Fouling substances causing variable rejection of a small and uncharged trace organic chemical by reverse osmosis membranes

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Abstract

The safety of recycled water for potable water reuse can be enhanced by improving the reliability of reverse osmosis (RO) treatment for the removal of trace organic chemicals. This study assessed the mechanisms underlying the variable rejection of a carcinogenic *N*-nitrosamine, namely *N*-nitrosodimethylamine (NDMA), caused by RO membrane fouling. Foulants that cause the variable rejection were evaluated through rejection tests and foulant characterization. The RO treatment of wastewaters with and without pre-treatment using an ultrafiltration or nanofiltration membrane showed that NDMA rejection commonly increased with increasing membrane fouling. The characterization of organics in the treated wastewater samples revealed that increased NDMA rejection can be caused by foulants composed of low-molecular-weight organics (< 300 Da), including tryptophan (or tryptophan-like substances). It is speculated that small organics such as tryptophan form a densely packed cake layer on the membrane surface, which may function as an additional barrier for the membrane transport of NDMA. The results of this study indicate that RO membrane fouling that occurs during long-term wastewater treatment can increase NDMA rejection. The enhanced separation performance can yield positive consequences for the credibility of RO treatment in potable water reuse.

Keywords: membrane fouling; *N*-nitrosamine; micropollutant; reverse osmosis; potable water reuse.

1. Introduction

Ensuring sufficient removal of trace organic chemicals (TOrCs) from wastewater is critical to protect public health in potable water reuse (Villanueva et al., 2014). This removal is particularly important in direct potable reuse, which is the direct transportation of recycled water to drinking water supply systems. In an advanced wastewater treatment system, two types of treatment—reverse osmosis (RO) and advanced oxidation processes (AOP)—are essential to reduce TOrCs (Warsinger et al., 2018). The RO membrane process typically achieves high removal for most TOrCs (Verliefde et al., 2008). However, this process alone can be insufficient for the removal of some TOrCs (Doederer et al., 2014). The commonly used polyamide RO membrane has been developed for salt rejection and water permeability. Therefore, its separation performance for the removal of TOrCs in small polar or hydrophobic organic compounds remains a challenge (Tang et al., 2018). A notable example of this type of compound includes *N*-nitrosodimethylamine (NDMA)—a probably carcinogenic *N*-nitrosamine (Sgroi et al., 2018). Because of its potential impact on public health, NDMA has been proposed as a health-based contaminant in monitoring programs for potable water reuse projects (CSWRCB, 2016).

High concentrations of NDMA (>20 ng/L) are typically found in the feedwater of RO processes (Fujioka et al., 2012a; Sedlak et al., 2005). Raw wastewater usually contains NDMA (Wang et al., 2014). Moreover, NDMA can also be formed as a by-product of the pre-disinfection process (e.g., chloramination), which is performed prior to RO processes to reduce membrane fouling (Farré et al., 2011; Zeng et al., 2016; Zhang et al., 2014). As a result, NDMA in RO permeate can be found at concentrations higher than 10 ng/L (Fujioka et al., 2012a), which exceed the guideline value (10 ng/L) in the California regulatory notification level for drinking water and the Australian Guidelines for water recycling for indirect potable water reuse (CDPH, 2015; NRMMC et al., 2008). Although a subsequent treatment process (i.e., AOP) can reduce NDMA

concentrations to below guideline levels, any improvement in the confidence on RO processes for NDMA removal can enhance the reliability of the recycled water safety.

In general, the credibility of RO processes for NDMA removal is low due to the high variation on its efficacy (negligible to 80%) (Fujioka et al., 2012a). Low-pressure RO membranes that are used for water recycling are capable of rejecting approximately 50% of NDMA (Fujioka et al., 2012a). As a small and uncharged substance, NDMA can permeate through free-volume holes of RO membranes, resulting in a low rejection rate. Previous studies (Fujioka et al., 2012b; Steinle-Darling et al., 2007) indicate that process operating conditions such as permeate flux, feed temperature, feed pH, and permeate recovery can influence NDMA rejection. In addition, the impact of membrane fouling is of great concern for long-term operations because it inevitably occurs during RO treatment of treated wastewater (Jacob et al., 2010).

The impact of complex foulants on the rejection of NDMA has not been fully clarified despite several efforts (Fujioka et al., 2013a; Steinle-Darling et al., 2007). A previous study (Fujioka et al., 2013a) demonstrated that membrane fouling caused by actual treated wastewater can increase NDMA rejection. Another study (Fujioka et al., 2017) showed that membrane fouling caused by large model organic foulants (e.g., sodium alginate, bovine serum albumin, and humic acid) do not significantly impact NDMA rejection, whereas small ones such as fulvic acid have the potential to influence it. However, the mechanisms suggested in the study were based on empirical information using model foulants, which are different from organics in wastewaters. Therefore, further understanding the impacts of membrane fouling can improve the credibility of RO treatments for TOrC removal.

