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Graphical abstract

Defect-free highly selective polyamide thin-film composite membranes for desalination and boron removal

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Abstract

Removal of boron from saline water sources has presented a major challenge for commercially available reverse osmosis desalination membranes. In this work, we report the boron and sodium chloride separation properties of truly *defect-free*, highly selective, interfacially polymerized aromatic polyamide thin-film composite membranes. The fabricated membranes show potential for separating sodium chloride with a maximum rejection of 99.6% obtained for the optimized film-forming protocol under lab-scale brackish water desalination conditions. This translated into promising boron rejection performance with rejections of up to 99% at pH 10, higher than a number of commercially available reverse osmosis membranes tested in-house. Comprehensive characterization including X-ray photoelectron spectroscopy, atomic force microscopy, scanning electron microscopy, ellipsometry, and surface charge measurements revealed intimate insights on interfacially polymerized polyamide membrane structure-property relationships. Increased membrane crosslinking was shown to be the primary determining factor for membrane permselectivity performance. Furthermore, relationships were established between microstructural properties such as crosslinking and morphological characteristics like surface roughness, highlighting an intricate and complex structure formation mechanism.

1. Introduction

Over one billion people worldwide have extremely limited availability of safe drinking and irrigation water and by 2030 the demand is predicted to further increase by 50% [1,2]. This requires the development of more energy-efficient desalination processes. Over the past decades, reverse osmosis (RO) has established itself as a low-cost, high-efficiency method for water desalination. Currently, over 60% of the total world desalination capacity is provided by RO-based desalination plants [3]. The success of the process can be accredited to development of Filmtec's revolutionary aromatic polyamide thin-film composite (TFC) reverse osmosis (RO) FT-30 membranes made by interfacial polymerization of *m*-phenylene diamine (MPD) and trimesoyl chloride (TMC), which exhibit high water flux and salt rejection [4]. Such membranes are fabricated using interfacial polymerization (IP), an easily scalable fabrication process [5]. Despite their tremendous success for desalination with >99% salt rejection, FT-30-type membranes tend to have lower rejection towards small uncharged solutes such as alcohols, ketones, esters and boric acid.

Boron originated from either natural and/or anthropogenic sources is widely present in surface water, groundwater, and oceans with a wide range of concentrations. However, the majority of boron is found in seawater with an average concentration of about 4.5 mg/L [6]. The World Health Organization (WHO) recommends boron concentration of 2.4 mg/L for drinking water while for irrigation purposes concentrations of < 1 mg/L are advised for agricultural crops including wheat, carrots and potatoes among others [7,8]. In plants, high boron concentration can reduce root division, root growth and inhibit photosynthesis [9] whereas in humans and animals, it is correlated with diseases in the alimentary, cardiac and nervous systems [10]. Therefore, it is essential to regulate boron concentration but boron species can diffuse through RO membranes due to their small size and their uncharged nature in the form of boric acid in seawater with pH around 8 [11,12]. Boron rejection of several commercially available FT-30-type RO membranes is shown in **Table 1**. Because of the relatively low boron rejection of FT-30 type membranes, a two-stage RO process is

typically employed in desalination plants to decrease boron concentration to acceptable limits. This adds both capital and operating costs to the desalination process [13,14].

Table 1. Boron rejection for commercially available FT-30-type membranes.

Year	Membrane type	pH	Temperature (°C)	Experimental conditions	Boron rejection (%)	Ref.
2000	Hydranautics 4040-LHACPA2	6.5	-	15.5 bar, 5 ppm boron, no NaCl ^a	40	[15]
2001	Toray SUL-C10	9.5	-	15.5 bar, 4 ppm boron, no NaCl ^a	60	[16]
2001	Toray UTC-80-LB	-	25-30	55 bar, 4 ppm boron, 35,000 ppm NaCl ^b	75-90	[17]
2008	DOW SW-30-HR	8.2	23	48 bar, 5.1 ppm boron, 38,000 ppm NaCl ^a	88	[18]
2008	GE Osmonics AG	11	34	20 bar, 40 ppm boron, no NaCl ^b	95	[19]
2011	Toray TM-820A-400	8	25	55 bar 5 ppm boron, 40,200 ppm NaCl ^c	93	[20]
2018	Hydranautics SWC5 max	7	-	55 bar, 5 ppm boron, 32,000 ppm NaCl ^b	59	[21]
2018	Hydranautics SWC4B	7	-	55 bar, 5 ppm boron, 32,000 ppm NaCl ^b	68	[21]
2019	Toray TM820S-400	8	25	55 bar, 5 ppm boron, 32000 ppm NaCl ^a	60-85	[22]
2019	Toray TM820L-440	8	25	55 bar, 5 ppm boron, 32000 ppm NaCl ^a	85-90	[22]

Note: ^a Pilot/plant scale study; ^b lab study; ^c manufacturer data.

