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Rejection of small and uncharged chemicals of emerging concern by reverse osmosis membranes: The role of free volume space within the active skin layer

Takahiro Fujioka

University of Wollongong, tf385@uowmail.edu.au

Nagayasu Oshima

National Institute Of Advanced Industrial Science And Technology (Aist)

Ryoichi Suzuki

National Institute Of Advanced Industrial Science And Technology (Aist)

Stuart J. Khan

University Of New South Wales, s.khan@unsw.edu.au

Annalie Roux

Seqwater

See next page for additional authors

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Abstract

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Keywords

concern, reverse, osmosis, membranes, role, free, volume, space, within, emerging, active, rejection, skin, layer, chemicals, uncharged, small

Disciplines

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Authors

Takahiro Fujioka, Nagayasu Oshima, Ryoichi Suzuki, Stuart J. Khan, Annalie Roux, Yvan Poussade, Jörg E. Drewes, and Long D. Nghiem

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Takahiro Fujioka ¹, Nagayasu Oshima ², Ryoichi Suzuki ², Stuart J. Khan ³,
Annalie Roux ⁴, Yvan Poussade ⁵, Jörg E. Drewes ^{3, 6}, and Long D. Nghiem ^{1,*}

¹ Strategic Water Infrastructure Laboratory, School of Civil Mining and Environmental Engineering, The University of Wollongong, NSW 2522, Australia

² National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568, Japan

³ UNSW Water Research Centre, School of Civil and Environmental Engineering, The University of New South Wales, NSW 2052, Australia

⁴ Seqwater, Level 2, 240 Margaret St, Brisbane, QLD 4000 Australia

⁵ Veolia Water Australia, Level 15, 127 Creek Street, Brisbane, QLD 4000, Australia

⁶ Advanced Water Technology Center (AQWATEC), Department of Civil and Environmental Engineering, Colorado School of Mines, Golden, CO 80401, USA

* Corresponding author: Long Duc Nghiem, Email: longn@uow.edu.au, Ph +61 2 4221 4590

Abstract

Free-volume hole-radii of the active skin layer of one seawater and two low pressure reverse osmosis (RO) membranes – namely SWC5, ESPAB, and ESPA2 respectively – were evaluated using positron annihilation lifetime spectroscopy (PALS) with a slow positron beam. The results were related to the rejection of boric acid and eight N-nitrosamines to provide insights to the transport of these small solutes through RO membranes. At pH 8 (which is the experimental pH in this study), these solutes are uncharged. PALS analysis showed that the SWC5 has the smallest mean free-volume hole-radius (0.259 nm) among the three RO membranes investigated here. Correspondingly, the SWC5 membrane exhibited the highest rejection of boric acid and all N-nitrosamines. Results reported here also showed that the rejection of these chemicals increased in the order of increasing molecular volume. In addition, the difference in their rejection amongst the three RO membranes investigated here was most apparent for those (i.e., boric acid and N-nitrosodimethylamine (NDMA)) with a small molecular volume. The EPSA2 and ESPAB were determined to have mean free-volume hole-radius of 0.289 nm. However, the ESPAB membrane had lower water permeability and showed considerably higher rejection of boric acid and NDMA than the ESPA2 membrane. These results suggest that in addition to the mean free-volume hole-radius, other membrane parameters and properties such as the free-volume hole-radius distribution and thickness of the active skin layer can also play a role in governing the rejection of small and uncharged solutes by RO membranes.

Keywords: N-nitrosamines, NDMA, boron, reverse osmosis, and positron annihilation lifetime spectroscopy (PALS).

1. Introduction

Water reuse is an economically attractive strategy in many water-stressed regions and countries to augment the supply of clean water. Because municipal wastewater contains a large number of contaminants, the quality of reclaimed water is strictly regulated, particularly when it is intended for potable water reuse. In many cases, water reclamation plants employ low pressure reverse osmosis (LPRO) membranes for removing pathogenic agents, salt, and trace organic chemicals [1-2]. However, a recent comprehensive review by Fujioka et al. [3] revealed significant variation in the rejection of N-nitrosodimethylamine (NDMA) by LPRO membranes in both pilot- and full-scale operations. NDMA is an N-nitrosamine which is known to be formed as a disinfection by-product during wastewater treatment. Other N-nitrosamines that have been reported to occur in treated wastewater include N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP), N-nitrosomorpholine (NMOR), N-nitrosodipropylamine (NDPA), N-nitrosodi-n-butylamine (NDBA) and N-Nitrosodiphenylamine (NDPhA) [4-5]. NDMA and most of the N-nitrosamines listed above are classified as probable human carcinogens by US EPA [6]. Although their concentrations in water intended for potable consumption have been increasingly regulated around the world [3], information about the fate and transport of these chemicals during reverse osmosis (RO) filtration processes remains scarce. Similar to N-nitrosamines, boron is another chemical of concern in water reuse, in particular for certain agricultural irrigation practices, and is ubiquitous in wastewater with a typical concentration range of 0.3 to 5 mg/L [7]. The rejection of boron by LPRO membranes reported in literature is also highly variable, ranging from 20–80% [8-10].