This study assessed the mechanisms governing the impacts of foulants on the rejection of NDMA. Foulants that influence NDMA rejection were evaluated through rejection tests using various fractionated wastewater samples. Based on the characterization of organic compounds

in the wastewater samples, a major foulant responsible for the varied rejection was further evaluated using its model foulant. The outcome of this research can help elucidate the reliability of RO membranes for small TOrC removal, which is crucial for potable water reuse.

2. Materials and methods

2.1. Chemicals

NDMA was obtained from Ultra Scientific (Kingstown, RI, USA). A stock solution of NDMA was prepared at 1 µg/mL in pure methanol. Tryptophan was purchased from Fluorochem Ltd. (Glossop, UK) and used as the model foulant. Chemicals used for background electrolyte ions (NaCl, $CaCl_2$, and $NaHCO_3$) were obtained from Wako Pure Chemical Industries (Tokyo, Japan). Secondary wastewater effluent samples were collected after the activated sludge process of a municipal wastewater treatment plant (WWTP) in Japan.

2.2. Membranes

Two low pressure RO membranes, namely ESPA2 and BW30, were obtained from Nitto/Hydranautics (Osaka, Japan) and Dow Chemical Company (Midland, MI, USA), respectively. ESPA2 RO membrane has been used in many full-scale water recycling systems in the USA and Australia (Fujioka et al., 2012a). This study used four different membranes for the pre-treatment of secondary wastewater effluent. Two polyether sulfone ultrafiltration (UF) membranes, QM and XT, were supplied by Synder Filtration (Vacaville, CA, USA). Their molecular weight cut-off (MWCO) were 50,000 and 1,000 Da, respectively. A polysulfone UF membrane with MWCO of 10,000 Da (Q0100-07) was supplied by Advantec (Tokyo, Japan). Finally, nanofiltration (NF) membranes with MWCO of 300 Da (Filmtec^{TM} NF270) were supplied by Dow Chemical Company (Midland, MI, USA).

2.3. Membrane treatment system

The rejection of NDMA by RO membranes was evaluated using a laboratory-scale RO treatment system **(Fig. 1)**. The system comprised a stainless steel cross-flow membrane cell (Iwai Pharma Tech, Tokyo, Japan), high-pressure pump (KP-12, FLOM, Tokyo, Japan), flow meter (F7M, Azbil Co., Tokyo, Japan), pressure regulating valve, and 2-L glass reservoir with a stainless steel heat exchanging coil connected to a temperature control unit (NCB-500, Tokyo Rikakikai, Tokyo, Japan). The membrane cell was designed to hold a flat sheet membrane coupon with an effective surface area of 36.3 cm^2. To minimize the impact of concentration polarization on the solute rejection, the membrane cell has a built-in magnetic stirrer above the membrane surface.

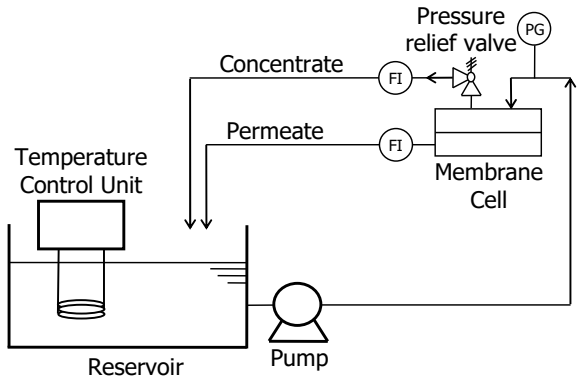


Fig. 1 Schematic diagram of the cross-flow RO filtration system.

