Environ. Sci.
410 Technol., 52 (2018) 13871-13878.

411 [29] T. Fujioka, H. Kodamatani, H. Takeuchi, H. Tanaka, L.D. Nghiem, Online monitoring
412 of N-nitrosodimethylamine for the removal assurance of 1,4-dioxane and other trace
413 organic compounds by reverse osmosis, Environ. Sci.: Water Res. Technol., (2018).

414 [30] A.R.D. Verliefde, S.G.J. Heijman, E.R. Cornelissen, G.L. Amy, B. Van der Bruggen,
415 J.C. van Dijk, Rejection of trace organic pollutants with high pressure membranes
416 (NF/RO), Environ. Prog., 27 (2008) 180-188.

417 [31] T. Fujioka, H. Kodamatani, W. Yujue, K.D. Yu, E.R. Wanjaya, H. Yuan, M. Fang, S.A.
418 Snyder, Assessing the passage of small pesticides through reverse osmosis membranes,
419 J. Membr. Sci., 595 (2020) 117577.

420 [32] H. Kodamatani, S.L. Roback, M.H. Plumlee, K.P. Ishida, H. Masunaga, N. Maruyama,
421 T. Fujioka, An inline ion-exchange system in a chemiluminescence-based analyzer for
422 direct analysis of N-nitrosamines in treated wastewater, J. Chromatogr. A, 1553 (2018)
423 51-56.

424 [33] H. Zhang, G.M. Geise, Modeling the water permeability and water/salt selectivity
425 tradeoff in polymer membranes, J. Membr. Sci., 520 (2016) 790-800.

426 [34] G.M. Geise, H.B. Park, A.C. Sagle, B.D. Freeman, J.E. McGrath, Water permeability
427 and water/salt selectivity tradeoff in polymers for desalination, J. Membr. Sci., 369
428 (2011) 130-138.

429 [35] T. Fujioka, S.J. Khan, J.A. McDonald, A. Roux, Y. Poussade, J.E. Drewes, L.D.
430 Nghiem, *N*-nitrosamine rejection by nanofiltration and reverse osmosis membranes:
431 The importance of membrane characteristics, Desalination, 316 (2013) 67-75.

432 [36] T. Fujioka, B.E. O'Rourke, K. Michishio, Y. Kobayashi, N. Oshima, H. Kodamatani,
433 T. Shintani, L.D. Nghiem, Transport of small and neutral solutes through reverse
434 osmosis membranes: Role of skin layer conformation of the polyamide film, J. Membr.
435 Sci., 554 (2018) 301-308.

436