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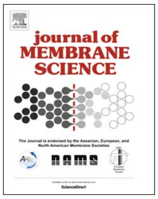

Transport of small and neutral solutes through reverse osmosis membranes: Role of skin layer conformation of the polyamide film

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ABSTRACT

The polyamide skin layer of reverse osmosis (RO) membranes was characterised using advanced and complementary analytical techniques to investigate the mechanisms underlying the permeation of contaminants of emerging concern in potable water reuse – *N*-nitrosodimethylamine (NDMA) and *N*-nitrosomethylethylamine (NMEA). This study used five RO membrane samples with similar membrane properties. The five RO membrane samples spanned over a large range of water permeance (0.9–5.8 L/m^2 h bar) as well as permeation of NDMA (9–66%) and NMEA (3–29%). Despite these differences among the five RO membranes, characterisations of the skin layer using positron annihilation lifetime spectroscopy, atomic force microscopy and field emission scanning electron microscopy revealed almost no variation in their free-volume hole-radius (0.270–0.275 nm), effective surface area (198–212%) and thickness (30–35 nm) of the skin layer. The results suggest that there could be other RO skin layer properties, such as the interconnectivity of the protuberances within the polyamide skin layer additional to the free-volume hole-size and thickness of the skin layer, which can also govern water and solute permeation.

1. Introduction

N-nitrosodimethylamine (NDMA; $C_2H_6N_2O$) and *N*-nitrosomethylethylamine (NMEA; $C_3H_8N_2O$) are micropollutants of significant concern in potable water reuse since they are probable carcinogenic chemicals [1]. With a molecular weight of 74 g/mol, NDMA is the smallest in the *N*-nitrosamine group. NDMA and NMEA are neutral and hydrophilic compounds at environmental pH (i.e. pH 6–8). Although reverse osmosis (RO) membrane separation can achieve excellent rejection of a range of impurities in reclaimed water including salts, macro-organics, and many micropollutants, the rejection of NDMA, NMEA and several other *N*-nitrosamines is low and highly variable because of their small molecular size and lack of charge [2–5]. Thus, they are often detectable in RO permeate at concentrations higher than guideline or target values set by water authorities around the world. For example, California has established a notification level of 10 ng/L for NDMA and a public health goal of 3 ng/L [6]. Similarly, in Australia, the guideline value of NDMA in water intended for potable reuse has been also set at 10 ng/L [7]. The low and highly variable separation performance of RO with respect to NDMA rejection necessitates post treatment by advanced oxidation (UV irradiation and H_2O_2) [8]. Recent research [9] suggests that NDMA rejection by RO membranes varies significantly amongst the many RO membranes available on the market. Thus, further insights which lead to better membrane selection and improvement of the separation performance of RO for *N*-nitrosamines can directly contribute to the economic viability and public safety of potable water reuse.

Given the significant importance of low molecular weight micropollutants in potable reuse, numerous previous studies have been conducted to reveal the permeation mechanisms of micropollutants through RO membranes [10–13]. The significance of steric (size) interaction between solutes and the free-volume holes within the RO membrane active skin layer has been clearly demonstrated from the viewpoint of solute properties. A strong correlation between molecular size (e.g. minimum molecular width or projected area) of uncharged solutes and their removals by RO has been established [14,15].

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Nevertheless, mechanisms underlying the difference in NDMA permeation among RO membranes are still poorly understood from the perspective of membrane properties. This is mainly due to analytical limitations in characterising the membrane skin layer at sub-nanometre scale resolution.

The free-volume holes – holes in the membrane skin layer in polymeric matrix – are thought to play an important role in water and solute transport through the RO membrane. Nevertheless, findings to date remain inconclusive. The free-volume hole size can be determined by positron annihilation lifetime spectroscopy (PALS) [16]. Previous measurements of the free-volume hole-radius of commercial RO membranes [16–18] varied considerably from 0.20 and 0.29 nm. Several previous studies [18–20] have demonstrated a strong correlation between solute permeation and free-volume hole-size. In contrast, no clear correlation between solute permeation and free-volume hole-size was reported by several other studies [17,21,22]. To date, there have been very few PALS studies on the characterisation of RO membranes due to the limited availability of slow positron beam based instruments.