2.4. Experimental protocols

Prior to the rejection tests using RO membranes, the secondary wastewater effluent was pre-filtered using UF or NF membranes. For the tests using the BW30 RO membrane, the wastewater effluent was pre-filtered with a UF (MWCO = 10 kDa) or NF270 (MWCO = 300 Da) membrane. For the tests using the ESPA2 RO membrane, one of the three membranes (i.e., QM, XT, or NF270) was used for pre-filtration. Rejection tests using BW30 or ESPA2 RO membranes started by conditioning the RO membrane using deionized water (Q 18.0 MΩcm) at 2,000 kPa until the permeate flux was stabilized. The deionized water was then replaced with

112 treated wastewater or the model foulant solution. The model solution contained 100 mg/L of
113 tryptophan in deionized water with background electrolytes (20 mM NaCl, 1 mM $NaHCO_3$,
114 and 1 mM $CaCl_2$). Thereafter, the NDMA stock solution was spiked into the RO feed at a
115 concentration of 500 ng/L. The RO treatment was conducted at a constant permeate flux of 60
116 L/m^2h (BW30) or 80 L/m^2h (ESPA2), constant feed flow rate of 30 mL/min, and constant feed
117 temperature of 25°C. The feed pressure was periodically adjusted to keep up with the constant
118 permeate flux, and the transmembrane pressure (TMP) was continuously recorded. A high
119 permeate flux was applied to accelerate the membrane fouling. To evaluate the changes in
120 NDMA rejection during the fouling development, both RO feed and permeate were collected
121 periodically in amber vials (1.5 mL).

122 ## *2.5. Analytical techniques*

123 Concentrations of NDMA were determined using high-performance liquid chromatography-
124 photochemical reaction-chemiluminescence (HPLC-PR-CL) (Kodamatani et al., 2018;
125 Kodamatani et al., 2009). The detection limit of NDMA was 0.4 ng/L. The excitation–emission
126 matrix (EEM) fluorescence spectra of organics were analyzed using Aqualog (Horiba, Kyoto,
127 Japan). All EEM spectra were corrected through blank subtraction to reduce the impact of the
128 scattered light emitted from the water and the Raman peak (Park and Snyder, 2018). The size
129 distribution of organics in each sample was analyzed using a liquid chromatography-organic
130 carbon detection (LC-OCD) system (DOC-LABOR, Karlsruhe, Germany) coupled with a 250
131 mm × 20 mm chromatographic column (TSK HW 50S, Toso, Japan) (Henderson et al., 2011;
132 Huber et al., 2011). The chromatographic column was based on a hydroxylated methacrylic
133 polymer with a pore size of 12.5 nm and separation range of 0.1–10 kDa (Huber et al., 2011).
134 Before entering the organic carbon detector, the sample solution was acidified, and carbonates
135 were converted to carbonic acid. Thereafter, the organic concentrations measured at the organic
136 carbon detector were converted to relative signal response using a software program (DOC-

LABOR, Karlsruhe, Germany). The LC-OCD was capable of subdividing the organic matter in water into four sub-fractions: biopolymers (molecular weight, MW of ≥ 20,000 Da), humics (MW of approximately 1,000 Da), building blocks (MW of 300–500 Da), and low molecular weight (LMW) compounds (MW of <350 Da). The mobile phase used in the system was a phosphate buffer at KH_2PO_4 and Na_2HPO_4 concentrations of 2.5 g/L and 1.2g/L, respectively.

3. Results and discussion

3.1. Membrane fouling and separation performance

The progress of membrane fouling during the RO of the treated wastewater samples varied depending on the type of pre-treatment. When the BW30 RO membrane treatment was applied to the secondary wastewater without any pre-treatment, membrane fouling progressed rapidly and the normalized TMP increased by 27% within 4.5 h **(Fig. 2a)**. The membrane fouling rate decreased from UF (MWCO = 10 kDa) to NF (MWCO = 300 Da). A similar trend was observed for the ESPA2 RO membranes. The RO treatment of the UF (MWCO = 50 kDa)-treated wastewater increased the normalized TMP by 14% within 3.5 h. The membrane fouling rate decreased with smaller pore sizes and from UF (MWCO = 10 kDa) to NF (MWCO = 300 Da) membranes **(Fig. 2b)**. These results indicate that pre-treatment with a tight membrane can induce less membrane fouling.