In the pH range of natural waters (i.e., pH 6 – 8), N-nitrosamines including NDMA and boron (pKa 9.23 [7]) exist as uncharged solutes. The rejection of these uncharged solutes is governed by the relationship between their molecular dimensions and the membrane pore size [11]. Several previous laboratory-scale studies have examined the passage of NDMA through RO membranes and showed that rejection can vary quite significantly due to the very small molecular size and uncharged characteristic of the NDMA molecule [4, 12-13]. RO membranes are also highly permeable to boric acid at or below pH 8 [7, 10].

The rejection of solutes through the active skin layer of RO thin-film composite membranes is usually described using indirect molecular transport measures such as salt rejections [11]. This simplification is due to the unavailability of any techniques for directly analysing the free-volume distribution of these membranes in the past. Recently, positron annihilation lifetime spectroscopy (PALS) has been successfully applied to quantify free-volume hole-radii within the active skin layers of NF/RO membranes [14-20]. In a pioneering study, Kim et al. [18] applied the PALS technique to several surface-modified RO membranes and reported that permeability increased with increasing free-volume hole-radius of the active skin layer. A recent PALS study by Chen et al. [19] also revealed that the rejection of several uncharged compounds (i.e., urea, ethylene glycol, and 1- or 2-propanol) by NF/RO membranes increased with decreasing free-volume hole-radii. To date, no studies have applied PALS to examine the impact of free-volume hole-radius on the rejection of water contaminants of significant health and environmental concern such as N-nitrosamines and boron.

The aim of this study was to provide an understanding of uncharged solute transport through nanoscale free-volume structure within RO membranes. A PALS technique with a slow positron beam was used to analyse the free-volume hole-radii within the active skin layers of commercial RO membranes. The relationship between the free-volume hole-radius of the active skin layer of three different RO membranes and the transport of boric acid and N-nitrosamines was examined.

2. Materials and methods

2.1. RO membranes

Specimens of three RO membranes – namely SWC5, ESPAB, and ESPA2 – were used in this study and supplied by Hydranautics (Oceanside, CA, USA) as flat sheet membrane samples. These are thin-film composite membranes that possess an ultrathin polyamide active skin layer on top of a porous polysulphone supporting layer. Because the supporting layer only provides mechanical strength, the separation efficiency and water permeability of these membranes are exclusively governed by the characteristics of their active skin layer. The SCW5 is a typical seawater RO (SWRO) membrane which is often employed in the first pass of RO desalination plants. The ESPA2 membrane is a LPRO membrane which is typically

used for water reclamation applications [3]. The ESPAB membrane is also an LPRO membrane but has been specifically developed for high boron rejection for the second pass of seawater desalination RO plants. The nominal salt rejections of these membranes specified by the membrane manufacturer are summarised in Table 1.

Table 1: Nominal salt rejection of the membranes used in this study.

Membrane	Membrane type	Manufacturer	NaCl rejection [%]
ESPA2	LPRO	Hydranautics	99.6 ^a
ESPAB	LPRO	Hydranautics	99.3 ^a
SWC5	SWRO	Hydranautics	99.8 ^b

^a Filtration condition: 1,500 ppm NaCl, 1.05 MPa, 25 °C and pH 6.5 - 7.0.

^b Filtration condition: 32,000 ppm NaCl, 5.5 MPa, 25 °C and pH 6.5 - 7.0.

