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Removal of haloacetic acids from swimming pool water by reverse osmosis and nanofiltration

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Abstract

Recent studies report high concentrations of haloacetic acids (HAAs), a prevalent class of toxic disinfection by-products, in swimming pool water (SPW). We investigated the removal of 9 HAAs by four commercial reverse osmosis (RO) and nanofiltration (NF) membranes. Under typical SPW conditions (pH 7.5 and 50 mM ionic strength), HAA rejections were $> 60\%$ for NF270 with molecular weight cut-off (MWCO) equal to 266 Da and equal or higher than 90% for XLE, NF90 and SB50 with MWCOs of 96, 118 and 152 Da, respectively, as a result of the combined effects of size exclusion and charge repulsion. We further included 7 neutral hydrophilic surrogates as molecular probes to resolve the rejection mechanisms. In the absence of strong electrostatic interaction (e.g., pH 3.5), the rejection data of HAAs and surrogates by various membranes fall onto an identical size-exclusion (SE) curve when plotted against the relative-size parameter, i.e., the ratio of molecular radius over membrane pore radius. The independence of this SE curve on molecular structures and membrane properties reveals that the relative-size parameter is a more fundamental SE descriptor compared to molecular weight. An effective molecular size with the Stokes radius accounting for size exclusion and the Debye length accounting for electrostatic interaction was further used to evaluate the rejection. The current study provides valuable insights on the rejection of trace contaminants by RO/NF membranes.

Keywords: Reverse osmosis, Nanofiltration, Haloacetic acids, Swimming pool water, Empirical formula

1. Introduction

Swimming is a popular activity for exercise and entertainment. Disinfection by chlorine gas, sodium hypochlorite or calcium hypochlorite is commonly practiced to keep swimming pool water (SPW) microbiologically safe and hygienic (WHO, 2006). However, these disinfectants can react with water constituents of natural and anthropogenic origin (e.g., natural organic matter and body fluid) to produce toxic disinfection by-products (DBPs) (Fischer et al., 2012). Haloacetic acids (HAAs) are a prevalent class of DBPs characterized by their high frequency of occurrence, considerable concentrations and potent toxicity (Richardson et al., 2007). HAAs are mutagenic in bacteria, and induce DNA damage and chromosomal aberrations in mammalian cells in vitro (IARC, 2004; Richardson et al., 2007). Besides, some HAAs cause liver tumors, leukemias and abdominal cavity mesotheliomas in experimental animals (Richardson et al., 2007). These concerns led to the regulation over HAAs for drinking water by the Environmental Protection Agency (EPA) in 1998, with a maximum contaminant level (MCL) of 60 µg/L for the sum of five HAAs (EPA, 1998). However, so far no regulation has been enacted for HAAs in SPWs. The presence of HAAs in SPWs has also raised significant concerns, with recent studies reporting their HAA concentrations of more than an order of magnitude higher than the MCL in drinking water (Wang et al., 2014; Yang et al., 2016).

The traditional SPW treatment system follows “flocculation-filtration-disinfection”, which is sometimes combined with activated carbon adsorption and/or ozonation to minimize DBP formation (Zwiener et al., 2007). In some cases, especially for private pools, water might be refreshed regularly. The large amount of HAAs accumulated in the recirculated SPW treatment system or formed in the regularly refreshed system

reveals that the current approaches are insufficient to sustain good water quality. One way to minimize HAAs is to control the human related HAA precursors by raising the public awareness of the importance of hygiene behavior, i.e., have a shower before entering into the pools, do not urinate during swimming, etc. Alternatively, more effective technologies are needed for HAA removal. There are several reports about the biodegradation of HAAs in drinking water systems (Bayless and Andrews, 2008; Grigorescu et al., 2010; Zhang et al., 2009). However, extrapolation of such technology to SPW treatment may raise uncertainties due to its distinguishing water matrix compared to drinking water. Photodegradation and thermal degradation are two possible HAA treatment methods while still encountering the problems of complex post-processing (e.g., the removal of the titanium dioxide suspensions) and/or high heating cost (Lifongo et al., 2004; Lifongo et al., 2010).

Reverse osmosis (RO) and nanofiltration (NF) have been widely used for the treatment of trace organic compounds in water and wastewater (Doederer et al., 2014; Dong et al., 2016; Kimura et al., 2003; Nghiem et al., 2004; 2005; Verliefde et al., 2008). The high efficiency in rejection and simple operation make them promising candidates for the potential removal of HAAs or other DBPs. There have been a handful of studies reporting the effective rejections of HAAs by NF/RO membranes (Chalatip et al., 2009; Kimura et al., 2003). Chalati et al. (2009) reported the high HAA rejections of 90-100% by a dense negatively charged NF membrane (i.e., ES10) using a mixture of five regulated HAAs as the feed solution. Kimura et al. (2003) found the rejections of two HAAs (i.e., dichloroacetic acid and trichloroacetic acid) reached 91-96% by two NF/RO membranes (i.e., ESNA and XLE) under a feed solution containing single HAA of 100 µg/L. A pilot-scale RO plant demonstrated high rejections (86-94%) for charged