Most research aimed at increasing boron rejection of membranes has investigated the effects of desalination process operating conditions such as pH, temperature, salinity and pressure [23,24]. For example, a recent study by Nir et al. demonstrated the effectiveness of pH adjustment to enable efficient boron removal in a single-stage pass using ultra-low energy, high-flux RO membranes [25–27]. Other efforts include: (1) process flow optimization approaches [13,28]; (2) modification of commercially available membranes as well as using novel materials [12,29,30] to reduce either boron affinity or pore

size of the membranes [21]. Recently, Shultz et al. used hydrophobic aliphatic amines as a “caulking” agent to tighten the pore structure and simultaneously altered membrane surface chemistry, both favorable for enhanced boron rejection. Successful scale-up of such approach was later demonstrated in a spiral-wound seawater RO pilot study with increased boron rejection, a moderate decrease in water permeability, and essentially no change in salt rejection due to the effective sealing of large defects in the membranes using “hydrophobic molecular plugs” [21,31].

It is well established that FT-30-type RO membranes contain micro- and mesoporous defects in the dry state, clearly indicated by Knudsen selectivity for small gas molecules [32,33]. In the dry state, these defects have a significant impact on the gas separation capabilities of such membranes. Recently, our group fabricated *defect-free*, ultra-selective FT-30-type RO membranes with excellent gas separation performance especially for hydrogen separation from mixtures containing CO₂ [34]. Our study showed that “in-situ” plugging of defects in FT-30-type RO membranes, by increasing reaction time and reaction temperature, changed penetrant transport mode from Knudsen diffusion to solution-diffusion as illustrated in **Figure 1**. Even further performance enhancement was achieved by increasing the degree of membrane crosslinking by varying organic solution temperature and organic monomer concentration. The gas separation properties showed a significant performance boost, *e.g.*, H₂/N₂ pure-gas selectivity was increased from ~4 for traditional FT-30-type fabrication conditions to ~600 with our optimized fabrication procedure. If gas separation properties are any indicator for separation performance in the liquid state, the membranes should also demonstrate improvement in permselectivity performance over currently available RO membranes.

Figure 1. Proposed *in-situ* pore plugging process during interfacial polymerization of thin-film composite membranes.

In this work, the performance of *defect-free*, highly selective MPD-TMC polyamide thin-film composite membranes are reported for boron and NaCl RO separation under brackish water operating conditions. Boron rejection was measured at three different pH values and compared to a number of commercially available sea- and brackish water type RO membranes in both dead-end and crossflow modes. The membranes were characterized using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), ellipsometry, atomic force microscopy (AFM) and surface charge measurements. The defect-free membranes show potential for improving boron and sodium chloride rejection of traditional TFC membranes through *in-situ* plugging and/or self-healing using modified interfacial polymerization conditions. Various characterization techniques combined with boron and NaCl

separation performance of the modified membranes reveal structure-transport property relationships for FT-30-type RO membranes.

2. Experimental

2.1. Materials

Trimesoyl chloride (TMC), 98% pure, and *m*-phenylene diamine (MPD), 99% pure, were obtained from Aldrich. The TFC membranes were prepared on polysulfone (PS) ultrafiltration supports provided by Sepro Membranes Inc. (Carlsbad, CA, USA). Isoparaffin G (Isopar®) was acquired from ExxonMobil. Distilled water was obtained from a Millipore Advantage A10 system. Boric acid and sodium bicarbonate (Na_2CO_3) were purchased from Sigma. Isopropanol (IPA), 99.5+% ACS reagent, was acquired from Sigma Aldrich. Commercial TFC RO membranes were purchased from different RO membrane manufacturers. The manufacturer specifications of these commercial membranes are given in **Table 2**.

Table 2. Manufacturer specifications of commercial RO membranes used in this study. LMH denotes $\text{liters/m}^2 \cdot \text{h}$.

Membrane	Flux (LMH)	NaCl rejection (%)	Test pressure (bar)	Test conditions
Koch XR	44	99.75	22.1	BWRO
Sepro RO4	34	99.50	55.2	SWRO
Toray UTC-80B	30	99.80	55.2	SWRO
Toray UTC-80LB	46	99.80	55.2	SWRO

2.2. Membrane fabrication

The fabrication method to produce defect-free TFC membranes was described in our previous publication [34]. Briefly, FT-30-type membranes were modified by varying three parameters: (i) reaction time, (ii) organic solution temperature, and (iii) TMC concentration. Porous polysulfone support sheets (11.5 x 15.5 cm) were immersed in 2 wt/vol% of MPD dissolved in distilled water for 5 minutes. The support was then passed through a rubber roller and fixed in a Teflon frame. Isopar® was either used at room temperature (20 °C) or heated to 60 or 100 °C and TMC was dissolved at 0.1, 1 or 10 wt/vol% as specified. The TMC solution was then poured on the polysulfone surface. After a specific reaction time, between 10 to 600 s, excess solution was poured off. The membrane was washed with Isopar® and stored in a desiccator until testing. **Table S1** lists the conditions of TFCs prepared in this study. The membrane designation is defined by: xs (reaction time between organic TMC and aqueous diamine phases in seconds); yTMC (TMC concentration in weight/volume percent); zC (organic phase temperature in °C), resulting in a final designation of: xs-yTMC-zC, *e.g.*, 300s-0.1TMC-100C. Data for at least three samples are reported for each test.