2.2. Chemicals

Analytical grade N-nitrosamines and boric acid were obtained from by Sigma-Aldrich (St Louis, MO, USA). A stock solution of N-nitrosamines of 10 mg/L of each compound was prepared in pure methanol. A surrogate stock solution of 100 µg/L of each deuterated N-nitrosamines (i.e. N-nitrosodimethylamine-D6, N-nitrosomethylethylamine-D3, N-nitrosopyrrolidine-D8, N-nitrosodiethylamine-D10, N-nitrosopiperidine-D10, N-nitrosomorpholine-D8, N-nitrosodipropylamine-D14 and N-nitrosodi-n-butylamine-D9) was also prepared in pure methanol. These deuterated N-nitrosamines were purchased from CDN isotopes (Pointe-Claire, Quebec, Canada). A stock solution of boric acid of 1 g-boron/L was prepared in Milli-Q. Key physicochemical properties of these N-nitrosamines and boric acid are summarised in Table 2. The N-nitrosamine stock solutions were kept at -18 °C in the dark while the boric acid stock solution was kept at 4 °C. All stock solutions were used within 1 month of preparation. Analytical grade NaCl, CaCl₂ and NaHCO₃ were purchased from Ajax Finechem (Taren Point, NSW, Australia) and used as the background electrolytes for the filtration experiments. Stock solutions of these background electrolytes were also prepared in Milli-Q water at 2M (NaCl) and 0.1M (CaCl₂ and NaHCO₃) concentrations.

Table 2: Physicochemical characteristics of the selected N-nitrosamines and boric acid.

2.3. Name	2.4. B (Boric acid)	2.6. ND MA	2.7. NM EA	2.8. NPY R	2.9. NDE A	2.10. NPIP	2.11. NMO R	2.12. NDPA	2.13. NDBA
2.14. Structure	2.15.	2.16.	2.17.	2.18.	2.19.	2.20.	2.21.	2.22.	2.23.
Molecular	61.83	74.05	2.24. 88.0	2.25. 100.0	2.26. 102.0	2.27. 114.0	2.28. 116.06	2.29. 130.11	2.30. 158.14

weight			6	6	8	8			
[g/mol]									
Log K_{ow} ^a	-0.62	-0.50	0.01	-0.09	0.52	0.44	-0.81	1.54	2.56
Molecular	0.071	0.124	0.151	0.134	0.178	0.161	0.145	0.232	0.286
volume ^b			2.31.	2.32.	2.33.	2.34.	2.35.	2.36.	2.37.
V_m									
[nm ³ /mole									
cule]									

2.38. ^a ACD/PhysChem Suite software (Advanced Chemistry Development, Inc., Ontario, Canada)

2.39. ^b The molecular volume of each molecule was estimated with the equation ($V_m = \text{Molecular volume [nm}^3/\text{mol}]/N_A$) where Avogadro constant (N_A) is 6.022×10^{23} 1/mol. The molecular volume of each molar was obtained from ACD/PhysChem Suite software.

2.40. Membrane filtration system

A laboratory-scale cross flow RO filtration system was used in this investigation (Figure 1). The system consisted of a stainless steel membrane cell with an effective membrane area of 40 cm² (4 cm × 10 cm) and a channel height of 2 mm. The feed solution was transferred from a stainless steel reservoir to the membrane cell by a high pressure pump (Hydra-Cell, Wanner Engineering Inc., Minneapolis, MN, USA). The permeate and concentrate streams were recirculated into the feed reservoir. The permeate flow rate and cross flow velocity were regulated by a bypass valve and back-pressure regulator (Swagelok, Solon, OH, USA). The permeate flow was monitored using a digital flow meter (FlowCal, GJC Instruments Ltd, Cheshire, UK) which was connected to a personal computer and the concentrate flow was monitored using a rotameter. The feed solution temperature was controlled using a temperature control unit (Neslab RTE 7, Thermo Scientific Inc., Waltham, MA, USA) which was equipped with stainless steel heat exchanging coil directly submerged in the feed reservoir.

Figure 1

Experimental protocols

Prior to each filtration experiment, the membrane sample was compacted at 1,800 kPa using Milli-Q water until permeate flux has been stabilised. The cross flow velocity and solution temperature were 0.42 m/s and 20.0 ± 0.1 °C, respectively. Following the compaction step, the feed water solution was conditioned using 20 mM NaCl, 1mM CaCl₂ and 1 mM NaHCO₃ by adding appropriate volumes of the stock solutions of each background electrolyte. The

stock solutions of N-nitrosamines and boric acid were also introduced into the feed to obtain approximately 250 ng/L of each N-nitrosamine and 1.0 mg/L of boron. Thereafter, the permeate flux was adjusted with 20 L/m²h. The system was continuously operated for 2 h before the first permeate and concentrate samples were taken for analysis.