HAAs and low rejections (as low as 55%) for neutral and low-molecular-weight DBPs, e.g., trihalomethanes (Agus and Sedlak, 2010). In the context of SPWs, Klüpfel et al. (2011) applied NF in a by-pass (with the membrane installed at the outlet of a traditional sand filter) to investigate the effects on a large pool. These authors found that the rejections of DBPs and DBP precursors reached as high as 80% and 70%, respectively. Glauner et al. (2005) applied ultrafiltration (UF) or NF prior to some advanced oxidation processes (AOPs) for the treatment of SPWs in a laboratory scale using a 2-L reactor. The overall eliminations of DBPs and DBP precursors reached up to around 80% by NF and AOPs and 50% by UF and AOPs. In a parallel study, we reported the effective removal of major dissolved ions, e.g., Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , etc. from real SPWs by NF membranes (Yang et al., 2017). Current studies have demonstrated membrane filtration a promising method to control the SPW quality, particularly in terms of HAAs. Nevertheless, the detailed rejection mechanisms and controlling factors in the SPW context are yet to be systematically investigated.

Molecular weight cut-off (MWCO) concept has been widely used to describe the pore size property of the membranes (Chalatip et al., 2009; Do et al., 2012a; López-Muñoz et al., 2009). Molecular weight is also commonly used to model the size exclusion of neutral solutes by membranes (Chen et al., 2004; Ozaki and Li, 2002; Yangali-Quintanilla et al., 2010). Nevertheless, these weight-related parameters only give a rough estimation of membrane retention characteristics and are often inadequate to explain the distinctive rejection values of solutes with similar molecular weights. Size-related parameters, e.g., Stokes radius, are more accurate size-exclusion descriptors than weight-related ones, as the former considers the molecular geometry (Van der Bruggen et al., 1999; Van der Bruggen and Vandecasteele, 2002). For charged solutes,

size exclusion and electrostatic interaction are two major rejection mechanisms, commonly modelled by the extended Nernst-Planck equation, originally developed by Bowen et al. (1997). This model contains complex calculation and limits the total number of ions in the solution. Thus, a simple and reliable estimation approach is needed to fill in the literature gap.

The systematic changes in the molecular structures of HAAs (sharing the same acetic acid structure with varied degrees of halogenation) prompt us to perform a comprehensive study on their removal by membranes. Specifically, we tested the rejection performance of 9 HAAs by four RO/NF membranes under different water chemistry conditions. Seven neutral hydrophilic surrogate compounds (Table 1) were used as molecular probes to evaluate the pore properties of these membranes. By correlating their rejections to various physicochemical properties of membranes and solutes, mechanisms governing HAA rejections in SPW matrix were revealed in detail.

2. Materials and methods

2.1 Chemicals and materials

General chemicals. All the general chemicals used in this study were analytical grade (> 99%), unless otherwise specified. Sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%) and sodium chloride (NaCl) were obtained from Merck. MilliQ water was used in all stock solution preparations and experiments (Millipore, Billerica, MA).

HAAs. Nine HAAs were tested, including chloroacetic acid (CAA), bromoacetic acid (BAA), dichloroacetic acid (DCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), trichloroacetic acid (TCAA), bromodichloroacetic acid (BDCAA),

dibromochloroacetic acid (DBCAA) and tribromoacetic acid (TBAA) (Table 1). HAA standards were analytical grade with $\geq 97\%$ purity (Sigma Aldrich). Solvents, including methyl tert-butyl ether (MTBE) and methanol, were GC grade. Other chemicals for HAA quantification, e.g., sulfuric acid (98%), sodium bicarbonate, copper sulfate and sodium sulfate, were at least ACS reagents.

Surrogate molecules. Seven surrogates, namely glycerol, erythritol, xylose, glucose, maltose, sucrose and raffinose, were analytical grades with $\geq 99\%$ purity. All surrogates were obtained from Sigma Aldrich except sucrose from USB.

RO/NF membranes. Four commercial flat sheet RO/NF membranes, including two NF membranes (NF90 and NF270) and two RO membranes (XLE and SB50), were investigated. SB50 was from TriSep with cellulose acetate as an active surface layer and the others were from Dow Filmtec with polyamide as the selective layer. All these membranes were stored at 4 °C in the dark. The virgin membrane properties, including water permeability, NaCl rejection, MWCO, ζ potential (at pH 7.5), pore radius, and roughness, are listed in Table 2.

2.2 Membrane characterization

FE-SEM. Field emission scanning electron microscopy (FE-SEM, JSM-7600F) was used to characterize the topography of membrane surfaces at an accelerating voltage of 2 keV. The wet membranes were dried in a vacuum at an ambient temperature (25 ± 1 °C). Before measurements, the membrane surface was coated with a layer of platinum by a sputter coater (Emitech SC7620, Quorum, UK) (Zhang et al., 2014).

ATR-FTIR. The chemical bonds of the membranes were characterized by attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR, Shimadzu IR Prestige 21). The spectrum was obtained from an average of 45 scans with a resolution of 4 cm⁻¹ within the scanning range of 400-4000 cm⁻¹ under absorbance mode.