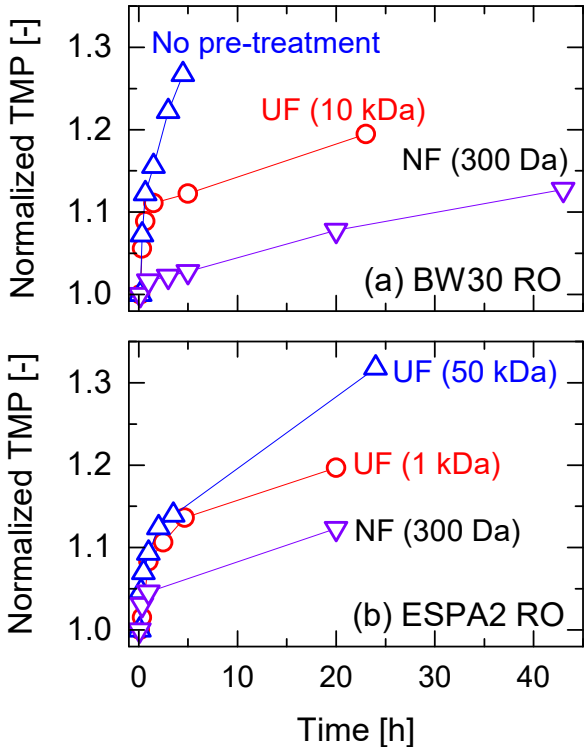


Fig. 2 Normalized transmembrane pressure (TMP_t/TMP_0) during reverse osmosis (RO) of treated wastewaters using: (a) BW30 and (b) ESPA2 RO membrane with permeate flux of 60 and 80 L/m^2h, respectively.

The impact of membrane fouling in the performance of NDMA separation by RO membranes was evaluated. The rejection of NDMA by both BW30 and ESPA2 RO membranes gradually increased according to the progress of membrane fouling (i.e., an increase in the normalized TMP) for all treated wastewater samples **(Fig. 3)**. Considering that *N*-nitrosamine rejection is primarily governed by size exclusion (Fujioka et al., 2013b), the increased NDMA rejection due to membrane fouling can be attributed to the reduced clearance between solutes and the passage from RO feed to permeate. Potential causes include: (a) small foulants penetrate into free-volume holes and are trapped or adsorbed in their interior gap, thus the passage of the RO membrane for the permeation of solutes is restricted; and (b) foulants deposited on the membrane surface form a tight layer, in which the gap among foulants is so small that solutes are less likely to permeate through. The effects of pre-treatment on NDMA rejection varied between the two RO membranes. For BW30 and ESPA2 membranes, NF pre-treatment resulted

in the lowest and highest NDMA rejections, respectively. The secondary wastewater effluent samples used in both experiments were collected at different sampling occasions. Therefore, the variation in the organic composition of the wastewaters may have caused the different NDMA rejection values.

