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# Boron as a surrogate for N-nitrosodimethylamine rejection by reverse osmosis membranes in potable water reuse applications

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**Abstract**

The results of this study reveal a strong linear correlation (R2 = 0.95) between the rejections of boron and N-nitrosodimethylamine (NDMA) by six different reverse osmosis (RO) membranes, suggesting that boron can be used as a surrogate for NDMA rejection. This proposal is based on the premise that the rejection of both boric acid and NDMA is governed by steric hindrance and that they have similar molecular dimensions. The concept proposed here is shown to be valid at pH 8 or below where boron exists as the neutral boric acid species and NDMA is also a neutral solute. Observed changes in the rejections of these two species, as a function of permeate fluxes and feed solution temperatures, were also almost identical. Boron rejection increased from 21 to 79%, and the correlation coefficient of the linear regression between boron and NDMA rejections was 0.99 as the permeate flux increased from 5 to 60 L m−2 h−1. Similarly, a linear correlation between boron and NDMA rejections was observed as the feed solution temperature increased from 10 to 40 °C. This linear correlation was also validated in a tertiary treated effluent matrix.

**Disciplines**

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# Boron as a surrogate for N-nitrosodimethylamine (NDMA) rejection by reverse osmosis membranes in potable water reuse applications

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KEYWORDS: N-nitrosodimethylamine, N-nitrosamines, boron, reverse osmosis (RO), surrogate, potable reuse.

ABSTRACT: The results of this study reveal a strong linear correlation ($R^2 = 0.95$) between the rejections of boron and N-nitrosodimethylamine (NDMA) by six different reverse osmosis (RO) membranes, suggesting that boron can be used as a surrogate for NDMA rejection. This proposal is based on the premise that the rejection of both boric acid and NDMA is governed by steric hindrance and that they have similar molecular dimensions. The concept proposed here is shown to be valid at pH 8 or below where boron exists as the neutral boric acid species and NDMA is also a neutral solute. Observed changes in the rejections of these two species, as a function of permeate fluxes and feed solution temperatures, were also almost identical. Boron rejection increased from 21 to 79% and the correlation coefficient of the linear regression between boron and NDMA rejections was 0.99 as the permeate flux increased from 5 to 60 $Lm^{-2}h^{-1}$. Similarly, a linear correlation between boron and NDMA rejections was observed as the feed solution temperature increased from 10 to 40 ºC. This linear correlation was also validated in a tertiary treated effluent matrix.

## 1 Introduction

The presence of N-nitrosodimethylamine (NDMA) in recycled water and drinking water has recently emerged as a significant concern for human health.[1] NDMA can be formed when precursor-containing wastewater effluents are disinfected with chloramines or chlorine. NDMA is known to induce tumors at multiple sites in rodents exposed by various routes and has been classified as a probable human carcinogen.[2, 3] As a result, water authorities in Australia, the United States, and several other countries have set a limit on NDMA concentration in drinking water and recycled water intended for potable water reuse of 10 $ngL^{-1}$ or below. NDMA

concentrations in secondary treated effluents are commonly above this guideline value.[1] Thus, in many potable water reuse schemes, NDMA concentration is reduced by a sequence of reverse osmosis (RO) filtration and UV/advanced oxidation processes. NDMA rejection by RO membranes can be profoundly influenced by the types of membrane used [1, 4] and operating conditions such as permeate flux and temperature.[5] This can present a major water quality compliance challenge for potable water reuse schemes and can have a significant impact on overall plant design and operation such as inclusion of UV/advanced oxidation processes in the treatment train.[4] Reliable chemical analysis at low part per trillion levels ($ngL^{-1}$) is a further significant technical challenge for the control of NDMA. In fact, despite their significance in drinking water, reliable analytical methods for N-nitrosamines are only available at a few commercial and research laboratories around the world.

Boron is ubiquitous in municipal wastewater. It is an important ingredient of soaps, detergents, and glassware products.[6] In municipal wastewater, boron commonly occurs at concentrations in the range of 0.3 – 4 $mgL^{-1}$.[7] In some water reuse applications, boron removal may also be required, particularly if the reclaimed water is used for irrigation because boron can be toxic to a range of plant species at concentrations as low as 0.5 $mgL^{-1}$.[8] In the aqueous phase, at pH values below the $pK_a$ of 9.2 (which is typical for secondary treated effluent), boron exists predominantly as neutral boric acid. Being a low-molecular-weight and neutral species, boric acid rejection by RO membranes is also strongly dependent on operating conditions.[8, 9] Similar to NDMA, boron rejection by RO membranes has been a subject of significant interest in separation science and technology.[8-11] However, unlike NDMA, boron concentration in an aqueous solution can be readily measured using a range of conventional analytical techniques including ion chromatography [12, 13] or online probes.[14] In addition, boron rejection can also be modelled and simulated using currently available commercial software packages (e.g. ROSA, TorayDS/DS2,

and IMSDesign provided by Dow FilmTec, Toray, and Hydranautics, respectively). By contrast, no commercial software packages are currently available for modelling NDMA rejection by RO membranes.