Zeta potential. Membrane surface charge quantified as zeta potential was measured by an electrokinetic analyzer (SurPASS, Anton Paar GmbH, Austria). The channel height of two 20 × 10 mm adjustable gap cells was kept at 100-150 μm. The measurement was performed in 0.05 M NaCl as a background electrolyte over a pH range of ~2-11 at an ambient temperature (25 ± 1 °C). The NaCl electrolyte solution was first manually adjusted to pH ~11 by 1 M NaOH. The pH was decreased with an interval of ~0.5 by automatic titration with 0.05 M HCl during the entire measurement. Zeta potential was computed according to the Helmholtz-Smoluchowski (HS) equation (Chun et al., 2003).

2.3 Membrane filtration experiments

Membrane setup. The bench scale RO/NF filtration system consisted of four identical rectangular cross-flow CF042 cells (Delrin Acetal, Sterlitech, Kent, WA, USA). Each cell held an active membrane area of 42 cm² (4.6 cm × 9.2 cm) and possessed a spacer with a thickness of 1.2 mm (GE Osmonics, Minnetonka, MN, USA). Both permeate and retentate were recycled back to the feed tank (20 L) to keep a constant feed concentration. The temperature was maintained at 25 °C by a chiller (Polyscience, Niles, IL, USA).

Permeability, salt rejection and HAA rejection. The virgin membrane coupons were soaked in the MilliQ water for 24 h before being loaded into the test cells. The

membranes were filtered with MilliQ water for at least 24 h until the flux remained constant to eliminate the effect of membrane compaction. The rejection tests were performed using a feed water containing 0.05 M NaCl (reflecting the typical salinity for local SPWs, sodium concentration reached at 1062 ± 90 mg/L based on our field test (Yang et al., 2017)) and 100 μ g/L of each HAA (Table 1). The HAA concentration (900 μ g/L for the sum of nine HAAs) used in the current study was comparable to that we or other researcher observed in the real outdoor pools (798 ± 448 and 808 ± 464 μ g/L, respectively) (Simard et al., 2013; Yang et al., 2017). Other ionic and organic species, e.g., Ca^{2+} , Mg^{2+} , urea, etc., that may be present in the real SPWs (Yang et al., 2017) were excluded to eliminate the potential interference (e.g., fouling) in order to better resolve the detailed mechanisms governing HAA rejection by membranes. Filtration tests were performed at 100 psi at a fixed cross-flow of 0.8 L/min (corresponding to 18.1 cm/s cross-flow velocity) under a constant temperature of 25 °C. Preliminary experiments showed that pressures higher than 100 psi could enhance the the effect of concentration polarization and therefore discarded. The pHs of the feed were adjusted to 3.5, 5.5, or 7.5 by the addition of 0.1 M HCl or NaOH. To eliminate the minor difference caused by membrane materials, the same membrane coupons were used in different pH conditions. Upon changes of pHs, the system was run for at least 2 h to ensure system stabilization. Both feed and permeate were collected for HAA analysis. Water flux was monitored manually by weighting the mass of permeate at a predetermined time interval. Conductivity was continually measured by a conductivity meter (Myron L's Ultrameter II 4P) for the calculation of salt rejection.

MWCO and membrane pore radius. The surrogates used in the current study were neutral hydrophilic compounds (Table 1) to ensure that their rejections were primarily

based on size exclusion. The molecular weight (MW) of these surrogates spans over 92-504 g/mol, which allows them to be used as molecular probes for examining pore properties of the RO/NF membranes. Rejection tests for surrogates were performed at a feed concentration of 200 mg/L of each surrogate without pH adjustment (~ pH 6.7). Additional solution pHs of 3.5, 5.5, and 7.5 were included for verification purpose. According to our prior study, solution pHs had no significant effect on membrane pore size (Yang et al., 2017). In addition, the coincident rejection of surrogates at various pHs further indicated the negligible effect of pHs on pore size estimation (see Section 3.2). NaCl was not added in these rejection tests to avoid its interference with the surrogate analysis by high-performance liquid chromatography coupled with refractive index detector (HPLC-RID). The MWCO for each membrane was determined as the MW corresponding to a 90% solute rejection by interpolating the surrogate rejection curve.

Molecular radii of both surrogates and HAAs were calculated according to the Stokes-Einstein equation (Eq. (1)) based on the assumption of spherical solutes (Deen, 1987; Einstein, 1956). It should be noted that the actual molecular shape in the solution can be non-sphere which may somehow affect the rejection evaluation and different orientations of a non-sphere molecule in a pore may influence its rejection behavior as well (Deen, 1987; Kiso et al., 2010). The diffusivity in Eq. (1) was obtained from Wilke-Chang equation (Geankoplis, 1993) as shown in Eq. (2) or (3):

$$r_s = \frac{kT}{6\pi\eta_B D_{AB}} \quad (1)$$

$$D_{AB} = 1.173 \times 10^{-16} (\Phi M_B)^{0.5} \frac{T}{\eta_B V_A^{0.6}} \quad (\text{for } V_A \leq 0.5 \text{ m}^3/\text{kmol}) \quad (2)$$

$$D_{AB} = \frac{9.96 \times 10^{-16} T}{\eta_B V_A^{1/3}} \quad (\text{for } V_A > 0.5 \text{ m}^3/\text{kmol}) \quad (3)$$

where D_{AB} is the diffusivity in the bulk solution (m^2/s), k is the Boltzmann constant (J/K), T is the absolute temperature (K), η_B is the solvent viscosity ($\text{Pa}\cdot\text{s}$), r_s is the solute radius (m), Φ is the association parameter of the solvent (dimensionless), M_B is the molecular weight of the solvent (g/mol), and V_A is the solute molar volume at the boiling point (m^3/kmol).