2.41. Analytical technique

2.41.1. PALS

The free-volume hole-radii of the RO membranes were analysed using a PALS technique with a pulsed slow positron beam at the National Institute of Advanced Industrial Science and Technology (AIST) in Tsukuba, Japan [21]. Details of this PALS analysis are available elsewhere [19, 22-23]. In brief, the PALS technique with a slow positron beam is capable of measuring free-volume hole-radius within a sub-nanometer range within the membrane active skin layer [19]. In principal, when positrons are injected into a solid sample, the positrons annihilate with electrons of the solid sample and emit gamma-rays. Application of PALS relies on the fact that some positrons combine with an electron to form the hydrogen-like bound state, positronium (Ps). The intrinsic lifetimes of spin-antiparallel *para*-positronium (*p*-Ps) and spin-parallel *ortho*-positronium (*o*-Ps) in vacuum are 0.125 ns and 142 ns, respectively. In a polymer sample, a typical positron lifetime spectrum of a polymer contains three exponentially decaying components, due to the intrinsic *p*-Ps, free positron (non-Ps) and *o*-Ps annihilation. Although *o*-Ps annihilates with a lifetime much shorter than 142 ns in a polymer sample, *o*-Ps still survives far longer than the *p*-Ps and free positrons which indicates that *o*-Ps is the longest lifetime component.

Lifetime of *o*-Ps (τ_{o-Ps}) is affected by the free-volume size in insulating materials including polymer and their relationship is given by the Tao-Eldrup model as follows [24-25]

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

where r (≤ 1 nm) is the radius of the free-volume hole approximated as a spherical shape. Consequently, the free-volume hole-space (V_f) can be calculated with the following formula.

$$V_f = \frac{4}{3} \pi r^3 \quad (2)$$

It should be noted that the evaluated r (calculated by Eq. 1) represents the mean radius of free-volume holes which were probed by o -Ps. Although this indicates that the PALS technique is expected to have a limited range for evaluating the size of free-volume hole [22-23], the mean free-volume hole-radius based on the PALS technique was referred simply as “mean free-volume hole-radius” in this study.

Positron lifetime was measured as the time difference between the pulsing trigger from the beam pulsing system and the detection timing of annihilation gamma-ray detected by a BaF₂ scintillation detector [21] (Figure 2). The analysis was carried out under vacuum at 10^{-5} Pa. The mean implantation depth of positrons was adjusted by changing positron incident energy of the slow positron beam. During the PALS analysis in this study, positron incident energy was set at 1.0 keV which corresponds to a mean depth of around 40 nm. This energy (1 keV) and corresponding implantation depth (~ 40nm) of slow positron was decided reasonably for our sample evaluation based on previous investigations. For example, previous studies investigated the mean free-volume hole-radius in variable implantation depths using composite polyamide RO membranes and reported that smallest mean free-volume hole-radii were found at mean implantation depth of 40-100 nm [19, 26] where the active skin layer is expected to exist. In fact, for LPRO and SWRO membranes the total thickness of about 200 nm active skin layers has been estimated with transmission electron microscopy by Freger et al. [27].

Approximate 2×10^6 events of positron annihilation were collected for obtain one positron lifetime spectrum for each sample. The positron lifetime spectra were analysed assuming three exponential components to deduce the lifetime, $\tau_{o\text{-Ps}}$, using a non-linear least-squares fitting program. The relative measurement uncertainty of $\tau_{o\text{-Ps}}$ was evaluated not more than 5%.

2.41.2.

N-nitrosamine analysis

N-nitrosamine concentrations were determined using a method previously described by McDonald et al [28], which involves solid phase extraction (SPE) and subsequent quantification by gas chromatography – tandem mass spectrometry (GC-MS/MS) with electron ionisation. Prior to GC-MS/MS analysis, 200 mL of sample was extracted to a SupelcleanTM Coconut Charcoal (2 g) SPE cartridge (Supelco, St Louis, MO, USA). To correct for any variation in the recovery efficiency of the SPE procedure, 50 ng deuterated surrogate of each N-nitrosamine was added to all samples. The concentrations of N-nitrosamines were quantified using a GC-MS/MS system consisting of an Agilent 7890A gas chromatograph coupled with an Agilent 7000B triple quadrupole mass spectrometer. The limit of quantification of this GC-MS/MS method is less than 5 ng/L for all N-nitrosamines investigated here.