Given the co-occurrence of both NDMA and boron in wastewater effluents, the aim of this study was to demonstrate the prospect of using boron as a viable surrogate for NDMA rejection by RO membranes. Boron rejections by six different RO membranes were correlated to those of NDMA under similar operating conditions. The impact of permeate flux and temperature on the rejection of both boron and NDMA was also evaluated.

## 2 Materials and Methods

### *2.1 Chemicals and reagents*

Stock solution of 10 $mgL^{-1}$ of NDMA (Sigma–Aldrich, St Louis, MO, USA) was prepared in pure methanol, in the dark at -18 ºC, and was used within one month. $B(OH)_3$, NaCl, $CaCl_2$, $NaHCO_3$, NaOH, and HCl (Ajax Finechem, Taren Point, NSW, Australia) were used for preparing the feed solution. Suprapur $HNO_3$ (Merck Co., Darmstad, Germany) was used for sample dilution prior to inductively-coupled plasma mass spectrometry (ICP-MS) analysis. Milli-Q water (Millipore, Billerica, MA, USA) was used for the preparation of stock and feed solutions. All chemicals used are analytical grade. Tertiary treated effluent was collected from a water reclamation plant in New South Wales, Australia which was comprised of primary screening followed by an activated sludge treatment process and microfiltration. The tertiary treated effluent sample was collected after microfiltration. The effluent had a boron concentration of 0.1 $mgL^{-1}$, conductivity of 720 μS/cm and a pH of 7.1. The detailed characteristics of this tertiary treated effluent have been reported elsewhere. [15]

## 2.2 Membranes

Six RO membranes were used in this study, including BW30 (Dow FilmTec, Minneapolis, MN, USA), ESPA1, ESPA2, ESPAB, SWC5 (Hydranautics, Oceanside, CA, USA), and TFC-HR (Koch Membrane Systems, San Diego, CA, USA) membranes. The SWC5 is a high-pressure seawater RO membrane and the others are low-pressure RO membranes commonly used for water reuse applications. These are thin-film composite membranes consisting of an ultra-thin polyamide (or polyamide derivative) skin layer on top of a micro-porous support layer. Key properties of these membranes are summarised in Table 1.

**Table 1.** Water permeability and salt rejection of the selected RO membranes. (The SWC5 is a high-pressure seawater RO membrane and the others are low-pressure RO membranes commonly used for brackish water or wastewater reclamation applications.)

| Membrane | Water permeability [a] [$Lm^{-2}h^{-1}bar^{-1}$] | TDS rejection [b] [%] | Na rejection [b] [%] |
|---|---|---|---|
| SWC5 | 2.63 | 99.2 | 99.3 |
| TFC-HR | 3.12 | 98.8 | 99.2 |
| BW30 | 3.88 | 92.8 | 93.3 |
| ESPAB | 4.55 | 98.4 | 98.5 |
| ESPA2 | 6.15 | 95.8 | 96.1 |
| ESPA1 | 7.80 | 95.5 | 95.8 |

[a] Measured with milli-Q water at 1,000 kPa and 20 ºC.

[b] Measured at 20 $Lm^{-2}h^{-1}$ permeate flux, 20 $mmolL^{-1}$ NaCl and pH 8.

## 2.3 NF/RO filtration system and experimental protocol

Prior to each experiment, the membrane sample was rinsed with Milli-Q water to remove any preservative chemicals. Membrane compaction was then conducted using Milli-Q water at 1,800

kPa for at least 1 h until a stable permeate flux had been achieved. Following the membrane compaction, the pressure was reduced to 1,000 kPa for the pure water permeability measurement. The Milli-Q water was then replaced by a 10 L standard feed solution containing 250 $ngL^{-1}$ NDMA, 5.75 $mgL^{-1}$ $B(OH)_3$ (1 $mgL^{-1}$ B), 20 $mmolL^{-1}$ NaCl, 1 $mmolL^{-1}$ $CaCl_2$, and 1 $mmolL^{-1}$ $NaHCO_3$. The NDMA and boron concentrations were chosen to represent concentrations previously observed in secondary treated effluent. The pH of the feed solution was adjusted and kept constant at pH 8 by adding a small volume of either 1 $molL^{-1}$ NaOH or 1 $molL^{-1}$ HCl solution. When tertiary treated effluent was used as the feed, an appropriate volume of NDMA stock solution was used to obtain of concentration of 250 $ngL^{-1}$ NDMA in the feed; no further chemical addition or pH adjustment were required. The operational parameters were set at 20 $Lm^{-2}h^{-1}$ permeate flux, 20 ºC temperature, and 42 $cms^{-1}$ cross-flow velocity unless otherwise stated. These parameters are similar to those commonly used in full-scale RO installations for wastewater reclamation.[4] Permeate and retentate were circulated back to the feed reservoir to maintain the same feed solution composition throughout the experiment. Experiments with variable permeate flux were conducted by first adjusting the permeate flux to 60 $Lm^{-2}h^{-1}$ followed by a stepwise reduction in 5 $Lm^{-2}h^{-1}$ increments. For experiments with variable temperature, the feed temperature was incrementally increased from 10 to 40 ºC. The permeate flux and feed solution temperature were selected for further examination since these two parameters are known to have strong effects on the rejection of boric acid and NDMA.[4, 8] In all experiments, once the target operational parameters were achieved, the filtration system was operated at steady state for 1 h prior to the collection of feed and permeate samples for analysis. At each sampling event, 200 mL of feed and permeate samples were collected simultaneously. Isotope standard (50 ng) of NDMA was added to the samples and solid phase extraction (SPE) was conducted immediately.