To estimate the average pore radius of each membrane, we used the pore transport model developed by Nghiem et al. (2004). Although solution-diffusion model may commonly be used to interpret the transport of solutes through RO membranes, the current model has also been attempted to estimate the pore sizes of both NF and RO membranes by other researchers (Kiso et al., 2011; Kiso et al., 2010; Nghiem et al., 2004; Xie et al., 2012), since the latter takes both diffusion and convection into consideration. This model assumes size exclusion as the sole mechanism for rejection. By treating the membrane as a rejection layer which consists of parallel cylindrical pores of identical radius, both convective and diffusive transport of the solutes can be modeled. Detailed information on the calculation of membrane pore radius is presented in Supporting Information (S1 and S2). The calculated pore radii for NF90 and NF270 were comparable to those reported by Nghiem et al. (2004) (Table 2).

2.4 Analytical methods

HAA quantification. HAAs were analyzed based on a modified EPA 552.3 Method (Domino et al., 2003). The sample (40 mL) was acidified with 2 mL concentrated H_2SO_4 (98%) to reach $\text{pH} \leq 0.5$. The CuSO_4 (2 g) and Na_2SO_4 (16 g) were added to

achieve a clear phase separation and a saturated solution, respectively. The HAAs were extracted by adding 4 mL methyl tert-butyl ether (MTBE) followed by 30 min shaking. The MTBE extract (3 mL) with the addition of 1 mL acidic methanol (10% H₂SO₄ in methanol) was heated at 50 °C for 1.5 hours for HAA derivatization. The extract was quickly cooled down by the ice bath. Solution neutralization was completed by the addition of saturated NaHCO₃ (4 mL) followed by 2 min shaking before venting the CO₂. After 1 min standing for phase separation, the methylated HAAs (1 mL) was extracted into a 2 mL vial. The methylated HAAs were quantified by gas chromatography–mass spectrometry (GCMS, 7890B GC, 5977A MS, Agilent) coupled with an HP-5MS UI column (J & W Scientific, (5% - phenyl) - methylpolysiloxane, 30 m × 0.25 mm ID, 0.25 µm film thickness). The oven program was controlled as: 1) hold 35 °C for 9 min; 2) increase to 150 °C by 10 °C/min; 3) increase to 250 °C by 20 °C/min. The temperatures of the transfer line, MS quadrupole and ion source were 280, 150 and 300 °C, respectively. The sample (1 µL) was injected by an auto-sampler into the GCMS in a splitless mode and run for 25.5 min (with 5.40 min solvent delay) with a constant flow of the carrier gas (helium, 0.6 mL/min). The MS scanned at a range of m/z 50–300 amu with a rate of 5.5 scans/sec under electron ionization (EI) mode at 70 eV. The quality control of this method has been described elsewhere in detail (Yang et al., 2016).

Surrogate quantification. The surrogates were analyzed by HPLC-RID (Agilent 1260 Infinity) with Hi-Plex Pb (7.7 × 300 mm, 8 µm)/(7.7 × 50 mm, 8 µm) as guard/analytical columns. The 20 µL sample was injected with freshly prepared ultra-pure water as the mobile phase at a flow rate of 0.25 mL/min. The column and RID temperatures were kept at 70 °C and 55 °C, respectively. The samples were run for 65 min, and analyzed

and quantified using a calibration curve fitted by at least 6 standard points between 1 and 200 mg/L. The chromatogram of a standard with a concentration of 200 mg/L is shown in Supporting Information (S3).

3. Results and discussion

3.1 Membrane properties

Figure S2 in Supporting Information S4 shows the SEM images of the membrane surfaces. Both XLE and NF90 had rough surfaces with ridge-and-valley structures. FTIR results (Figure 1A) reveal their fully aromatic polyamide chemistry, with characteristic absorption bands of 1659 cm^{-1} (amide I band), 1611 cm^{-1} (aromatic amide band) and 1547 cm^{-1} (amide II band) (Tang et al., 2009). The semi-aromatic polyamide NF270, indicated by an absence of the aromatic amide band and amide II band (Tang et al., 2009), had a relatively smooth surface. SB50 was a cellulose acetate membrane with a smooth surface and was characterized by intense absorption bands at 1368 cm^{-1} (-OH bending vibration) and 1034 cm^{-1} (C-O-C ether linkage from the glycosidic units) (Kamal et al., 2014).