2.3. Liquid permeation and rejection

For liquid permeation tests, dry membrane coupons were activated by dipping in IPA for 5 min followed by washing with running water for 15 min. All permeation tests were conducted at a feed pressure of 15.5 bar (225 psi) and the temperature was maintained at 23 °C using a heat exchanger. Dead-end filtration was used to measure pure water flux and boron rejection. A Sterlitech HP4750 dead-end cell was used and the schematic of the setup is shown in **Figure S1**. The coupons had an active area of 13 cm² and a stirrer operating at 420 rpm was used to minimize concentration polarization. The dead-end cell was loaded with 250 ml of test solution and the system was pressurized with cylinder nitrogen. Pure water measurements were made using distilled water. A solution containing 5 ppm boron was prepared

by dissolving boric acid in distilled water. The pH of the solution was adjusted to 6, 8 or 10, respectively, using 0.1 to 1M sodium bicarbonate solutions. Flux and rejection measurements were taken every 2 h until steady state was achieved.

Crossflow permeation tests were conducted using a custom-made RO system employing Sterlitech crossflow cells (CF016), as shown in **Figure S2**. A crossflow velocity of 0.37 m/s was used and spacers were placed in the feed channel to minimize concentration polarization. The coupons had an active area of 33.5 cm². Standard brackish water reverse osmosis (BWRO) sodium chloride rejection measurements were performed using 2000 ppm (mg/L) sodium chloride solutions prepared with distilled water at pH 8. Crossflow experiments with boron were conducted using 5 ppm boron solutions (as described above) at pH 6, 8 and 10. Rejection and flux measurements were taken every 24 h up to 100 h to ensure steady-state values.

A Myron L Ultrameter II conductivity meter was used to measure sodium chloride concentrations. Boron concentration was measured using an Avio 500 of Perkin-Elmer Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The equipment was calibrated with standard solutions and each sample was replicated three times and average values are reported. All pH measurements were conducted using a Thermo Scientific Orion 8 pH meter.

Rejection was calculated using the following equation:

$$Rejection = 100 \times \left[1 - \frac{c_{permeate}}{\left(\frac{c_{feed} + c_{retentate}}{2} \right)} \right] \quad (\text{Eq. 1})$$

where c_{feed} , $c_{permeate}$ and $c_{retentate}$ are the feed, permeate and retentate salt concentrations (wt/vol%), respectively. Rejection is reported in %.

Water flux J_w (L/m²·h) can be calculated as:

$$J_w = \frac{m}{Area \cdot t \cdot \rho} \quad (\text{Eq. 2})$$

where m is the mass of water (kg) collected in time t (h), $Area$ is the membrane active area (m^2) and ρ (kg/L) is the density of water. Water permeance ($\text{L}/\text{m}^2 \cdot \text{h} \cdot \text{bar}$ or LMH/bar), A , is calculated as:

$$A = \frac{J_w}{(\Delta p - \Delta \pi)} \quad (\text{Eq. 3})$$

where Δp is the pressure difference across the membrane (bar) and $\Delta \pi$ is the differential osmotic pressure (bar).

For sodium chloride solutions, $\Delta \pi$ is given by;

$$\Delta \pi = \frac{2\Delta c_s \cdot R \cdot T}{M_w} \quad (\text{Eq. 4})$$

where M_w = molecular mass sodium chloride (g/mol), R = universal gas constant ($\text{cm}^3 \cdot \text{bar}/\text{K} \cdot \text{mol}$), T = temperature (K) and Δc_s (g/cm^3) = differential mass concentration of sodium chloride in water which is defined as:

$$\Delta c_s = c_{feed} - c_{permeate} \quad (\text{Eq. 5})$$

Normalized permeance of water P_w/l ($\text{cm}^3/\text{cm}^2 \cdot \text{s}$ or cm/s) can be calculated using a previously reported method [35,36] as:

$$\frac{P_w}{l} = \frac{A \cdot R \cdot T}{M_w} \quad (\text{Eq. 6})$$

Eq. 6 is used to convert pressure-normalized flux to concentration-normalized flux to ensure fair comparison between water and salt flux.

The salt flux J_s ($\text{kg}/\text{m}^2 \cdot \text{h}$) through the membrane is defined as;

$$J_s = J_w \cdot c_{permeate} \quad (\text{Eq. 7})$$

Salt permeance B ($\text{m}^3/\text{m}^2 \cdot \text{h}$ or m/h) can then be defined as;

$$B = \frac{J_s}{\Delta c_s} \quad (\text{Eq. 8})$$

Normalized salt permeance P_s/l equals B .