### *2.4 Analytical method*

The concentration of NDMA was determined using an Agilent 7890A gas chromatograph (GC) coupled with an Agilent 7000B triple quadrupole mass spectrometer (MS/MS) (Agilent Technologies, Wilmington, DE, USA). The obtained limit of quantification of NDMA by this analytical method is 0.45 $ngL^{-1}$ in ultrapure water.[16] Details of the SPE procedure and validation of the methods in different matrix solutions are available elsewhere.[16] The concentrations of boron and sodium were analysed using an Agilent 7500cs ICP-MS. A Merck ICP multi-element standard solution was used for calibration. Detection limits for $^{11}B$ and $^{23}Na$ (expressed as total B and Na) were approximately 50 $ngL^{-1}$ and 140 $ngL^{-1}$, respectively. The details of this analytical method have been described in a previous publication.[17] Conductivity and pH were measured using an Orion 4-Star Plus pH/conductivity meter (Thermo Scientific, Beverly, MA).

## 3 Results and discussion

### 3.1 *Correlation between boron and NDMA rejection by RO membranes*

The RO membranes used in this study were systematically selected to span a wide range of permeability (Table 1). As a result, the rejection values of boron also covered a large range from approximately 10% (by the ESPA1 membrane which has the highest water permeability) to as high as 80% (by SWC5 which is a seawater RO membrane). The range of NDMA rejection by these membranes was similar to that of boron, ranging from 22 – 74%. The linear correlation ($R^2$ = 0.95) between the rejection values of boron and NDMA shown in Figure 1 has an F-value of 104 corresponding to a p-value of 0.000517. In addition, the slope of the linear regression is 0.82 indicating that the absolute values of boric acid rejection and NDMA rejection by a specific membrane are comparable to each other, especially by the higher-rejection membranes such as ESPAB and SWC5.

The strong correlation between boron and NDMA rejections by RO membranes observed here can be attributed to the similarity in their molecular dimensions, charge, and rejection mechanism. Possessing a $pK_a$ value of 9.2 (Table 2), boric acid can speciate and transform from its neutral boric acid form to the negatively charged borate species as a function of pH (Figure 2). As a result, in aqueous solution, boron exists predominantly (> 90%) in the neutral boric acid form at or below pH 8 (Figure 2). On the other hand, NDMA only exists as an uncharged species in the normal wastewater pH range due to its negative $pK_b$ value (Table 2). As a result, at or below pH 8, both boron and NDMA exist in their uncharged forms and steric hindrance is the only mechanism governing their rejection by RO membranes.[5, 18, 19] With the steric hindrance rejection mechanism, rejection is governed by the size of the solute. Boric acid and NDMA have comparable molecular dimensions (Table 2) and thus their rejection values as well as behaviour are comparable. In addition, boric acid and NDMA are both hydrophilic (Table 2) and thus are not expected to adsorb to the membrane polymeric matrix. It is noteworthy that NDMA has a significantly higher dipole moment than that of boric acid (Table 2). The dipole moment can influence the orientation of cylindrical molecules as they approach the membrane surface. [20] NDMA and boric acid have comparable molecular length and height (Table 2) and since the relative rejection for both solutes was similar the influence of dipole moment on their rejection appears to be insignificant.