Zeta potential of the four membranes was measured in a 0.05 M NaCl solution over a pH range of ~2-11 (Figure 1B). Overall, zeta potential increased from negative to positive with the decreasing pH. Compared to the cellulose acetate membrane SB50, the polyamide membranes appeared to be more charged, which can be explained by their amine and carboxylic functional groups (Tang et al., 2006). The isoelectric points were between 2.5-3.5 for XLE, NF270 and SB50, and slightly higher at ~4.0 for NF90, comparable to the literature (Do et al., 2012b). At pH 7.5 (representing the typical SPW pH range of 7.2-7.8), the zeta potentials were -33, -33, -36 and -13 mV for XLE, NF90,

NF270 and SB50, respectively.

The MWCOs, evaluated based on the rejections of neutral hydrophilic surrogates, were determined to be 96, 118, 266 and 152 Da for XLE, NF90, NF270 and SB50, respectively (Figure 1C). The reported MWCOs for NF90 and NF270 were 180 and 340 Da by López-Muñoz et al. (2009) and ~200 and ~300 Da by Do et al. (2012a). The difference of MWCOs could be explained by different steric characteristics of solutes, i.e., chain for polyethylene glycols (PEGs) and circular for most surrogates. Corresponding to its highest MWCO value, NF270 had the lowest NaCl rejection (30.6%) and the largest membrane pore radius (0.44 nm).

3.2 Rejection of HAAs

3.2.1 Effect of size exclusion

Rejection by RO/NF can be affected by both size exclusion and electrostatic interaction (Nghiem et al., 2004). The sorption effect by the membrane material could be neglected due to the hydrophilic properties of HAAs. For example, we observed a stable rejection of HAAs and surrogate molecules over time. Our results are consistent with Kimura et al. (2003) who reported the time-independency of HAA rejections by NF/RO membranes. In contrast, hydrophobic compounds such as some estrogens show a decreasing rejection over time as the hydrophobic molecules “break-through” the ultrathin rejection layer (Hu et al., 2007; Jin et al., 2010; Jin et al., 2007; Nghiem et al., 2004). In order to isolate the effect of size exclusion, we performed some HAA rejection tests at pH 3.5. At this pH, the electrostatic interaction was negligible as the membranes were uncharged or only weakly charged (Figure 1B), although HAAs were partially or almost completely negatively charged (based on the pKa values in Table 1). Figure 2

presents the effect of molecular weight on the rejections of both HAAs and surrogate molecules by the four membranes, with a vertical dash line representing the MWCO of each membrane. A general trend of increased rejection at higher molecular weight was observed, which confirms the critical role of size exclusion. However, the rejection data of HAAs had some significant scattering possibly due to the different molecular structure caused by various halogen numbers. More importantly, the rejection behavior of HAAs deviated apparently from that of the surrogate molecules. For molecules with similar molecular weights, HAAs had consistently lower rejections compared to the surrogates. The difference between the two groups was most significant for NF270 (Figure 2C), which was also the membrane having the largest pore radius of 0.44 nm. The MWCOs were somehow overestimated due to the use of observed rejection instead of the real rejection of the surrogates, however, the error should be insignificant as we used a relatively low pressure (100 psi) to minimize the concentration polarization effect. Indeed, the MWCO concept commonly used as a membrane characterization parameter (Chalatip et al., 2009; Do et al., 2012a; López-Muñoz et al., 2009) was inadequate to explain the low rejection values of equal or less than 40% for those HAAs having molecular weights around or even greater than the MWCO of NF270 (266 Da).

The discrepancy in rejection performance between HAAs and the surrogate molecules can be attributed to their difference in molecular structure (Table 1). The HAAs have a basic structure of acetic acid, with some hydrogen atoms substituted by halogens. In contrast, a number of the sugar-based surrogate molecules have circular structures, making them bulkier compared to the chain-like HAAs. For example, the Stokes radius of glucose (MW = 180 g/mol) is approximately 0.323 nm, which is significantly larger than the sizes of HAAs with similar or even greater molecular weights. The current

study suggests that the molecular weight, despite being the most commonly used parameter for modeling size exclusion (Chen et al., 2004; Ozaki and Li, 2002; Yangali-Quintanilla et al., 2010), is inadequate due to its inability to capture the molecular structure. Other studies similarly demonstrated that molecular weight was not the most appropriate parameter to indicate the rejection as it does not consider the molecular geometry (Van der Bruggen et al., 1999; Van der Bruggen and Vandecasteele, 2002). However, for the determination of Stokes radius, solute molar volume (deemed as V_A in Eqs. (2) and (3)) was used as a major distinctive parameter (Section 2.3).

Figure 3 plots the rejections of HAAs and surrogates as a function of their molecular radii. Where applicable, the rejections of linear PEG molecules obtained from Do et al. (2012a), have been included for comparison purpose. Figure 3 shows a clear and consistent trend of increased rejections for molecules with greater molecular radii. For solutes with their radii bigger than the membrane pore size ($r_s > r_p$), both the HAAs and surrogates were highly rejected ($R > 98\%$). The small percentage of the solutes passing through the membranes can be explained by a distribution of pore sizes and shapes in the membranes (Guillen and Hoek, 2010). The rejection decreased significantly for molecules with smaller molecular radii. The collapse of data points of both HAAs and surrogate molecules into a single trend line in Figure 3 reveals a more fundamental role of molecular radius in comparison to molecular weight in governing the solute transport through membranes. Since molecules with similar molecular weights can have drastically different molecular radii and thus rejection behavior, future studies shall consider the use of the latter as a preferred indicator for the description of size exclusion effect. Other researchers similarly found that size-related parameters are more accurate for the estimation of solute rejection than molecular weight (Van der Bruggen et al.,

1999; Van der Bruggen and Vandecasteele, 2002).