Water/sodium chloride selectivity $\alpha_{\text{Water/NaCl}}$ is calculated as:

$$\alpha_{\text{Water/NaCl}} = \frac{P_w/l}{P_s/l} = \frac{P_w}{P_s} \quad (\text{Eq. 9})$$

Boron flux, permeance and water/boron selectivity ($\alpha_{\text{Water/Boron}}$) were also calculated by applying Eqs. 7-9.

2.4. Membrane characterization

X-ray photoelectron spectroscopy (XPS) studies were carried out using a Kratos Axis Supra spectrometer equipped with a monochromatic Al Ka X-ray source ($h\nu = 1486.6$ eV) operating at 150 W, a multi-channel plate and delay line detector under a vacuum of $\sim 10^{-9}$ mbar. All spectra were recorded using an aperture slot of $300 \mu\text{m} \times 700 \mu\text{m}$. Survey spectra were collected using pass energy of 160 eV and step size of 1 eV. Samples were mounted in floating mode to avoid differential charging. Charge neutralization was required for all samples. Binding energies were referenced to the C 1s binding energy of sp^2 -hybridized carbon taken to be 284.4 eV. The data were analyzed with commercially available software, CASAXPS. The atomic percentage concentrations of carbon, nitrogen and oxygen obtained were used to calculate the degree of crosslinking, *i.e.*, the ratio of nitrogen to oxygen atoms (N/O) [37,38].

Atomic force microscopy (AFM) was used to characterize the surface morphology of the membranes, specifically surface roughness. Measurements were conducted for 8-points on each sample using a Bruker Dimension Icon SPM AFM and average values are reported. A FESPA (Bruker) AFM probe with spring constant of 2.8 N/m was used employing a tapping in air imaging mode with a scanning speed of 1 Hz. Commercially available Gwyddion software was used to analyze raw data to obtain the

roughness ratio (RR) which is defined as the ratio of the AFM measured membrane surface area accounting for roughness divided by the membrane surface area assuming a flat surface.

Membrane surface charge was measured using the Anton Paar/SurPASS electrokinetic analyzer. The cell gap height was adjusted to approximately 100 μm . A 0.001M NaCl solution was used as an electrolyte and the pH was adjusted manually using 0.1M HCl and 0.1M NaOH. The surface charge (or zeta potential) was calculated using the Helmholtz-Smoluchowski equation.

A spectroscopic ellipsometer M-2000 UI operating in a wavelength range 192 – 1690 nm coupled with light focusing optics (300 micron, short axis) and modeling software CompleteEASE v.5.24 was used to perform polyamide layer thickness measurements. The procedure is described in detail elsewhere [39,40]. In brief, the ellipsometric spectra were recorded over a square sample in equal steps in x and y directions to produce 4 x 4 mm maps. Afterwards, the raw data, represented by ellipsometric angles ψ and δ , were converted into IP film thickness and its refractive index by numerical fitting using a single layer, isotropic optical model. The properties of the bare substrate were recorded separately and subsequently fixed in the optical model of the IP membrane.

3. Results and discussion

It has been well established that for FT-30-type RO membranes very high rejection for sodium chloride translates to high boron rejection [41]. In this study, we used sodium chloride rejection as a screening tool to identify membranes with potential for high boron rejection. Commercially manufactured FT-30-type RO membranes exhibit micro- and mesoporous defects in the dry state but are known for their high rejection of sodium chloride in the wet state [42]. It has been proposed that under RO conditions the polyamide layer swells, possibly self-plugging the majority of defects in the ultrathin polyamide layer [43]. Transport through such membranes has been defined by ‘solution-diffusion’ and ‘solution-diffusion with defects’ models [22,44,45]. In commercial production of FT-30-type RO membranes a

short reaction time is used, with the idea to minimize the thickness of the barrier layer and hence, maximize water flux. Sodium chloride rejection of the tested membranes is tabulated in **Table 3**. Similar flux and rejection performance for FT-30 variant Sepro RO4 compared to in-house fabricated 10s-0.1TMC-20C implies similar fabrication conditions. **Figure 2a** shows how defect-free properties, as illustrated by higher rejection, start to develop at longer reaction times. As reaction time was increased from 10 to 300 s, the pure water permeance decreased from 1.65 to 0.83 LMH/bar showing a linearly decreasing correlation with the reaction time. In this study, SEM and ellipsometry were used to qualitatively characterize polyamide thickness. Ellipsometry data, **Table S2**, show an increase of film thickness from 107 nm to 151 nm as reaction time was increased from 10 to 300 s, which can explain the decreasing water permeance. However, when the reaction time was further increased to 600 s, an increase in water permeance was observed despite increasing thickness. This increase in permeance can possibly be explained by the increase in effective surface area of the membrane due to increased roughness, described by the roughness ratio (*RR*) in **Table S2** [46].

Table 3. Membrane water flux, permeance and sodium chloride rejection performance parameters (15.5 bar; T = 23 °C). A is water permeance and P_w/P_s is water over sodium chloride selectivity.