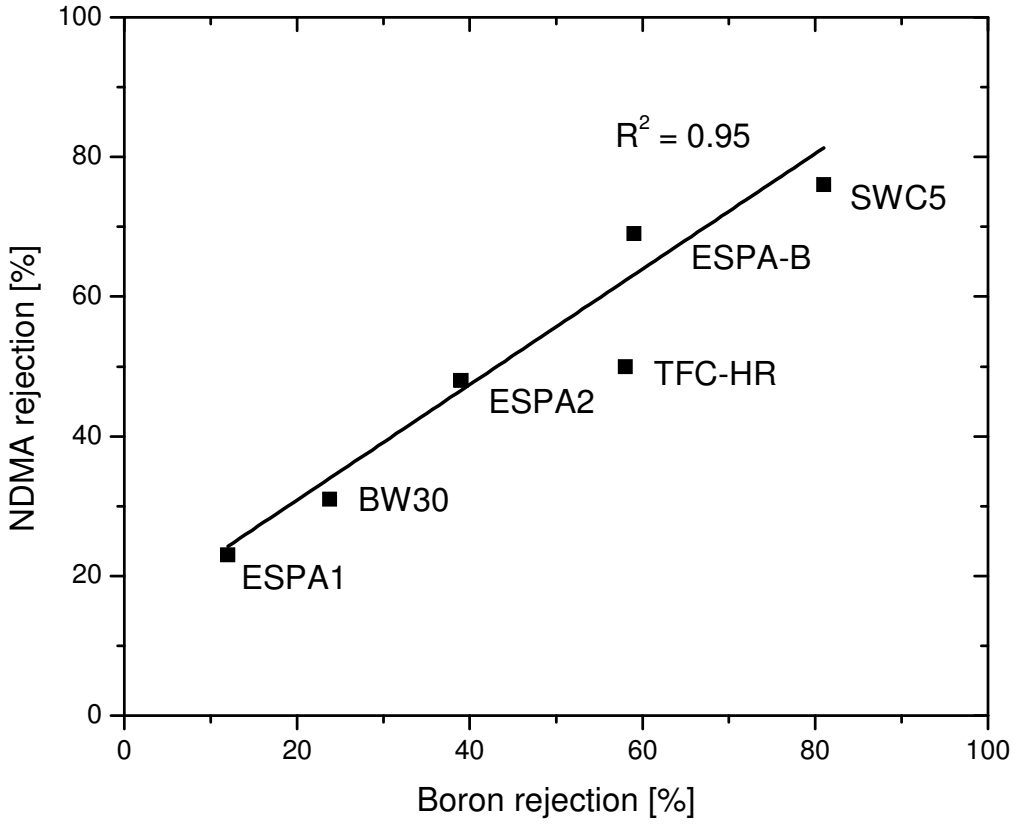
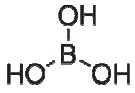
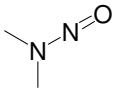



**Figure 1.** The correlation between the rejections of boron and NDMA by different membranes at pH 8. Feed water contains 250 $ngL^{-1}$ NDMA, 5.75 $mgL^{-1}$ $B(OH)_3$, 20 $mmolL^{-1}$ NaCl, 1 $mmolL^{-1}$ $NaHCO_3$, and 1 $mmolL^{-1}$ $CaCl_2$; temperature 20 ºC, permeate flux 20 $Lm^{-2}h^{-1}$, cross-flow velocity 42 $cms^{-1}$.

**Table 2.** Properties of boric acid and NDMA.

| | Boric acid | NDMA |
|---|---|---|
| Molecular weight [$gmol^{-1}$] | 61.83 | 74.05 |
| Molecular dimensions [Å] [a] | | |
| Length | 4.52 | 4.10 |
| Height | 3.08 | 3.46 |
| Width | 0.85 | 1.73 |

| Molecular structure |  |  |
|---|---|---|
| $pK_a/pK_b$ [b] | 9.2 | -3.63 |
| $LogK_{ow}$ [b] | -0.64 | -0.50 |
| Dipole moment [D] [c] | 1.11 | 3.71 |

[a] Calculated using the ChemBio3D Ultra software.

[b] From SciFinder Scholar (obtained from the *Advanced Chemistry Development Software)*.

[c] Calculated using the Millsian 2.1 software.

The correlation between boron and NDMA rejections reported in Figure 1 creates a perspective for monitoring and predicting the fate and transport of NDMA during RO membrane filtration using boron rejection as a surrogate. Boron rejection could serve as a reference for selecting membranes for NDMA removal purposes. However, the correlation shown in Figure 1 was obtained under a specific filtration operating condition. By contrast, the operating condition in full-scale RO installations may vary quite significantly. Thus, it is necessary to establish a range where the above correlation is valid.