3.2.2 Effect of electrostatic interaction

To investigate the effect of electrostatic interaction, solute rejections at different pHs were compared. Solution pHs had a negligible effect on the rejection of the neutral surrogate molecules (see Figure 4A for NF270 and Supporting Information S5 for other membranes). This pH-independent rejection behavior can be attributed to the lack of solute-membrane electrostatic interaction. The trend line in Figure 4A, which fits the surrogate data well at all pHs, provides a useful baseline for size exclusion (SE baseline).

Figure 4B presents the rejection of HAAs by NF270 at different pHs. To resolve the relative importance of size exclusion and charge interaction, the SE baseline obtained for the surrogates (Figure 4A) is also shown. The rejection data of HAAs at pH 3.5 and 5.5 falls nicely onto this baseline, suggesting that their rejection behavior was dominated by the size exclusion effect. At these pHs, most of HAAs (~85-100%) were dissociated to their anion forms. Nevertheless, NF270 was non-charged or weakly charged at pH 3.5 and 5.5 (Figure 1B), which explains such dominance of size exclusion over charge interaction at these pHs. The fitting by an identical baseline in Figure 4A and 4B reveals that the effect of size exclusion may be adequately described by the molecular radius regardless of the detailed molecular structure.

Increasing pH from 3.5 to 7.5 significantly enhanced the rejection of HAAs by NF270 (> 60%, see Figure 4B). At pH 7.5, the membrane became more negatively charged (zeta potential ~ -36 mV, see Table 2), resulting in enhanced charge repulsion between the membrane and HAA anions (pKa values (Bhattacharyya and Rohrer, 2012; Kong et

al., 2014) in a range of 0.05-2.73, see Table 1). The contribution of charge repulsion to solute rejection is represented by the vertical distance of the rejection data to the SE baseline. Figure 4B reveals several important trends with regard to the effect of electrostatic interaction on solute rejection: (1) solute rejection was greatly enhanced in the presence of strong charge repulsion; (2) charge repulsion played a more critical role for molecules with smaller molecular radii, i.e., molecules experiencing relatively weaker size exclusion effect; (3) the rejection of charged molecules had a much weaker dependence on the molecular radius (represented by a smaller slope) as a result of combined effects of charge interaction and size exclusion. The rejection enhancement due to charge repulsion was less significant for XLE, NF90, and SB50 (Supporting Information S5). These membranes had much smaller pore sizes (0.30-0.33 nm) compared to the loose NF270 (pore radius = 0.44 nm), implying a more important role of size exclusion over charge repulsion for these tight membranes. Nevertheless, the role of charge repulsion for these membranes was still non-trivial, resulting in consistently high rejections of equal or higher than 90% that would be otherwise difficult to achieve for the smaller molecules on the basis of size exclusion alone.

3.3 A unified approach for assessing size exclusion and charge repulsion

Figure 4 demonstrates the feasibility of an SE baseline for resolving the role of size exclusion and charge repulsion on solute rejection by NF270. However, each membrane would require a separate SE baseline as a result of its different pore size (e.g., see Supporting Information S5). Since the effect of size exclusion is ultimately determined by the size of the solute (r_s) relative to the membrane pore size (r_p), we attempted to use a normalized molecular size ($\lambda = r_s/r_p$) to assess the importance of size exclusion. Figure 5A shows the rejection for both HAAs and surrogates by various membranes at

a solution pH of 3.5. At this pH, size exclusion would be the dominant rejection mechanism due to the absence of charge repulsion. In Figure 5A, solutes with radii bigger than the pore size ($\lambda > 1$) were nearly completely rejected ($R = \sim 100\%$). For smaller solutes ($\lambda < 1$), the rejection decreased significantly at reduced λ . In addition, all the data points can be approximately fitted by an identical trend line (the solid curve in Figure 5A) regardless of the membranes or solutes used, indicating λ as the single most important parameter affecting size exclusion. Its invariance with respect to the properties of membranes and solutes may further allow the trend line in Figure 5A to be used as a unified baseline for evaluating size exclusion.