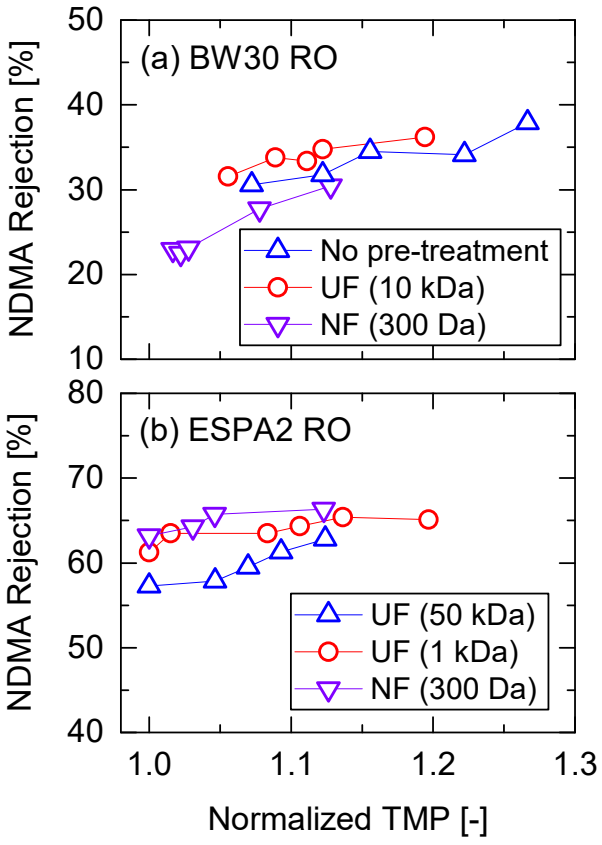


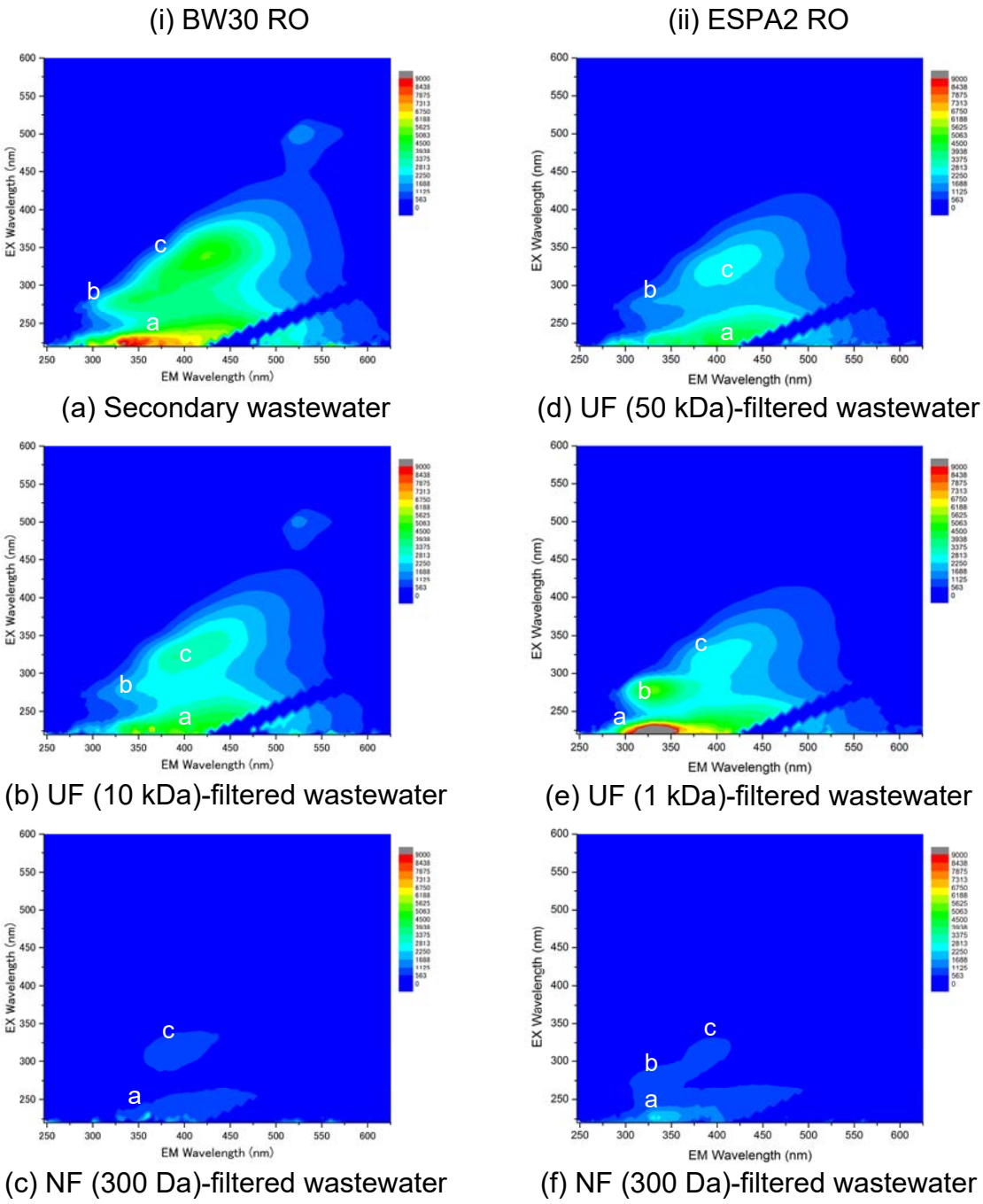
Fig. 3 *N*-nitrosodimethylamine (NDMA) rejection by (a) BW30 membranes and (b) ESPA2 reverse osmosis (RO) membranes in treated wastewater as a function of normalized transmembrane pressure (TMP_t/TMP_0).

3.2. Identification of responsible foulants

3.2.1. Excitation–emission matrix (EEM) fluorescence spectroscopy

Fouling substances responsible for the increased NDMA rejection were evaluated by identifying the variety of organic compounds in the treated wastewaters using EEM fluorescence spectroscopy. The EEM fluorescence spectrum of the secondary wastewater effluent **(Fig. 4a)** presented three strong peaks at an Ex/Em of 230/335–360 nm (aromatic amino acid, denoted by "a"), 275/350 nm (tryptophan, denoted by "b"), and 340/425 nm

(humic-like substances, denoted by "c") (Chen et al., 2003; Nam and Amy, 2008). Similarly, the UF-treated wastewater samples used for BW30 and ESPA2 RO membranes presented three strong peaks in the same areas **(Fig. 4b, 4d, and 4e)**. However, the intensity of these peaks were lower than those of the secondary wastewater effluent. Moreover, the NF-treated wastewater samples commonly showed weak peaks in the same areas **(Fig. 4c and 4f)**. The tests using BW30 and ESPA2 RO membranes were conducted using different secondary wastewater effluent samples collected on a separate day. Thus, water quality in the permeate of the NF treatment also varied. Overall, the UF and NF pre-treatments reduced the intensity of all three peaks. These major organic compounds can remain in the permeate, indicating that they can be foulants in the RO treatment.