2.41.3. General analytical techniques

Concentrations of boron and sodium were analysed using an Inductive Coupled Plasma – Mass Spectrometer (7500CS, Agilent Technologies, Wilmington, DE, USA) as described in a previous study [9]. A calibration of these ion concentrations was carried out using a Merck ICP multi-element standard solution. Their detection limits using this technique are 50 ng/L

for boron ions and 140 ng/L for sodium ions. Conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, USA).

3. Results and discussion

3.1. PALS analysis

The *o*-P_s lifetime (τ_{o-Ps}) of the LPRO membranes (i.e. ESPA2 and ESPAB) obtained here were almost identical ($\tau_{o-Ps} = 2.07$ ns) and, as a result, these two membranes were determined to have the same mean free-volume hole-radii (r) of 0.289 nm (Table 3). The *o*-P_s lifetime (τ_{o-Ps}) of the SWC5 membrane was 1.75 ns and the corresponding mean free-volume hole-radius (r) was determined to be 0.259 nm. In good agreement with our results, Lee et al. [20] used the PALS technique and obtained a mean free-volume hole-radius of 0.278 nm for the SW30 which is commonly used as seawater RO membrane. Pure water permeability was generally membrane dependent and increased in the order of the SWC5, ESPAB and ESPA2 membranes and sodium ion rejection decreased following the same order (Table 3).

Although the mean free-volume hole-radii of the ESPA2 and ESPAB probed by *o*-Ps are both 0.289 nm, a notable variation was found for their pure water permeability and sodium ion rejections (Table 3). In general, pure water permeability of RO membranes increases and solute rejection decreases with increasing mean free-volume hole-radius (r) and with decreasing the effective thickness of the membrane active skin layer [29], thus these two parameters (i.e, mean hole-radius and effective thickness) are likely to be key factors differentiating permeability and solute rejections among these membranes. Although not reported in this study, it is noteworthy that the distribution of the free-volume hole-radii may also play a role in permeability and solute rejection. Freger [27] measured the membrane thickness of LPRO and SWRO membranes by transmission electron microscopy and reported that the LPRO membrane have thinner active skin layer than the SWRO membrane, which is consistent with the fact that it is an SWRO membrane with lower permeability and higher sodium ion rejection than the ESPA2 and ESPAB membranes (Table 3). In addition, Prakash et al. [30] reported a strong correlation between the effective thickness of active skin layer and pure water permeability of RO membranes. It is also noteworthy that the ESPAB is likely to be a modified version of the ESPA2 (which may explain the same calculated free-volume hole-radii of these two membranes). The details of this modification are proprietary

information of the manufacturer. However, it can be speculated that the lower pure water permeability and higher sodium ion rejection of the ESPAB compared to the ESPA2 is attributed to a thicker active layer thickness and different free-volume hole-radius distribution of the ESPAB. Although it is beyond the scope of this study, measurement of the active layer thickness and distribution of free-volume hole-radius within the active skin layer would be useful to substantiate this hypothesis.

Table 3: Mean free-volume hole-size and hole-space, pure water permeability and sodium ion rejection of the RO membranes.

Membrane	σ_{PS} [ns]	Mean free-volume hole-radius, r [nm]	Mean free-volume hole-space, V_f [nm ³]	Pure water permeability ^a [L/m ² hbar]	Na ⁺ rejection ^b [%]
ESPA2	2.07	0.289	0.101	5.9 ± 0.3	97.1 ± 1.4
ESPAB	2.07	0.289	0.101	4.6 ± 0.1	99.0 ± 0.1
SWC5	1.75	0.259	0.073	2.6 ± 0.1	99.2 ± 0.4

^a Determined with Milli-Q water at 1,000 kPa and 20 °C feed temperature. Values reported here are average and ranges of duplicate results.

3.2. ^b *Analysed with feed solution contained 20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂ at permeate flux 20 L/m²h, cross flow velocity 40.2 cm/s, feed pH 8.0 ± 0.1 and feed temperature 20.0 ± 0.1 °C. Values reported here are average and ranges of duplicate results. Rejection of boric acid and N-nitrosamines*