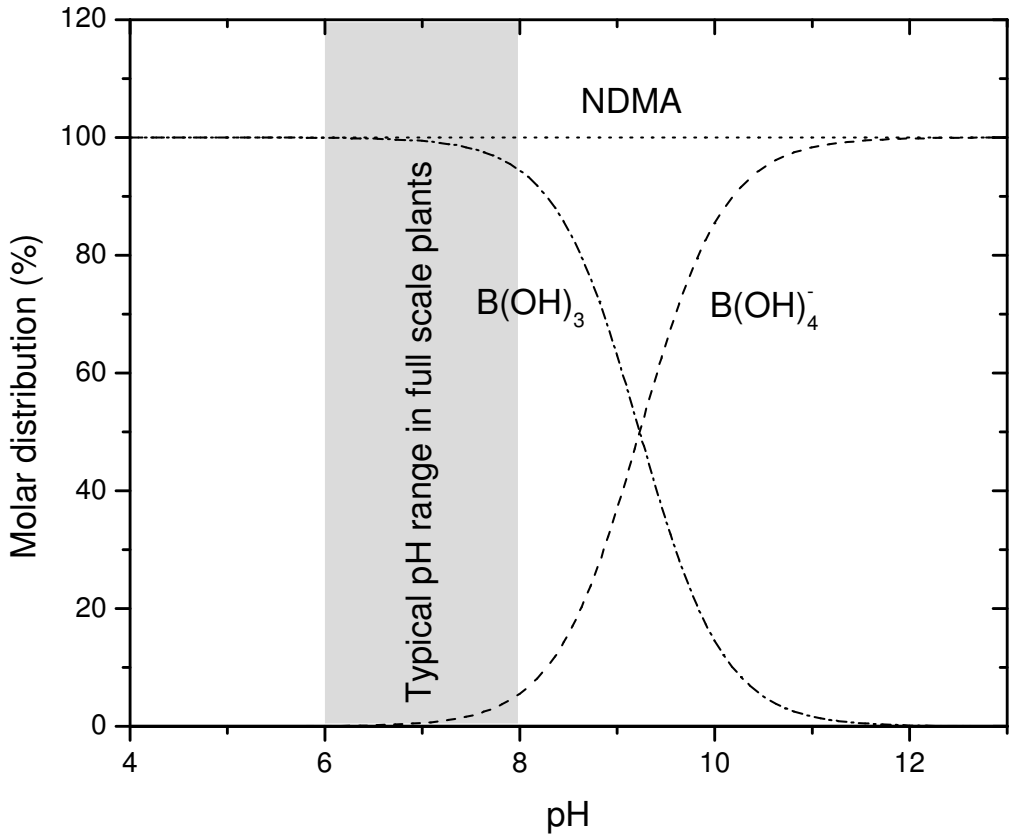



**Figure 2.** The speciation of boric acid and NDMA in de-ionised water matrix, temperature 25 ºC, pressure 1 atm.

## *3.2 Effects of operating conditions on boron and NDMA rejection*

In a full-scale RO installation, in addition to the solution pH, temporal variation in other operating parameters including solute concentration, ionic strength, permeate flux and temperature can be expected. Some of these parameters do not affect solute rejection while others can exert a significant impact on the separation efficiency of RO membranes. It has been consistently reported that the rejections of boron and NDMA by RO membranes are independent of their concentrations in the feed water.[4, 8] Thus, the concentration is not expected to affect the correlation between NDMA and boron rejection. Similarly, it has also been revealed that the impact of ionic strength variation on the rejection of neutral solutes is not significant.[21, 22] NDMA

rejection by RO membranes was reported to decrease by only 17% as the feed ionic strength increased from 26 to 260 $mmolL^{-1}$.[5] Steinle-Darling et al.[23] reported a 15% decrease in NDMA rejection by the ESPA3 membrane when the NaCl concentration increased from 0 to 100 $mmolL^{-1}$. Similarly, the impact of ionic strength (within the range encountered during water reuse) on boron rejection was not significant. Tu et al.[17] reported a slight increase in boron rejection when the feed water ionic strength was raised from 16 to 43 $mmolL^{-1}$, and there exists a coupling effect between the water ionic strength and pH on boron rejection. Given the small impact of feed concentration and ionic strength on the rejection of boron and NDMA reported in the literature, the influence of these two parameters on the correlation between boron and NDMA rejections was not examined here. Instead, we have sought to demonstrate the correlation between boron and NDMA rejections under a range of permeate fluxes and feed solution temperatures since these parameters are known to exert a significant impact on the rejection of boron and NDMA.

An increase in the permeate flux led to a substantial increase in the rejection of both boron and NDMA (Figure 3a). This result is consistent with the literature [5, 24] and can be systematically described by the irreversible thermodynamic model [5] wherein solute rejection approaches the intrinsic membrane reflection coefficient ($\sigma$) as the permeate flux increases. As a result, an increase in permeate flux will result in an increase in solute rejection. At pH 8, a linear correlation ($R^2 = 0.99$) between the rejections of boron and NDMA at various permeate flux was observed (Figure 3b). However, it is noteworthy that the boron rejection can significantly increase when boron exists as the negatively charged borate ion at pH values above 8. At pH 6 and 8, NDMA and boron rejections were comparable, whereas at pH 10.5, boron rejection was substantially higher (Figure 3a). This result implies that boron can only be used as a surrogate for

NDMA rejection at pH values equal or below 8.