195 **Fig. 4** Excitation–emission matrix (EEM) fluorescence spectrum of (a) secondary wastewater
196 effluent and (b)–(f) pre-filtered wastewater effluent upon use of (i) BW30 and (ii) ESPA2
197 reverse osmosis (RO) membranes for fouling and rejection tests.

198 The peak of tryptophan at Ex/Em of 275/350 nm was further evaluated using a model
199 tryptophan solution. Tryptophan ($C_{11}H_{12}N_2O_2$) is a hydrophilic chemical (Log*D* = -1.1 at pH
200 8.0) with a low molecular weight of 204 Da. The EEM fluorescence spectrum of a 1000-fold
201 diluted tryptophan solution confirmed that the areas denoted by “a” and “b” were aromatic

amino acid and tryptophan, respectively **(Fig. 5)**. Tryptophan is a non-polar aromatic amino acid and the main component of protein fluorescence. Thus, it can appear at the area of both aromatic amino acid and tryptophan. Many bacteria (including *E. Coli*) produce tryptophan and can release tryptophan-like substances in the water when they rupture after death (Arana et al., 2004; Elliott et al., 2006). Wastewater contains high concentrations of bacteria, which can still exist at high concentrations in the feed of RO (Ishida and Cooper, 2015). Therefore, the characterized organics in the NF-treated wastewater can be tryptophan or tryptophan-like substances. Molecules, including tryptophan and tryptophan-like substances, that are smaller than the NF membrane's MWCO (300 Da) could pass through the NF membrane and become foulants in the following RO membrane. However, the EEM fluorescence spectrum does not provide the molecular information associated with molecular sizes. Consequently, further evaluation focusing on organic molecular size was conducted and is detailed in the following section.

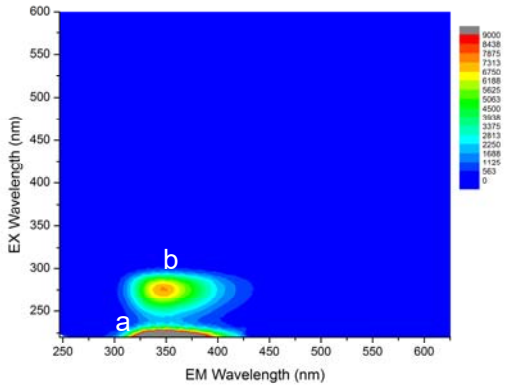


Fig. 5 Excitation–emission matrix (EEM) fluorescence spectrum of tryptophan solution.

3.2.2. Liquid chromatography-organic carbon detection (LC-OCD)

The size distribution of the organic constituents in the treated wastewater samples were characterized using LC-OCD. Most organics in the treated wastewater samples were hydrophilic, which can be further classified into four fractions: biopolymers, humics, building blocks, and low molecular weight (LMW) compounds in a LC-OCD chromatogram (Henderson

et al., 2010; Huber et al., 2011). The secondary wastewater effluent without any pre-filtration showed all four major fractions **(Fig. 6a)**. UF-treated wastewaters showed three major fractions, but the largest fraction (i.e., biopolymer) was not present **(Fig. 6b, 6d, and 6e)**. In samples treated using NF membrane (MWCO of 300 Da), the presence of building blocks (MW of 300–500 Da) and LMW compounds (MW of < 350 Da) were observed **(Fig. 6c and 6f)**. The properties of LMW compounds are consistent with the properties of tryptophan, which showed a peak in the area of LMW compounds **(Fig. 7)**.