The rejection of boric acid and N-nitrosamines by the three RO membranes used in this study generally increased in the increasing order of their molecular volume (Figure 3). Significant differentiation in solute rejection by the three membranes was observed for those smaller than 0.13 nm³/molecule. The ESPAB and SWC5 membranes exhibited similar rejection values for any given solute with boric acid and NDMA being the only notable exceptions (Figure 3) despite the fact that their mean free-volume hole-radii differ by 0.03 nm (Table 3). Likewise, although the mean free-volume hole-radii of the ESPAB and ESPA2 were both 0.289 nm, the

rejection values of small molecular volume solutes by these membranes were distinctly different. Once again, these results suggest that, in addition to the free-volume hole-radius, the rejection of small molecular volume solutes can also be influenced by other membrane characteristics such as thickness of the membrane active skin layer. Furthermore, hydrophobic interaction can also influence the permeation of small molecular volume solutes through the membrane. Due to hydrophobic interaction, solute adsorption onto the membrane surface followed by subsequent diffusion can facilitate the transport of small and hydrophobic solutes across the membrane active skin layer [31-32]. However, all three RO membranes investigated here have similar surface hydrophobicity. The contact angle values of these membranes are in the range from 47 to 61° [33]. Thus, hydrophobic interaction is not likely to play an important role in differentiating the rejection of boric acid and N-nitrosamines by these membranes.

3.3.

Rejection mechanisms

The rejection of boric acid, NDMA and sodium ion by the RO membranes was inversely correlated with their pure water permeability (Figure 4). The rejection of sodium ion was significantly higher than that of boric acid and NDMA (Figure 4) because sodium ion is strongly hydrated ($\text{Na}^+ \cdot 6\text{H}_2\text{O}$) at the tested pH and the charged sodium ion is rejected by both steric and electrostatic interactions [11]. For the case of the ESPA2 and ESPAB membranes both of which have 0.289 nm mean free-volume hole-radii, as described in a previous section the thicker active skin layer and different free-volume hole-radius distribution of the ESPAB membrane may be the reason why the rejection of small molecular volume solutes (i.e. boric acid, NDMA and sodium ion) by the ESPAB was higher than the ESPA2 membrane. On the other hand, the SWC5, being a SWRO membrane, is expected to have a thicker active skin layer than LPRO membranes [27]. Because the PALS analysis showed that the SWC5 membrane has a smaller mean free-volume hole-radius than the LPRO membranes, two parameters (i.e. mean free-volume hole-radius and/or its distribution and active skin layer

thickness) can be expected to contribute to the higher rejection of uncharged solutes by the SWC5 compared to the ESPA2 and ESPAB.

The effect of the size relationship between mean free-volume hole-space and solute volume on the rejection of the uncharged solutes was evaluated using the ratio of molecular volume (V_m) to the mean free-volume hole-space (V_f) (Figure 5). As a result, rejection increased drastically around V_m/V_f ratio of one with an increasing V_m/V_f ratio and reached almost constant value of 95 % over V_m/V_f ratio of two. Such significant changes in rejections were also observed in the similar range of the V_m/V_f ratio (between one and three) in previous studies [19, 26].

A previous study by Chen et al. [19] revealed that a correlation between V_m/V_f and the rejection of uncharged solutes among one RO and two NF membranes was approximately linear (Figure 5). They reported that the rejection of uncharged solute is highly associated with the mean free-volume hole-space of the membranes and the correlation is valid for different solutes and membranes (Figure 5). While our experimental results showed that the

correlation between rejection and V_m/V_f is not linear, rejection increased almost monotonically with increasing function of V_m/V_f for each membrane like the previous studies [19, 23]. These results indicate that the mean free-volume hole-space (V_f) is an important parameter determining uncharged solute rejection. It is also noteworthy that the rejections of solutes with molecular volume of less than $0.13 \text{ nm}^3/\text{molecule}$ by the three RO membranes differ considerably from one to another although the mean free-volume hole-space (V_f) of these membranes were similar. Thus, in addition to the mean free-volume hole-space (or mean radius), other membrane characteristics such as the free-volume hole-radii distribution and active skin layer thickness could also be important parameters governing the rejection of small and uncharged solutes by RO membranes.

Figure 5

4. Conclusions

PALS analysis with 1 keV slow positron beam revealed that the seawater reverse osmosis (RO) SWC5 membrane has the smallest mean free-volume hole-radius followed by the two low pressure RO membranes (ESPA2 and ESPAB). The SWC5 membrane also exhibited the highest rejection of uncharged solutes (i.e. boric acid and N-nitrosamines) and sodium ions. The ESPAB membrane revealed a lower pure water permeability and higher rejection of

uncharged solutes and sodium ions than the ESPA2 membrane, despite their identical mean free-volume hole-radii. The comparison between solute volume (V_m) and mean free-volume hole-space (V_f) evaluated by PALS exhibited a monotonically increasing factor of V_m/V_f , indicating the mean free-volume hole-space (or referred as hole-radii) is indeed an important factor determining uncharged solute rejection. Nevertheless, because the rejection of small and uncharged solutes by the three RO membranes differ considerably from one to another, other membrane parameters and properties such as the distribution of free-volume hole-radius and thickness of the active skin layer are also likely to play a role in governing the passage of solutes with small molecular volume. Thus, further research is necessary to examine the distribution of mean free-volume hole-radius and to measure the thickness of the active skin layer.