Membrane	Flux (LMH)	A (LMH/bar)	Rejection (%)	Pw/Ps
Sepro RO4	25.1	1.73	97.9	5053
10s-0.1TMC-20C	23.9	1.65	97.9	4881
60s-0.1TMC-20C	21.7	1.50	98.9	9213
300s-0.1TMC-20C	12.0	0.83	99.2	12849
600s-0.1TMC-20C	15.3	1.06	99.2	14299
300s-0.1TMC-60C	10.3	0.71	99.2	13009
300s-0.1TMC-100C (KRO-1*)	10.9	0.75	99.6	25804
300s-1TMC-60C	9.9	0.68	98.9	9131
300s-10TMC-60C	11.2	0.77	94.7	1898

* KRO-1 = Optimized KAUST TFC membrane made under the following conditions: reaction time: 300 s; 0.1 wt/vol% TMC in Isopar G; 100 °C organic solution temperature.

Meanwhile as reaction time was increased from 10 to 300 s, the rejection increased from 97.9 to 99.2%. Increasing overall membrane thickness with increasing reaction time ensures plugging of defects in the

polyamide layer as MPD continues to diffuse through the defects to react with TMC. This manifests itself as an increase in membrane rejection potentially due to change of transport from ‘solution-diffusion with defects’ to “pure” solution-diffusion mechanism [22,45].

Figure 2. a) Effect on water permeance and salt rejection of: a) reaction time at fixed organic solution temperature of 20 °C and b) organic solution temperature at fixed reaction time of 300 s. TMC concentration 0.1 wt/vol% in Isopar G.

From our previous work [34] we gained understanding that further performance enhancements can be achieved by increasing organic solution temperature. As illustrated in **Figure 2b**, a small decrease of water permeance from 0.83 to 0.71 LMH/bar was observed as organic solution temperature was increased from 20 to 60 °C. When the temperature was further increased to 100 °C, the water permeance increased slightly. It can be seen from **Figure 3** that as organic solution temperature was increased, a significant increase in membrane roughness was observed. Normalizing the water permeance A with the roughness ratio RR (A/RR) demonstrates a clear trend of linearly decreasing water permeance with increasing temperature. Meanwhile, rejection showed no variation when temperature was increased from 20 to 60 °C. When temperature was further increased to 100 °C, rejection significantly improved from 99.2 to 99.6%.

Figure 3. Surface AFM images of in-house fabricated polyamide thin-film composite membranes. RMS refers to root-mean-square roughness. Roughness ratio (*RR*) is described in **Section 2.4**.

The decrease in water flux with increasing organic solution temperature can be explained by an increase in membrane thickness, *e.g.*, membrane thickness increased from 151 to 231 nm as organic solution temperature was increased from 20 to 60 °C. Increasing the organic solution temperature decreased the solution viscosity, density and surface tension [47]. This increases the diffusivity of MPD through the reaction zone for further growth of the polyamide layer, which leads to formation of a thicker barrier layer with negligible changes in the polymer microstructure. Changes in polymer microstructure can be quantified using the degree of crosslinking represented by the N/O ratio deduced by XPS measurements. A fully crosslinked polymer has a N/O ratio of 1 whereas a fully linear polymer (no crosslinking) has a

N/O ratio of 0.50 [38]. Increasing the temperature from 20 to 60 °C had a negligible effect on the crosslinking ratio, as shown in **Table S2**, confirming minimal microstructural changes. This explains the small variation in membrane rejection.

On the other hand, increasing organic solution temperature to 100 °C resulted in a further decrease in water permeance (roughness ratio normalized) but rejection increased significantly to 99.6%. As temperature was increased to 100 °C, the crosslinking ratio increased from 0.79 to 0.93. Increased polymer crosslinking resulted in decreased water-induced swelling of the thin polyamide layer due to the reduced mobility of the polymer chains leading to a boost in rejection [48–50]. Increasing the organic solution temperature presumably increases the reaction zone temperature. This, in turn, increases the reaction rate for formation of amide linkages between the polymer chains resulting in increased crosslinking [34]. However, this change was not observed when the organic solution temperature was increased from 20 to 60 °C. Recently, attempts were made to measure reaction zone temperature for the MPD-TMC reaction and it was estimated that the reaction zone reaches ~ 80 °C during the polyamide formation processes [51]. To enable heat flow from the bulk organic solution to the reaction zone, a temperature of > 80 °C is required for the organic phase which can explain a lack of variation in crosslinking and rejection at 60 °C. The overall effect of increasing reaction time and organic solution temperature on membrane morphology agrees qualitatively with direct observations obtained from SEM analysis as highlighted in **Figure 4**.

Figure 4. Surface (a, c and e) and cross-section (b, d and f); SEM images of in-house fabricated membranes for varying reaction time and organic solution temperature. The dotted line is provided to guide the eyes in order to identify the interface of the polyamide layer and the porous polysulfone support.