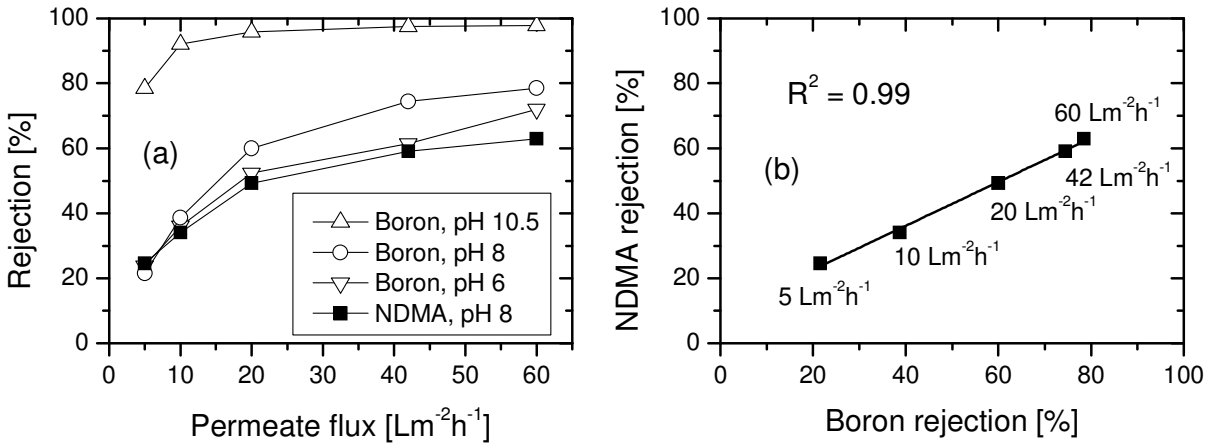



**Figure 3.** (a) The rejection of boron and NDMA as functions of permeate flux at different pH values; and (b) the correlation between boron and NDMA rejections at various permeate fluxes at pH 8. The TFC-HR membrane was used; feed water contains 250 $ngL^{-1}$ NDMA, 5.75 $mgL^{-1}$ $B(OH)_3$, 20 $mmolL^{-1}$ NaCl, 1 $mmolL^{-1}$ $NaHCO_3$, and 1 $mmolL^{-1}$ $CaCl_2$; temperature 20 ºC, cross-flow velocity 42 $cms^{-1}$.

The rejections of boron and NDMA decreased linearly as a function of feed solution temperature (Figure 4a). Similar results have also been reported elsewhere[5, 25] and were attributed to the swelling of the membrane structure [26, 27] as well as the increase in the solute diffusivities.[28] Boron rejection at pH 6 and 8 and NDMA rejection at pH 8 appeared to be comparable at various feed water temperatures (Figure 4a). Indeed, a linear correlation ($R^2$ = 0.98) between boron rejection and NDMA rejection at various feed water temperatures can be observed at pH 8 (Figure 4b). However, once again, at pH 10.5, boron rejection as a function of feed water temperature exhibited a very different behaviour (Figure 4a). These results reaffirmed that boron can only be used as a surrogate for NDMA rejection at pH 8 or below when both boron and NDMA exist as neutral species.

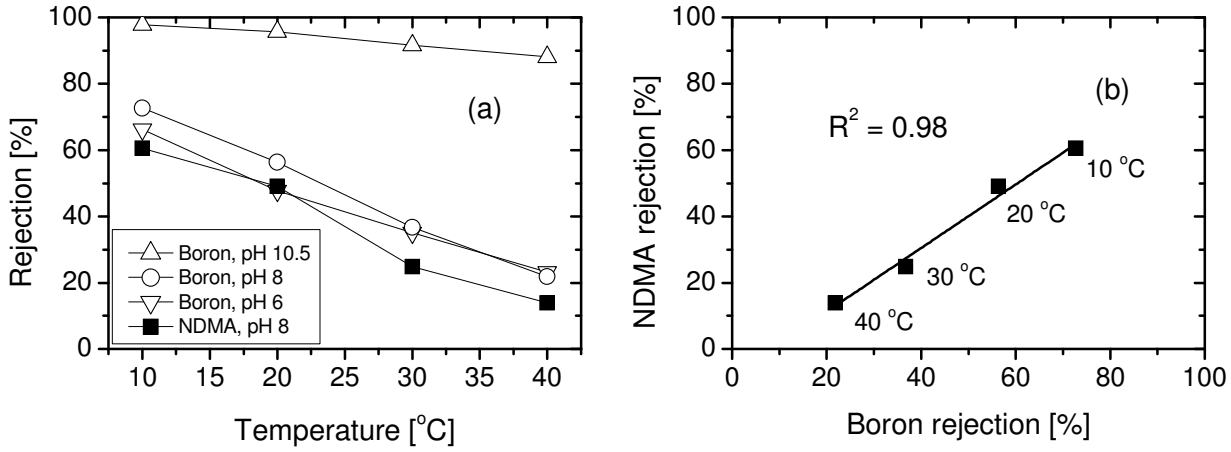



**Figure 4.** (a) The rejection of boron and NDMA as functions of temperature at different pH values; and (b) the correlation between boron and NDMA rejections at various temperatures at pH 8. The TFC-HR membrane was used; feed water contains 250 $ngL^{-1}$ NDMA, 5.75 $mgL^{-1}$ $B(OH)_3$, 20 $mmolL^{-1}$ NaCl, 1 $mmolL^{-1}$ $NaHCO_3$, and 1 $mmolL^{-1}$ $CaCl_2$; permeate flux 20 $Lm^{-2}h^{-1}$, cross-flow velocity 42 $cms^{-1}$.

The correlation between boron and NDMA rejections at different temperatures was also validated using a tertiary treated effluent matrix. The tertiary treated effluent had a pH value of 7.1 and thus both boron and NDMA exist in their neutral forms. As expected, a linear correlation between boron and NDMA rejections was observed with a correlation coefficient ($R^2$) of 0.94 as the feed solution temperature increased from 10 to 40 ºC (Figure 5a). However, it is noteworthy that the rejections of both boron and NDMA differ slightly from values reported in Figure 4. This variation can be attributed to the compositional difference between the tertiary treated effluent and the synthetic feed water solution used in this study.[29]