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6. References

- [1] A.A. Alturki, N. Tadkaew, J.A. McDonald, S.J. Khan, W.E. Price, L.D. Nghiem, Combining MBR and NF/RO membrane filtration for the removal of trace organics in indirect potable water reuse applications, *Journal of Membrane Science*, 365 (2010) 206-215.
- [2] T. Wintgens, T. Melin, A. Schäfer, S. Khan, M. Muston, D. Bixio, C. Thoeye, The role of membrane processes in municipal wastewater reclamation and reuse, *Desalination*, 178 (2005) 1-11.
- [3] 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, *Separation and Purification Technology*, 98 (2012) 503-515.
- [4] E. Steinle-Darling, M. Zedda, M.H. Plumlee, H.F. Ridgway, M. Reinhard, Evaluating the impacts of membrane type, coating, fouling, chemical properties and water chemistry on reverse osmosis rejection of seven nitrosoalkylamines, including NDMA, *Water Research*, 41 (2007) 3959-3967.

- [5] J.E. Drewes, C. Hoppe, T. Jennings, Fate and transport of N-Nitrosamines under conditions simulating full-scale groundwater recharge operations, *Water Environment Research*, 78 (2006) 2466-2473.
- [6] USEPA, N-Nitrosodimethylamine (CASRN 62-75-9) - Integrated risk information system (IRIS), <http://www.epa.gov/iris/subst/0045.htm> (1993).
- [7] K.L. Tu, L.D. Nghiem, A.R. Chivas, Boron removal by reverse osmosis membranes in seawater desalination applications, *Separation and Purification Technology*, 75 (2010) 87-101.
- [8] K. Rahmawati, N. Ghaffour, C. Aubry, G.L. Amy, Boron removal efficiency from Red Sea water using different SWRO/BWRO membranes, *Journal of Membrane Science*, 423–424 (2012) 522-529.
- [9] K.L. Tu, A.R. Chivas, L.D. Nghiem, Effects of membrane fouling and scaling on boron rejection by nanofiltration and reverse osmosis membranes, *Desalination*, 279 (2011) 269-277.
- [10] E. Huertas, M. Herzberg, G. Oron, M. Elimelech, Influence of biofouling on boron removal by nanofiltration and reverse osmosis membranes, *Journal of Membrane Science*, 318 (2008) 264-270.
- [11] C. Bellona, J.E. Drewes, P. Xu, G. Amy, Factors affecting the rejection of organic solutes during NF/RO treatment - A literature review, *Water Research*, 38 (2004) 2795-2809.
- [12] Y. Miyashita, S.-H. Park, H. Hyung, C.-H. Huang, J.-H. Kim, Removal of N-Nitrosamines and their precursors by nanofiltration and reverse osmosis membranes, *Journal of Environmental Engineering*, 135 (2009) 788-795.
- [13] 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, *Journal of Membrane Science*, 409–410 (2012) 66-74.
- [14] D. Nanda, K.-L. Tung, W.-S. Hung, C.-H. Lo, Y.-C. Jean, K.-R. Lee, C.-C. Hu, J.-Y. Lai, Characterization of fouled nanofiltration membranes using positron annihilation spectroscopy, *Journal of Membrane Science*, 382 (2011) 124-134.
- [15] K.-L. Tung, Y.-C. Jean, D. Nanda, K.-R. Lee, W.-S. Hung, C.-H. Lo, J.-Y. Lai, Characterization of multilayer nanofiltration membranes using positron annihilation spectroscopy, *Journal of Membrane Science*, 343 (2009) 147-156.
- [16] K. Boussu, J. De Baerdemaeker, C. Dauwe, M. Weber, K.G. Lynn, D. Depla, S. Aldea, I.F.J. Vankelecom, C. Vandecasteele, B. Van der Bruggen, Physico-Chemical Characterization of Nanofiltration Membranes, *ChemPhysChem*, 8 (2007) 370-379.
- [17] T. Shintani, A. Shimazu, S. Yahagi, H. Matsuyama, Characterization of methyl-substituted polyamides used for reverse osmosis membranes by positron annihilation