Because no further performance enhancement was observed by varying TMC concentration, the defect-free thin-film composite membrane made by the optimized 300s-0.1TMC-100C protocol (henceforth referred to as KRO-1) was chosen for boron separation studies due to its superb sodium chloride rejection. The pH dependent boron rejection of the membrane was explored and compared to some commercially available membranes for boron removal from water. The dead-end rejection data for the membranes are plotted in **Figure 5a**. Boron rejection for all tested membranes increased with increasing pH. Moderate enhancement in boron rejection was observed by increasing pH from 6 to 8, whereas significant improvement resulted as the pH was increased from 8 to 10. Under dead-end filtration conditions, defect-free KRO-1 membranes consistently demonstrated higher boron rejection than four tested commercial RO membranes at three pH values, and reached a high boron rejection of 94% at pH

10. The Toray UTC-80LB membrane showed the second highest rejection of 88% followed by UTC-80B membrane (84%), whereas Sepro RO4 showed a lower rejection of 80% at pH 10.

Figure 5. Boron rejection as function of pH for KRO-1 and some commercial RO membranes. a) Dead-end filtration and b) crossflow filtration. The highlighted area is $B(OH)_4^-$ ion dominated region.

At low concentrations (< 200 mg/L), boron is present in solution as mononuclear species, comprising boric acid $B(OH)_3$ and borate ions $B(OH)_4^-$ [45]. Such solutions have a pK_a of ~ 9.2 at $25^\circ C$ and distribution of boron in boric acid and borate ions is highly dependent on the pH of the solution. At $pH < 9.2$, boron is primarily present in the solution as boric acid while at $pH > 9.2$, boric acid rapidly disassociates into larger borate ions. Boric acid has a trigonal structure, is non-polar and smaller than the polar borate ion [14]. Boron rejection has previously been correlated with several parameters especially the membrane surface charge due to increased boron rejection at higher pH values and the polar nature of borate ions [2,45,52]. Surface charge of the tested membranes is tabulated in **Table S4**. As pH was increased, the surface charge of all tested membranes became more negative. For the commercial membranes, Toray UTC-80LB showed the highest negative surface charge (-48 mV) at pH 10 followed by Toray UTC-80B (-41 mV), Sepro RO4 (-16 mV) and Koch XR (-12 mV). The boron rejection of the

commercial membranes displayed some dependence on the surface charge as the boron rejection increased with increasing surface charge in the order of Koch XR < Sepro RO4 < Toray UTC-80B < Toray UTC-80LB, as shown in **Figure 6a**. Such correlation diminished as pH decreased to 8 and 6, as shown in **Figure S3**. This was expected because boric acid is the dominant boron species at lower pH, thus boron rejection should not show much charge dependence in this case. However, the defect-free KRO-1 consistently exhibited higher boron rejection despite having a much less negative surface charge across all pH conditions tested compared to both Toray UTC-80B and UTC-80LB membranes. Furthermore, KRO-1 retained the best boron rejection of all membranes in this test series even at pH 6 regardless of its moderate negative surface charge, suggesting a tighter membrane structure in accordance with its defect-free nature.

Crossflow separation experiments performed on the best performing commercial membrane in this study, Toray UTC-80LB, and the optimized in-house fabricated membrane highlight the separation capabilities of the defect-free KRO-1 with 99% rejection for boron at pH 10, as shown in **Figure 5b**. On the other hand, the Toray UTC-80LB membrane showed a maximum rejection of 95% at pH 10. This 4% increase in rejection compared to UTC-80LB represents a significant increase in permselectivity performance. Similar to trends observed in the dead-end testing mode, the KRO-1 TFC membrane consistently demonstrated higher boron rejection in crossflow mode compared to Toray UTC-80LB membrane at the lower pH 6 and 8. For both types of membranes crossflow mode displayed higher boron rejection compared to the dead-end mode testing, as illustrated in **Figure 5a** and **5b**. Increase of rejection in crossflow mode compared to dead-end mode is well known and results from the reduction of concentration polarization on the membrane surface. Performance can potentially be further enhanced when membranes are tested in commercial spiral wound modules due to flow optimizations when compared to lab-scale crossflow systems [53]. Furthermore, it is noteworthy that pKa of boric acid

decreases with increasing salt concentration in seawater feed. The higher ionic strength of the feed solution could lead to enhanced boron rejection due to the increased amount of borate ions under the same pH condition. However, the impact of increasing NaCl concentration in the feed on boron rejection can be highly dependent on the testing conditions [54,55]. In this study, we measured sodium chloride and boron rejection *independently* to decouple such effects. Meanwhile, increasing operating pressure always results in increased boron rejection [24] which must be considered when comparing membranes tested in this study under brackish conditions compared to those tested at seawater RO conditions (**Table 1**).

Rejection is typically used as a performance indicator for RO membranes but it is often misleading in characterizing the intrinsic salt transport properties. Here, similar to gas permeation studies, selectivity of water over boron (P_W/P_{Boron}) (as calculated in Eq. 9) was used to characterize intrinsic separation performance of membrane materials as illustrated in **Figure 6b-d**.