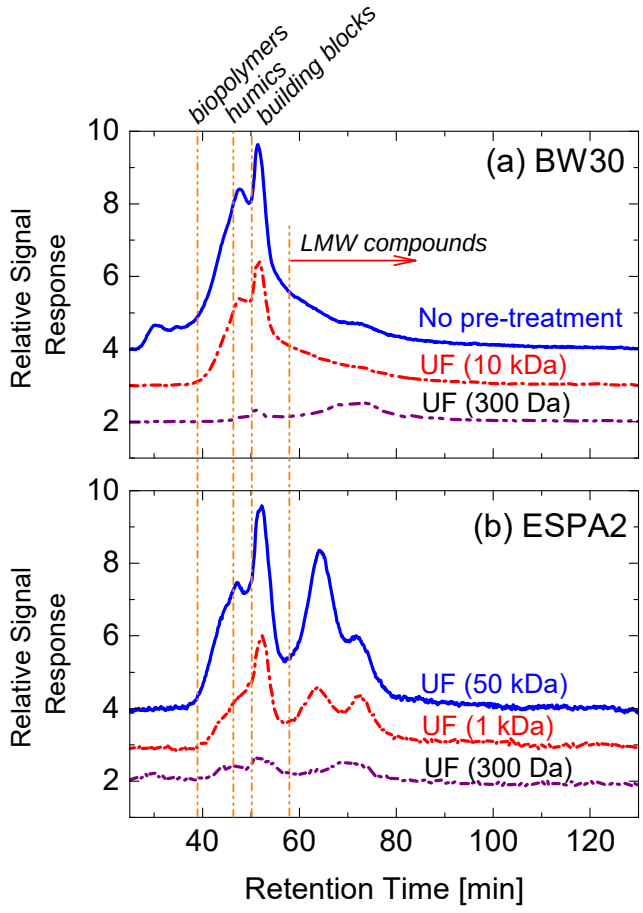


Fig. 6 Liquid chromatography-organic carbon detection (LC-OCD) chromatogram of (a) secondary wastewater effluent and (b)–(f) pre-filtered wastewater effluent upon use of (i) BW30 and (ii) ESPA2 reverse osmosis (RO) membranes for fouling and rejection tests.

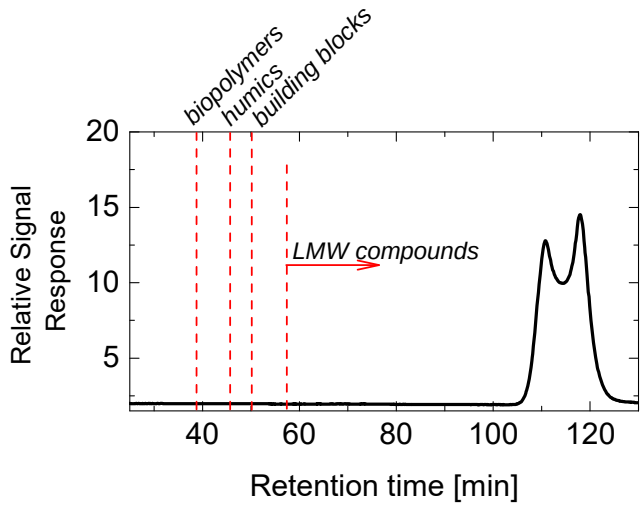


Fig. 7 Liquid chromatography-organic carbon detection (LC-OCD) chromatogram of tryptophan solution.

To verify that membrane fouling by tryptophan (or tryptophan-like substances) can increase NDMA rejection, another membrane fouling and separation performance test was conducted using a model foulant solution containing tryptophan. Similar to the treated wastewater samples, the rejection of NDMA progressively increased according to the progress of membrane fouling **(Fig. 8)**. The results confirmed that membrane fouling caused by low molecular weight organics such as tryptophan can increase NDMA rejection.

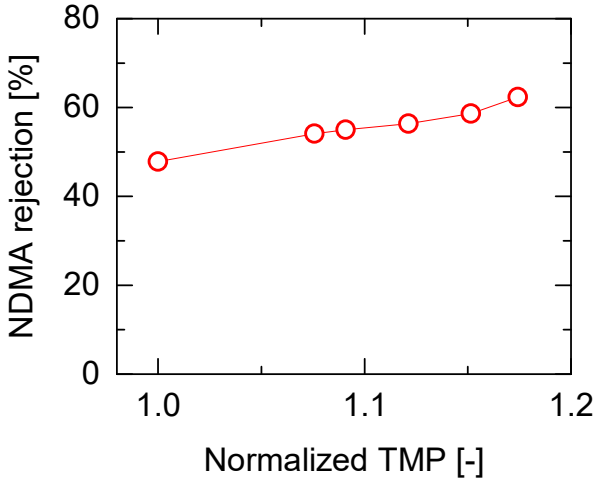


Fig. 8 *N*-nitrosodimethylamine (NDMA) rejection by ESPA2 reverse osmosis (RO) membrane in tryptophan solution as a function of normalized transmembrane pressure (TMP/TMP_0).