Figure S4 in Supporting Information S6 presents the rejection of HAAs and surrogates at pH 7.5. Compared to the surrogates, HAAs had significantly enhanced rejection with respect to the SE baseline. The relatively high rejection of HAAs (equal or higher than 90%) was achieved with the presence of strong electrostatic repulsion for $\lambda > 0.7$. However, such high rejection could not be maintained at smaller λ values. Conceptually, the combined effect of electrostatic repulsion and size exclusion for HAAs may be captured by defining an effective molecular size $r_{eff} = r_s + k \cdot \lambda_d$, with the Stokes radius r_s accounting for size exclusion and the Debye length λ_d for electrostatic interaction ($\lambda_d = 1.4$ nm at an ionic strength of 50 mM (Heimburg, 2008)), where k is a dimensionless fitting coefficient. Further study may take concentration polarization into consideration to determine the ionic strength in the membrane surface to obtain a more reliable Debye length. Figure 5B plots the HAA rejections as a function of the effective molecular size. By adopting a k value of 0.045 via the least square best-fit method, the HAA rejection data can be well fitted by the same baseline (i.e., the solid curves in Figure 5A and 5B). Thus, the concept of effective molecular size may potentially allow

a unified approach to account for the effects of both size exclusion and charge repulsion. Nevertheless, further studies are required to relate the constant k to solute and membrane properties (e.g., valence of the solutes and charge density of membranes).

3.4 Implications

The current study investigated the rejection of 9 HAAs and 7 surrogates by RO and NF membranes. Molecular radius was identified as a preferred parameter over molecular weight to capture the effect of size exclusion. In existing literature, the influence of size exclusion on rejection (defined as R) is often modeled by the Ferry's equation (Eq. (4)) (Ferry, 1936) or its modified version (Werber et al., 2016) (that takes account of the additional friction hindrance between solutes and pore walls, Eq. (5)):

Ferry's model:
$$R = \begin{cases} [\lambda(2-\lambda)]^2 & \lambda \leq 1 \\ 1 & \lambda > 1 \end{cases} \quad (4)$$

Modified Ferry's model:
$$R = \begin{cases} 1 - \left\{ 1 - [\lambda(2-\lambda)]^2 \right\} \exp(-0.7146\lambda^2) & \lambda \leq 1 \\ 1 & \lambda > 1 \end{cases} \quad (5)$$

These equations have been included in Figure 5A and 5B for comparison purpose. The current study shows that both the Ferry' model and its modified version overestimate the solute rejection by RO and NF membranes, particularly for λ equal or less than 0.7. Therefore, the application of the Ferry's model for RO and NF membranes requires further verification, noting that this model is derived based on continuum fluid mechanics (Ferry, 1936). On the basis of two boundary conditions ($\lambda=0, R=0$; $\lambda=1, R=1$) and the curve fitting the rejection results (nonlinear least square best-fit method), we propose the following empirical equation with good correlation to our experimental data (correlation coefficient $R^2=0.94$, and 0.3, 36, and 4.3 were fitting coefficients):

$$R = \begin{cases} \lambda^{0.3} \exp[-36(1-\lambda)^{4.3}] & \lambda \leq 1 \\ 1 & \lambda > 1 \end{cases} \quad (6)$$

Eq. (6) is applicable to both HAAs and surrogates for the four RO/NF membranes, where differences in molecular structures and membrane separation properties are taken care by the single relative-size parameter λ . Furthermore, the effect of electrostatic interaction can also be accounted for by using $r_{eff} (= r_s + k \cdot A_d)$ for the calculation of the effective relative-size parameter $\lambda_{eff} (= r_{eff}/r_p)$. This approach provides a simple and rational way to treat the combined effects of size exclusion and electrostatic interaction. Future studies are required to validate its application to a wider variety of trace contaminants.

4. Conclusions

In this study, we investigated the removal of 9 HAAs by four commercial RO/NF membranes. To resolve the rejection mechanism, 7 neutral hydrophilic surrogates as molecular probes were used. The following conclusions can be drawn:

- (1) HAA rejections were $> 60\%$ for loose NF270 membrane and equal or higher than 90% for other tighter membranes (XLE, NF90 and SB50) under typical SPW conditions (pH 7.5 and 50 mM ionic strength).
- (2) The relative-size parameter, i.e., the ratio of molecular radius over membrane pore radius was a better SE descriptor compared to molecular weight when electrostatic interaction (e.g., pH 3.5) was negligible.
- (3) An effective molecular size of the solutes considering both charge repulsion and size exclusion could be a valid indicator of rejection.
- (4) The empirical formula derived may provide a simple and rational way for pool managers to have a primary screening of membrane selection to achieve the

targeted rejection for contaminants of interest.

These mechanisms would not be limited to the HAAs in SPWs but, rather, should be applicable to HAAs in all types of water, e.g., drinking water, wastewater, etc. The real applicability of membrane technology to practical SPW conditions requires further investigation. For example, the polyamide-based membranes are not tolerant to chlorine. One possible way is to include a chlorine removal step before membrane treatment to protect the downstream polyamide-based membranes. In addition, other matrix effects, e.g. humic acids, a variety of metal ions, etc., on the membrane performance will be studied in our future work as well.

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Appendix A. Supplementary data

Supplementary data related to this article can be found in the online version.