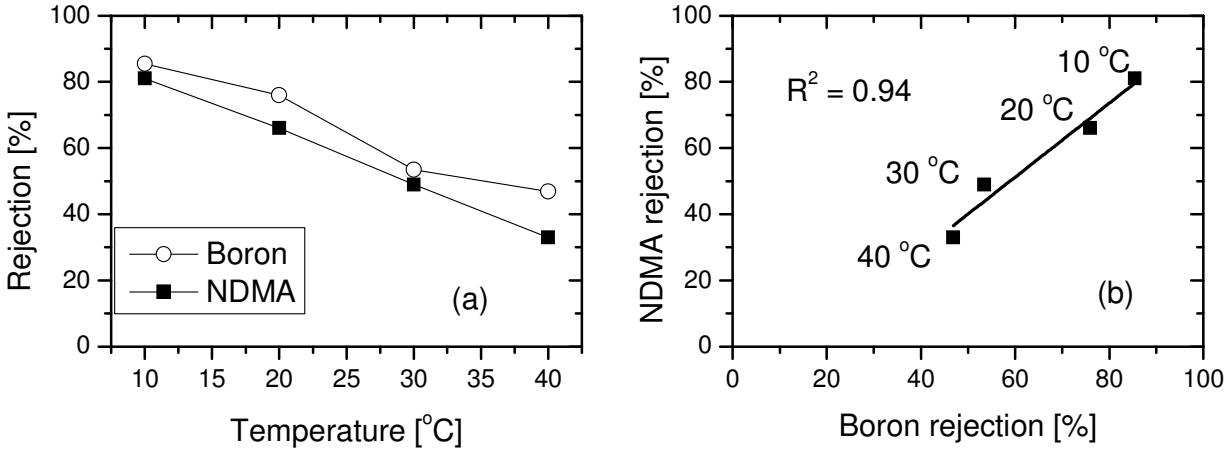



**Figure 5.** (a) The rejection of boron and NDMA as functions of temperature; and (b) the correlation between boron and NDMA rejections at various temperatures. The TFC-HR membrane was used. Tertiary treated effluent dosed with 250 $ngL^{-1}$ NDMA was used as feed solution. Permeate flux 20 $Lm^{-2}h^{-1}$, cross-flow velocity 42 $cms^{-1}$.

The strong correlation between boron and NDMA rejections reported in this study is valid at pH 8 or lower where boron exists in the form of boric acid (Figure 2). It is noteworthy that in full-scale RO plants for water reclamation applications, the feed water pH is usually in the range of pH 6 – 7.5 to minimize the precipitation of partially-soluble salts.[4] Thus, our proposal to use boron as a surrogate for NDMA rejection can be applied in the typical context of water reclamation. Given the recent availability of online boron monitoring techniques (e.g. online ion chromatography and boron-specific probe), boron can be a viable surrogate for NDMA rejection. Thus, the rejection of NDMA by RO membranes can be predicted without the burden of NDMA analysis. Nevertheless, this approach does not eliminate the need for compliance monitoring of NDMA in the RO permeate. Furthermore, caution is necessary when using boron as a surrogate for NDMA rejection. For example, the established correlation may be influenced by the interactions between boric acid with other constituents present in the water matrix. A notable example is the complexation between boric acid and poly-alcohols which can substantially

increase boric acid rejection by RO membranes.[30-32] Further studies are necessary to assess the validity of this concept in pilot- and full-scale operations and under the influence of parameters that have not been investigated in this study, such as the interaction of boric acid with traces of poly-alcohols in the feed solution.

## AUTHOR INFORMATION

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## REFERENCES

[1] Sedlak, D.L., Deeb, R.A., Hawley, E.L., Mitch, W.A., Durbin, T.D., Mowbray, S., and Carr, S. Sources and fate of nitrosodimethylamine and its precursors in municipal wastewater treatment plants. *Water Environment Research*. **2005**, 77, 32-39.

[2] US-EPA. *N-Nitrosodimethylamine (CASRN 62-75-9)*. 2008 25/09/2008]; Available from: http://www.epa.gov/ncea/iris/subst/0045.htm.

[3] WHO, *N-Nitrosodimethylamine in drinking-water*, 2006, World Health Organization: Geneva. p. 36.

[4] Fujioka, T., Khan, S.J., Poussade, Y., Drewes, J.E., and Nghiem, L.D. 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*. **2012**, 98, 503-515.

[5] Fujioka, T., Nghiem, L.D., Khan, S.J., McDonald, J.A., Poussade, Y., and Drewes, J.E. Effects of feed solution characteristics on the rejection of N-nitrosamines by reverse osmosis membranes. *Journal of Membrane Science*. **2012**, 409-410, 66-74.

[6] Argust, P. Distribution of boron in the environment. *Biological Trace Element Research*. **1998**, 66, 131-143.

[7] Butterwick, L., Oude, N.d., and Raymond, K. Safety assessment of boron in aquatic and terrestrial environments. *Ecotoxicology and Environmental Safety*. **1989**, 17, 339-371.

[8] Tu, K.L., Nghiem, L.D., and Chivas, A.R. Boron removal by reverse osmosis membranes in seawater desalination applications. *Separation and Purification Technology*. **2010**, 75, 87-101.

[9] Hilal, N., Kim, G.J., and Somerfield, C. Boron removal from saline water: A comprehensive review. *Desalination*. **2011**, 273, 23-35.