Figure 6. Water over boron selectivity (P_w/P_{Boron}) vs. a) surface charge at pH 10 and b-d) water permeance (P_w/l), for tested membranes at b) pH 10, c) pH 8 and d) pH 6. Membrane KRO-1 [CF] and UTC-80LB [CF] data were measured with crossflow system; all other membrane performance data were obtained with dead-end system.

It is apparent that the defect-free KRO-1 membrane exhibited the highest selectivity for water over boron compared to all tested commercial membranes across all pH values and under both dead-end and crossflow testing modes, as shown in **Figure 6b-d**. Defect-free KRO-1 TFC displayed an average of two to five times higher selectivity for water over boron compared to commercial membranes in dead-end operation at pH 10. In crossflow mode, defect-free KRO-1 demonstrated water over boron selectivity of 8300 compared to 1700 for the highest performing commercial membrane (Toray UTC-80LB) at pH 10.

At lower pH conditions, the differences of water over boron selectivity among the defect-free KRO-1 TFC membrane and four commercial membranes were less pronounced but the water over boron selectivity of defect-free KRO-1 TFC remained the highest even at pH 6. The influence of membrane surface charge would have minimal effects on boron rejection at pH 6 due to the predominant presence of boric acid, therefore, the highest water over boron selectivity indicates that the defect-free KRO-1 TFC membrane exhibits very strong size-sieving properties in line with its excellent gas separation performance reported in our previous study [34]. Notably, the crossflow mode showed significant increase in water over boron selectivity compared to dead-end mode as discussed previously. On the other hand, the increased water/boron selectivity of the defect-free membrane was coupled with a three-fold drop in water flux relative to that of the Toray UTC-80LB. This trend follows the water permeance/selectivity trade-off for desalination membranes as proposed by Geise et al. in Freeman's group [36]. Because the chemical composition and fabrication methods for the commercial membranes are proprietary, direct conclusions cannot be made between the structure-property relationships of all tested commercial membranes. To gain further insight into structure property relationships for FT-30-type MPD-TMC membranes, an extra fabrication variable, TMC concentration, was examined. As the TMC concentration was increased from 0.1 to 1 wt/vol%, a very small decrease was observed in the water permeance, from 0.71 to 0.68, LMH/bar and sodium chloride rejection, from 99.2% to 98.9%, as shown in **Figure S4**. As TMC concentration was increased to 10 wt/vol%, water permeance increased slightly to 0.77 LMH/bar but with a significant drop in rejection to 95%. It is important to note that as TMC concentration was increased, a significant decrease in roughness ratio was observed, as shown in **Table S2**. This implies an underestimation of the calculated permeance for increasing TMC concentration. Increasing the TMC concentration in the organic phase increases the ratio of the reactive COCl groups in the interfacial reaction zone compared to reactive NH₂ groups. This excess of COCl

groups promotes the formation of more linear, lesser crosslinked polyamide chains, which is confirmed by the crosslinking ratio [47]. The crosslinking ratio decreased from 0.79 to 0.74 and 0.66 as TMC concentration was increased from 0.1 to 1 and 10 wt/vol%, respectively. The decrease in crosslinking ratio with increasing TMC concentration was coupled with an expected decrease in rejection [48–50].

Figure 7. Surface (a, c and e) and cross-section (b, d and f) SEM images of in-house fabricated membranes for varying TMC concentration (0.1, 1 and 10 wt/vol%). The dotted line is provided to guide the eyes in order to identify the interface of the polyamide layer and the porous polysulfone support.

A significant change in surface morphology was observed by varying the TMC concentration, as illustrated in **Figure 7**. As TMC concentration was increased from 0.1 to 1 wt/vol %, membrane roughness decreases, *i.e.*, roughness ratio was reduced from 2.1 to 1.9. The surface of the membrane starts to flatten and ellipsometry data showed a significant decrease in membrane thickness from 231 to 139 nm. Thin "veils" of polyamide, which are almost transparent, start to appear over the initial thin film. These veils are only a few nm in thickness and very fragile (*i.e.*, sensitive to the electron beam). As

the concentration was increased to 10 wt/vol%, this effect appears further exaggerated. Top surface images show almost a flat structure, presumably due to the growth of the veils, partially covered by thin-walled ring-like structures. The apparent selective membrane thickness further decreased to about 20 nm.

Figure 8. Crosslinking N/O ratio vs a) membrane surface roughness ratio RR and b) water over sodium chloride selectivity (P_w/P_s) for in-house fabricated membranes with fixed reaction time (300 s).