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700

Table 1 Haloacetic acid and surrogate properties

Name	Abbreviation	Structure	Molecular weight g/mol	pKa ^a	Diffusivity ^b 10 ⁻⁹ m ² /s	Stokes radius ^c nm
HAA						
Chloroacetic acid	CAA	Chain	94.5	2.65	1.177	0.207
Bromoacetic acid	BAA	Chain	139.0	2.73	1.158	0.211
Dichloroacetic acid	DCAA	Chain	128.9	1.37	1.032	0.237
Bromochloroacetic acid	BCAA	Chain	173.4	1.39	1.018	0.240
Dibromoacetic acid	DBAA	Chain	217.8	1.47	1.004	0.243
Trichloroacetic acid	TCAA	Chain	163.4	0.09	0.926	0.264
Tribromoacetic acid	TBAA	Chain	296.8	0.22	0.895	0.273
Dibromochloroacetic acid	DBCAA	Chain	252.3	0.13	0.905	0.270
Bromodichloroacetic acid	BDCAA	Chain	207.8	0.05	0.915	0.267
Surrogate						
Glycerol	--	Chain	92.1	14.15	1.091	0.224
Erythritol	--	Chain	122.1	13.27	0.929	0.263
Xylose	--	Circular	150.1	12.15	0.842	0.290
Glucose	--	Circular	180.2	12.28	0.755	0.323
Maltose	--	Circular	342.3	11.94	0.511	0.478
Sucrose	--	Circular	342.3	12.62	0.511	0.478
Raffinose	--	Circular	504.4	12.74	0.418	0.585

Notes:

^aData from references (Bhattacharyya et al., 2012; Kong et al., 2014).^bThe diffusivity was calculated by the Wilke-Chang equation (Eq. (2) and (3)) at 25 °C (Geankoplis, 1993).^cStokes radius was calculated by Stokes-Einstein equation (Eq. (1)) (Deen, 1987).

Table 2 Membrane properties (all data were obtained in this study unless otherwise specified)

Membrane	Type	Surface layer material	Manufacturer	Water permeability ^a	NaCl Rejection ^b	MWCO	ζ potential at pH 7.5 ^c	Pore radius ^f	RMS roughness ^h
				L/m ² h bar	%	Da	mV	nm	nm
XLE	RO	Polyamide	Dow Filmtec	7.25	91.2	96	-33	0.30	129.5±23.4
NF90	NF	Polyamide	Dow Filmtec	7.69	82.7	118,180 ^e ,200 ^d	-33	0.31, 0.34 ^g	142.8±9.6
NF270	NF	Polyamide	Dow Filmtec	16.10	30.6	266,340 ^e ,300 ^d	-36	0.44, 0.42 ^g	9.0±4.2
SB50	RO	Cellulose acetate	TriSep	2.18	75.8	152	-13	0.33	NA

Notes:

^a Water permeability was obtained by compacting the membranes for 24 h under the defined conditions (100 psi, 25 °C, pH ~6.7, MilliQ water).

^b NaCl rejection was determined after NaCl was dosed to the feed tank for 24 h under defined conditions (100 psi, 25 °C, pH ~6.7, 0.05M NaCl).

^c Data from López-Muñoz et al. (2009), using polyethylene glycols with molecular weights of 62, 200, 300, 600, and 1500 Da as the probing molecules.

^d Data from Do et al. (2012), using polyethylene glycols with molecular weights of 200, 400 and 600 Da as the probing molecules.

^e Zeta potential values at pH 7.5 were interpolated from Figure 2B.

^f Pore radius was calculated according to Nghiem et al. (2004) (see details in Supporting Information S1 and S2).

^g Data from Nghiem et al. (2004).

^h Data from Tang et al. (2009).

Figure 1 FTIR, zeta potential and MWCO of the four membranes. A: FTIR spectra of virgin membranes. B: Zeta potential of virgin membranes (in a 0.05 M NaCl background electrolyte over pH ~2-11). C: MWCOs of the membranes obtained from the surrogate rejection tests (experimental conditions: 100 psi, pH ~6.7, 25 °C, feed water containing 200 mg/L of each surrogate).

Figure 2 Effect of the molecular weight on rejection. Experimental conditions: 100 psi, pH 3.5, 25 °C, feed water containing 100 $\mu\text{g/L}$ of each HAA and 0.05 M NaCl for HAA rejection tests or 200 mg/L of each surrogate for surrogate rejection tests. Vertical dash lines represent the membrane MWCOs.

Figure 3 Effect of the molecular radius on rejection. Experimental conditions: 100 psi, pH 3.5, 25 °C, feed water containing 100 $\mu\text{g/L}$ of each HAA and 0.05 M NaCl for HAA rejection tests or 200 mg/L of each surrogate for surrogate rejection tests. Vertical dash lines represent the membrane pore radii.

Figure 4 Effect of pH on rejections of surrogates (A) and HAAs (B) for NF270 membrane. Experimental conditions: 100 psi, pH over 3.5 to 7.5, 25 °C, feed water containing 100 $\mu\text{g/L}$ of each HAA and 0.05 M NaCl for HAA rejection tests or 200 mg/L of each surrogate for surrogate rejection tests.

Figure 5 Normalized rejection evaluation. A. Normalized rejection as a function of λ at pH 3.5. B. Normalized rejection as a function of λ_{eff} at pH 7.5. Vertical dash lines represent a critical point where λ or $\lambda_{eff} = 1$. The effective relative-size parameter λ_{eff} ($= r_{eff}/r_p$) is calculated based on an effective molecular radius r_{eff} given by $r_s + 0.045 \cdot \Lambda_d$.