The thickness of the skin layer has also been considered as an important property of an RO membrane governing water and solute transport. According to the solution-diffusion model [23–25], permeation of solutes and solution through RO membranes occurs via their penetration into the membrane material and diffusion through the RO membrane. The key role of the polymeric membrane thickness on solute permeation can also be supported by the finding that the thickness is inversely proportional to water permeance and there is a trade-off between water permeance and solute selectivity [26,27]. This mechanism is plausible, however, it is difficult to validate for commercial RO membranes. Recent RO membranes are designed with a rougher membrane surface that holds a higher surface area and a higher permeance [28–32]. As a result, they commonly have a so-called “ridge-and-valley” structure and hollow interior of crumpled nodules throughout the surface of the skin layer [29]. The entire thickness of the skin layer of commercial RO membranes is about 200–300 nm as reported by previous studies using transmission electron microscopy (TEM) [33–36]. The crumpled film forming the crumpled structure of the skin layer and the flat film comprising the interface between polyamide and polysulfone layers both have a thickness as low as 20 nm [31,37,38]. Characterisation using a field emission – scanning electron microscope (FE-SEM) [37] allows for a quantification of each polyamide film. Nevertheless, due to the complex inner structure and rough surface morphology of the RO membrane skin layer and its variation among RO membranes, it is still difficult to identify the location of the most important polyamide films and quantify their thickness for comparison among different RO membranes.

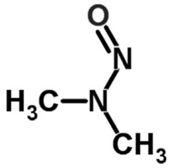
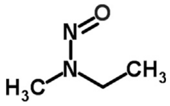
A systematic evaluation of several RO membranes with similar chemical ingredients can potentially yield new insights into the role of the membrane skin layer on solute permeation. This study aims to identify key structure parameters that govern NDMA transport in the RO process by characterising the skin layer properties of five RO membranes that have similar chemical composition and skin layer structure. State-of-the-art analytical techniques including PALS, FE-SEM and atomic force microscopy (AFM) were used for the characterisation of the skin layer including free-volume hole-size, thickness and surface area, respectively.

2. Materials and methods

2.1. Chemicals

Analytical grade NDMA and *N*-nitrosomethylethylamine (NMEA) (Table 1) were purchased from Ultra Scientific (Kingstown, RI, USA). All stock solutions were prepared in methanol to obtain 1 μg/mL of each chemical and were stored at 4 °C in the dark. Both chemicals can be classified as hydrophilic and neutral (uncharged) at environmental pH (pH 6–8) [39].

Table 1
Structure and properties of the selected *N*-nitrosamines.

Compound	NDMA	NMEA
Structure		
Molecular formula	$C_2H_6N_2O$	$C_3H_8N_2O$
Molecular weight [g/mol]	74.05	88.06
Log *D* at pH8[a] [-]	0.04	0.4
pKa at pH8[a] [-]	3.5	3.4
Minimum projection area[a,b] [nm^2]	0.20	0.22

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

[b] Minimum projection area is the area of the compound projected with the minimum plane of its circular disk, based on the van der Waals radius.

2.2. Membranes and membrane treatment system

Two commercially available RO membranes – namely ESPA2 and ESPAB – and a prototype RO membrane were obtained as flat sheet samples from Hydranautics/Nitto (Osaka, Japan). The active skin layers of these membranes have similar chemical ingredients although the detailed information is proprietary. The ESPA2 membrane has been employed in many potable water reuse schemes [14], while the ESPAB membrane is designed for boron removal and has been widely used in the second pass of RO in seawater desalination plants. In addition, samples of the ESPAB and Prototype membranes were also subjected to heat treatment to alter the physical properties. These heat-treated samples were designated as heated ESPAB and heated Prototype, respectively. Thus, in total, five different membrane samples were used in this investigation.

2.3. Experimental protocols

2.3.1. Heat treatment

Heat treatment was conducted by heating the RO membrane coupons in 80 °C ultrapure water solution. The RO membrane coupons were first rinsed with ultrapure water (18.0 MΩ cm). Thereafter, each coupon was stored in a 200 mL beaker filled with ultrapure water, and the beakers were placed in a temperature-controlled water bath (SWB-11A, AS ONE, Osaka, Japan) that maintained the water temperature at 80 °C. After 4 h of heat treatment, the membrane coupons were rinsed with ultrapure water and stored at 4 °C in the dark.

2.3.2. RO filtration experiments

The separation of NDMA and NMEA by each RO membrane was evaluated in ultrapure water using the bench-scale cross-flow RO system (Fig. S1). Filtration experiments were started with permeance evaluation in which RO membrane filtration experiments were conducted with ultrapure water at 2000 kPa to measure the pure water permeance. Thereafter, NDMA and NMEA stock solutions were added to obtain 200 ng/L of each compound in the feed solution. The membrane system was operated at a 20 L/m^2 h permeate flux and 20 °C feed temperature. Concentrations of NDMA and NMEA were determined by high-performance liquid chromatography-photochemical reaction-chemiluminescence as described in our previous studies [40,41]. The passage was defined as $R = 100 \times C_p/C_f$, where C_p and C_f are solute concentration in the permeate and feed, respectively.