3.3. Mechanisms

The mechanisms relating the increased NDMA rejection with membrane fouling were investigated based on the knowledge attained in this study and literature. The rejection of hydrophilic NDMA molecules by RO membranes is primarily governed by size exclusion, in which the solute rejection varies depending on the clearance between the solute and the inner wall of free-volume holes (Fujioka et al., 2013b). The minimum projection area (MPA), which is the two-dimensional projected area of a chemical calculated based on the van der Waals radius, has been suggested for this analysis (Fujioka et al., 2019). MPA is a suitable solute property because it is best correlated with *N*-nitrosamine rejection. The MPA of NDMA is 19.4 $Å^2$, which is smaller than the free-volume hole area of ESPA2 RO membranes (26.4 $Å^2$), and NDMA can readily pass through the free-volume hole. In contrast, the MPA of tryptophan (33.0 $Å^2$) is much larger than the membrane's free-volume hole-area **(Fig. 9)**. Therefore, it is unlikely that tryptophan will penetrate the free-volume hole, indicating that tryptophan is unlikely to reduce the inner passage of the free-volume hole in the membrane skin layer. Thus, a potential cause of the increased NDMA rejection can be attributed to the additional tight barrier, which consists of a membrane fouling layer on the membrane surface. In this context, a loose cake layer comprised of high molecular weight foulants (e.g., sodium alginate, bovine serum albumin, and humic acids) have negligible impact on NDMA rejection (Fujioka et al., 2017), whereas small compounds are expected to form a dense cake layer on the membrane surface (Ang et al., 2011). The clearance between tryptophan molecules in the dense cake layer can be significantly small, as illustrated in **Fig. 9**. The clearance reduced by the small foulants (i.e., tryptophan or tryptophan-like substances) likely enhances the rejection of *N*-nitrosamines, including NDMA. This implies that the same phenomena (i.e., reduced clearance caused by the deposition of small foulants) can increase the rejection of other uncharged TOrCs due to size

exclusion. Overall, the findings here suggest that the rejection of uncharged and small TOrCs is likely to increase according to the progress of membrane fouling.

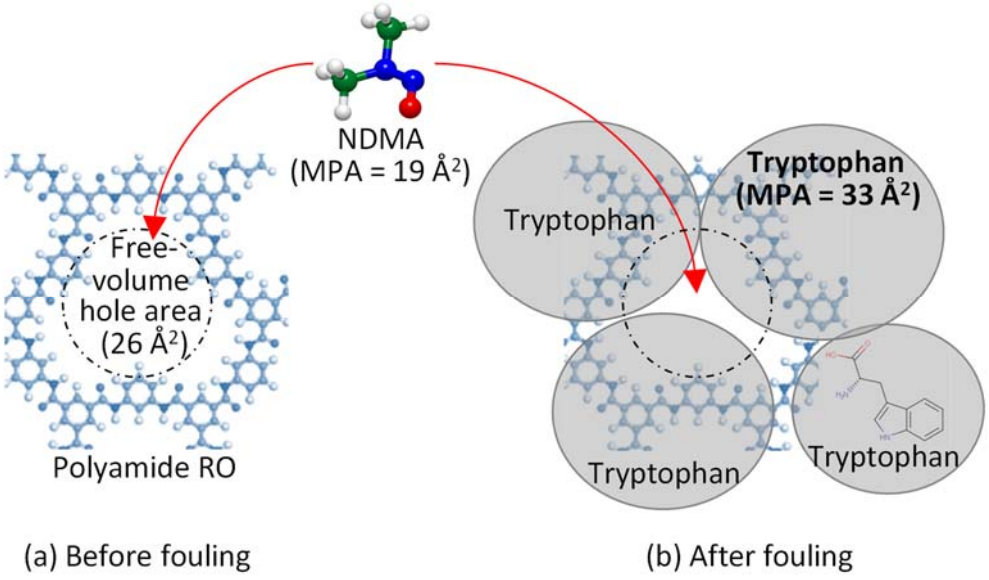


Fig. 9 – Example of *N*-nitrosodimethylamine (NDMA) transport through: (a) a free-volume hole, and (b) a free-volume hole covered by foulants composed of tryptophan. The area of the free-volume hole in the polyamide reverse osmosis (RO) membrane was calculated based on its free-volume hole-radius (2.9 Å), which was determined by positron annihilation lifetime spectroscopy found in the literature (Fujioka et al., 2013b).

4. Conclusions

This study evaluated fouling substances responsible for the variable rejection of TOrCs that occurs according to RO membrane fouling during wastewater treatment. Fouling of RO membranes and increased NDMA rejection commonly occurred for wastewaters pre-treated using UF and NF membranes. Characterization of fouling substances in the NF-treated wastewater found that fouling substances comprised of low molecular weight organics such as tryptophan (or tryptophan-like substances) can increase NDMA rejection. It is speculated that enhanced NDMA rejection can occur through a formation of a densely packed fouling layer, in which the clearance is too small for NDMA to pass through. This study proves that RO membrane fouling that occurs during long-term operation is likely to enhance the removal of

small and uncharged TOrCs, which yields positive consequences for the credibility of RO treatment in potable water reuse.

5. Acknowledgements

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