It was observed that, for fixed reaction time, a clear trend starts to emerge for membrane roughness with respect to the crosslinking N/O ratio, as shown in **Figure 8a**. RR shows a linearly increasing trend with increasing crosslinking ratio. MPD-TMC-based polyamide membranes are typically heterogeneous in nature with the polyamide layer consisting of large voids surrounded by thin polyamide layers [56,57]. The layers are formed by MPD diffusing from the aqueous into the organic phase and reacting with TMC molecules. Furthermore, formation of the MPD-TMC polyamide is an exothermic reaction [51]. Hence, as the reaction progresses to produce and crosslink the polyamide layer, heat is added to the reaction zone. The heat promotes turbulence at the interface due to increase in molecular kinetic energy. This leads to aggressive diffusion of MPD into the organic phase, which ultimately reacts with TMC to form the polyamide. This can explain the correlation between surface roughness and increased degree of crosslinking. Increasing the organic solution temperature adds further heat to the reaction zone which

forms the extremely rough membranes produced at 100 °C organic solution temperature. As a result, the KRO-1 (300s-0.1TMC-100C) membrane displayed the best salt and boron rejection of all tested membranes.

In this study, water permeance showed no clear correlation with the crosslinking ratio. It is well understood that membrane permeance varies significantly with membrane thickness as well as membrane roughness. Because only qualitative estimates of thickness were made in this study, no quantitative conclusions can be drawn about variation of intrinsic A with the crosslinking N/O ratio. On the other hand, gas permeation studies indicated that for defect-free membranes, selective layer thickness and surface area have little impact on membrane selectivity. Plotting P_w/P_s vs. crosslinking N/O ratio, as shown in **Figure 8b**, confirms a clear linear trend between increasing degree of crosslinking and membrane water over sodium chloride selectivity. An increase in crosslinking ratio results in restriction of polymer chain mobility, which, in turn, decreases water-induced polymer swelling and, thereby, enhances the size sieving properties of the polyamide layer.

Figure 9. Roughness ratio vs. water over boron selectivity (P_w/P_{Boron}) for KRO-1 and commercial RO membranes tested at pH 10.

Surface roughness of membranes tested for boron rejection experiments is illustrated in **Figure S6** and quantified in **Table S4**. It can be seen in **Figure 9** that membrane roughness ratio correlates much stronger with the membrane P_W/P_{Boron} selectivity compared to the membrane surface charge. This implies that the highly rejecting commercial RO membranes may have a higher crosslinking ratio compared to lower rejecting membranes. Furthermore, recent research [57] showed that the pH dependent performance of seawater polyamide RO membranes cannot be correlated with the pH dependence of the membrane charge. Similarly, in this study the brackish water type Koch XR membrane showed only a small increase in negative surface charge, from -11 to -12 mV, as pH was increased from 6 to 10 while its rejection increased significantly from 55 to 77%. The lowest boron rejection performance of the XR membrane was also found to be associated with its smoother surface roughness feature, as shown in **Figure S6**. Here it is more likely that the increase of boron rejection with increasing pH can be attributed primarily to the increased number of much larger borate ions, which are rejected significantly more by highly crosslinked membranes with rougher surfaces and stronger size sieving capabilities such as the defect-free KRO-1 (300s-0.1TMC-100C) membrane reported in this study [18,21,54].

4. Conclusions

Defect-free, highly selective MPD-TMC membranes were successfully fabricated showing potential for removal of boron and sodium chloride from water. The membranes exhibited improved boron rejection capabilities in crossflow operation, *i.e.*, up to 99% rejection at pH 10, higher than the commercial membranes tested in this study for comparison highlighting the impact of healing defects in FT-30-type RO membranes. The best performing commercial membrane in this study, Toray UTC-80LB, showed a maximum rejection of 95% under identical test conditions at pH 10. The membranes also exhibited improved sodium chloride rejection, reaching a maximum of 99.6% at lab-scale brackish water RO test

conditions, compared to the commercial FT-30 variant Sepro RO4 membrane with a maximum rejection of 97.9%.

It was demonstrated that *in-situ* plugging of defects in FT-30-type RO membranes can significantly improve performance by simply controlling the reaction time, *e.g.*, rejection improved from 97.9 to 99.2% when the reaction time was increased from 10 to 300 s. No change was observed in the degree of crosslinking of the polyamide layer as function of reaction time, which implied a pore plugging mechanism at play rather than changes in the intrinsic polymer microstructure. Further benefits were achieved by increasing the membrane crosslinking ratio, *e.g.*, increasing organic solution temperature to 100 °C resulted in maximum sodium chloride rejection of 99.6%. Although, the defect-free high boron rejection membranes displayed lower water flux compared to commercially available desalination membranes, the improved selectivity addresses a critical need for future development of such membranes [58]. Importantly, these membranes can be fabricated with small variations to the commercially used RO membrane manufacturing process enabling low-cost production as well as rapid scalability and reliability. Furthermore, the correlation found in this study between the high crosslinking ratio with rougher and tighter membrane structure and high water over boron selectivity provides an improved understanding of structure-property relationship of FT-30-type RO membranes and guidance toward development of high rejection RO membranes.

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Highlights

- Defect-free, highly selective MPD-TMC thin-film composite membranes were fabricated.
- Membrane performance was compared to a group of commercially available membranes.
- The fabricated membranes exhibited promising potential for improved boron and NaCl removal from water.
- Methods and mechanisms to improve membrane rejection are reported.