[10] Bick, A. and Oron, G. Boron removal from seawater reverse osmosis permeate: A Hasse diagram analysis of current technologies. *Desalination*. **2013**, 310, 34-38.

[11] Kabay, N., Güler, E., and Bryjak, M. Boron in seawater and methods for its separation - A review. *Desalination*. **2010**, 261, 212-217.

[12] Farhat, A., Ahmad, F., and Arafat, H. Analytical techniques for boron quantification supporting desalination processes: A review. *Desalination*. **2013**, 310, 9-17.

[13] Nir, O. and Lahav, O. Coupling mass transport and chemical equilibrium models for improving the prediction of SWRO permeate boron concentrations. *Desalination*. **2013**, 310, 87-92.

[14] *Sievers UPW boron analyzer, Fact Sheet*, in *Water & Process Technologies - Analytical Instruments* 2008, GE Analytical Instrument: Boulder, CO.

[15] Fujioka, T., Khan, S.J., McDonald, J.A., Henderson, R.K., Poussade, Y., Drewes, J.E., and Nghiem, L.D. Effects of membrane fouling on N-nitrosamine rejection by nanofiltration and reverse osmosis membranes. *Journal of Membrane Science*. **2013**, 427, 311-319.

[16] McDonald, J.A., Harden, N.B., Nghiem, L.D., and Khan, S.J. Analysis of N-nitrosamines in water by isotope dilution gas chromatography–electron ionisation tandem mass spectrometry. *Talanta*. **2012**, 99, 146-154.

[17] Tu, K.L., Nghiem, L.D., and Chivas, A.R. Coupling effects of feed solution pH and ionic strength on the rejection of boron by NF/RO membranes. *Chemical Engineering Journal*. **2011**, 168, 700-706.

[18] Oo, M.H. and Song, L. Effect of pH and ionic strength on boron removal by RO membranes. *Desalination*. **2009**, 246, 605-612.

[19] Bellona, C., Drewes, J.E., Xu, P., and Amy, G. Factors affecting the rejection of organic solutes during NF/RO treatment - A literature review. *Water Research*. **2004**, 38, 2795-2809.

[20] Van Der Bruggen, B., Schaep, J., Wilms, D., and Vandecasteele, C. Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration. *Journal of Membrane Science*. **1999**, 156, 29-41.

[21] Bartels, C., Franks, R., Rybar, S., Schierach, M., and Wilf, M. The effect of feed ionic strength on salt passage through reverse osmosis membranes. *Desalination*. **2005**, 184, 185-195.

[22] Childress, A.E. and Elimelech, M. Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. *Journal of Membrane Science*. **1996**, 119, 253-268.

[23] Steinle-Darling, E., Zedda, M., Plumlee, M.H., Ridgway, H.F., and Reinhard, M. Evaluating the impacts of membrane type, coating, fouling, chemical properties and water chemistry on reverse osmosis rejection of seven nitrosoalklyamines, including NDMA. *Water Research*. **2007**, 41, 3959-3967.

[24] Miyashita, Y., Park, S.-H., Hyung, H., Huang, C.-H., and Kim, J.-H. Removal of N-Nitrosamines and their precursors by nanofiltration and reverse osmosis membranes. *Journal of Environmental Engineering*. **2009**, 135, 788-795.

[25] Hung, P.V.X., Cho, S.-H., and Moon, S.-H. Prediction of boron transport through seawater reverse osmosis membranes using solution-diffusion model. *Desalination*. **2009**, 247, 33-44.

[26] Ben Amar, N., Saidani, H., Palmeri, J., and Deratani, A. Effect of temperature on the rejection of neutral and charged solutes by Desal 5 DK nanofiltration membrane. *Desalination*. **2009**, 246, 294-303.

[27] Sharma, R.R., Agrawal, R., and Chellam, S. Temperature effects on sieving characteristics of thin-film composite nanofiltration membranes: pore size distributions and transport parameters. *Journal of Membrane Science*. **2003**, 223, 69-87.

[28] Hyung, H. and Kim, J.-H. A mechanistic study on boron rejection by sea water reverse osmosis membranes. *Journal of Membrane Science*. **2006**, 286, 269-278.

[29] Hoek, E.M.V. and Elimelech, M. Cake-enhanced concentration polarization: A new fouling mechanism for salt-rejecting membranes. *Environmental Science and Technology*. **2003**, 37, 5581-5588.

[30] Tu, K.L., Chivas, A.R., and Nghiem, L.D. Enhanced boron rejection by NF/RO membranes by complexation with polyols: Measurement and mechanisms. *Desalination*. **2013**, 310, 115–121.

[31] Dydo, P., Nem , I., and Turek, M. Boron removal and its concentration by reverse osmosis in the presence of polyol compounds. *Separation and Purification Technology*. **2012**, 89, 171-180.

[32] Geffen, N., Semiat, R., Eisen, M.S., Balazs, Y., Katz, I., and Dosoretz, C.G. Boron removal from water by complexation to polyol compounds. *Journal of Membrane Science*. **2006**, 286, 45-51.