- lifetime spectroscopy and MD simulation, *Journal of Applied Polymer Science*, 113 (2009) 1757-1762.
- [18] S.H. Kim, S.-Y. Kwak, T. Suzuki, Positron Annihilation Spectroscopic Evidence to Demonstrate the Flux-Enhancement Mechanism in Morphology-Controlled Thin-Film-Composite (TFC) Membrane, *Environmental Science & Technology*, 39 (2005) 1764-1770.
 - [19] Z. Chen, K. Ito, H. Yanagishita, N. Oshima, R. Suzuki, Y. Kobayashi, Correlation study between free-volume holes and molecular separations of composite membranes for reverse osmosis processes by means of variable-energy positron annihilation techniques, *The Journal of Physical Chemistry C*, 115 (2011) 18055-18060.
 - [20] J. Lee, C.M. Doherty, A.J. Hill, S.E. Kentish, Water vapor sorption and free volume in the aromatic polyamide layer of reverse osmosis membranes, *Journal of Membrane Science*, 425–426 (2013) 217-226.
 - [21] R. Suzuki, Y. Kobayashi, T. Mikado, H. Ohgaki, M. Chiwaki, T. Yamazaki, T. Tomimasu, Slow Positron Pulsing System for Variable Energy Positron Lifetime Spectroscopy, *Japanese Journal of Applied Physics*, 30 (1991) 532-534.
 - [22] Y. Ito, H.F.M. Mohamed, V.P. Shantarovich, T. Suzuki, Vacancy Spectroscopy Using Positronium : What are we Looking at by Positronium in Polymers, *Membrane*, 34 (2009) 164-178.
 - [23] Y.C. Jean, P.E. Mallon, D.M. Schrader, Principles And Applications Of Positron And Positronium Chemistry, World Scientific, Singapore, 2003.
 - [24] M. Eldrup, D. Lightbody, J.N. Sherwood, The temperature dependence of positron lifetimes in solid pivalic acid, *Chemical Physics*, 63 (1981) 51-58.
 - [25] S.J. Tao, Positronium Annihilation in Molecular Substances, *The Journal of Chemical Physics*, 56 (1972) 5499-5510.
 - [26] K. Ito, Z. Chen, W. Zhou, N. Oshima, H. Yanagishita, R. Suzuki, Y. Kobayashi, Subnanoscopic Holes in Composite Membranes for Desalination Elucidated by Energy-Tunable Positron Annihilation, *Japanese journal of polymer science and technology*, 69 (2012) 443-447.
 - [27] V. Freger, Nanoscale Heterogeneity of Polyamide Membranes Formed by Interfacial Polymerization, *Langmuir*, 19 (2003) 4791-4797.
 - [28] J.A. McDonald, N.B. Harden, L.D. Nghiem, S.J. Khan, Analysis of N-nitrosamines in water by isotope dilution gas chromatography-electron ionisation tandem mass spectrometry, *Talanta*, 99 (2012) 146-152.
 - [29] Y. Kiso, K. Muroshige, T. Oguchi, M. Hirose, T. Ohara, T. Shintani, Pore radius estimation based on organic solute molecular shape and effects of pressure on pore radius for a reverse osmosis membrane, *Journal of Membrane Science*, 369 (2011) 290-298.

- [30] A. Prakash Rao, S.V. Joshi, J.J. Trivedi, C.V. Devmurari, V.J. Shah, Structure–performance correlation of polyamide thin film composite membranes: effect of coating conditions on film formation, *Journal of Membrane Science*, 211 (2003) 13-24.
- [31] L.D. Nghiem, A.I. Schäfer, M. Elimelech, Removal of natural hormones by nanofiltration membranes: Measurement, modeling, and mechanisms, *Environmental Science & Technology*, 38 (2004) 1888-1896.
- [32] B. Van der Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration, *Journal of Membrane Science*, 156 (1999) 29-41.
- [33] T. Fujioka, S.J. Khan, J.A. McDonald, A. Roux, Y. Poussade, J.E. Drewes, L.D. Nghiem, N-nitrosamine rejection by nanofiltration and reverse osmosis membranes: The importance of membrane characteristics, *Desalination*, 316 (2013) 67-75.