

1 **High rejection reverse osmosis membrane for**
2 **removal of *N*-nitrosamines and their precursors**

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17 **Abstract**

18 Direct potable reuse is becoming a feasible option to cope with water shortages. It requires
19 more stringent water quality assurance than indirect potable reuse. Thus, the development of
20 a high-rejection reverse osmosis (RO) membrane for the removal of one of the most
21 challenging chemicals in potable reuse – *N*-nitrosodimethylamine (NDMA) – ensures further
22 system confidence in reclaimed water quality. This study aimed to achieve over 90% removal
23 of NDMA by modifying three commercial and one prototype RO membrane using heat
24 treatment. Application of heat treatment to a prototype membrane resulted in a record high
25 removal of 92% (1.1-log) of NDMA. Heat treatment reduced conductivity rejection and
26 permeability, while secondary amines, selected as *N*-nitrosamine precursors, were still well
27 rejected (>98%) regardless of RO membrane type. This study also demonstrated the highly
28 stable separation performance of the heat-treated prototype membrane under conditions of
29 varying feed temperature and permeate flux. Fouling propensity of the prototype membrane
30 was lower than a commercial RO membrane. This study identified a need to develop highly
31 selective RO membranes with high permeability to ensure the feasibility of using these
32 membranes at full scale.

33 **Keywords:** *N*-nitrosodimethylamine; *N*-nitrosamine precursor; heat treatment; reverse
34 osmosis; potable water reuse.

35

36 **1. Introduction**

37 Potable reuse (PR) has been increasingly considered as a viable and powerful option to cope
38 with water scarcity in many parts of the world (Burgess et al., 2015). Most PR schemes
39 employed over the past decade are based on indirect potable reuse (IPR), which is
40 implemented through the augmentation of drinking water sources (e.g. dams and aquifers)
41 with highly treated wastewater. To make PR more economically feasible, the water industry
42 has devoted significant attention on direct potable reuse (DPR) (Arnold et al., 2012). In DPR,
43 recycled water with a short retention time is transported directly to the entrance of drinking
44 water treatment plants, so that capital and operating costs associated with infrastructure and
45 water quality monitoring can be reduced considerably. One of the critical considerations
46 when shifting from IPR to DPR is the quality assurance of recycled water (Drewes and Khan,
47 2015; Leverenz et al., 2011). In fact, a feasibility study of DPR initiated by the California
48 State Legislature (USA) has recommended greater focus on the identification and removal of
49 low molecular weight trace organic compounds (TOrcs) (CSWRCB, 2016).

50 Among low molecular weight TOrcs, *N*-nitrosodimethylamine (NDMA; C₂H₆N₂O) – a
51 probable carcinogenic chemical (USEPA, 1993) – is one of the more challenging compounds
52 in PR. For example, an adsorption process using granular activated carbon only removed
53 NDMA up to 50% (Fleming et al., 1996; Schmidt and Brauch, 2008). To date, NDMA is
54 essentially removed by a combination of direct photolysis by UV irradiation and an advanced
55 oxidation process (AOP) that is based on hydrogen peroxide dosage (Leverenz et al., 2011).
56 California has established a notification level (NL) of 10 ng/L for NDMA and a public health
57 goal (PHG) of 3 ng/L. No reliable removal credits for NDMA have been granted for the
58 application of a reverse osmosis (RO) process.

59 NDMA, an *N*-nitrosamine, is a hydrophilic compound with molecular weight of 74 g/mol and
60 is uncharged at pH 6–8. Because of its small molecular size and uncharged property, NDMA
61 readily permeates through an RO membrane. Brackish water RO membranes are typically
62 able to achieve 40–70% rejection of NDMA at lab-scale levels (Bellona et al., 2011; Fujioka
63 et al., 2012b; Hofs et al., 2013; Miyashita et al., 2009; Steinle-Darling et al., 2007) and at 5–
64 80% at pilot- to full-scale levels (Bellona et al., 2008; Farré et al., 2011a; Fujioka et al.,
65 2013b; Plumlee et al., 2008; Poussade et al., 2009). Any improvement to the selectivity of
66 RO membranes and assignment of removal credits for NDMA can improve the safety of
67 recycled water and possibly reduce the load on any UV or UV/AOP.

68 Formation of NDMA downstream of the RO process has also gained increased concern in
69 DPR. NDMA can form through a reaction between residual chloramine and NDMA
70 precursors in RO permeate (McCurry et al., 2017; Sgroi et al., 2015; Soltermann et al., 2013).
71 These NDMA precursors include dimethylamine (DMA) and tertiary amines (Mitch et al.,
72 2003; Schreiber and Mitch, 2005; Shah and Mitch, 2011). Although these precursors are well
73 removed by RO membranes (e.g. >99%) (Krauss et al., 2010; Miyashita et al., 2009),
74 significant NDMA precursors still remain in RO permeate (Farré et al., 2011b) that are not
75 degraded by UV/AOP (or are reaction products). Thus, the development of a highly selective
76 RO membrane for enhanced removal of NDMA and NDMA precursors could help to
77 improve on the safety of recycled water in DPR. In addition, improvement of the selectivity
78 of RO membranes is expected to become more important in PR to mitigate future water
79 quality issues associated with non-regulated or unidentified emerging TOxCs (Debroux et al.,
80 2012; Werber et al., 2016a).

81 To improve the rejection of RO membranes, a simple membrane modification technique
82 based on an immersion of RO membranes in high-temperature ultrapure water, has been

83 proposed (Fujioka et al., 2015). Heat treatment can enhance the rejection of uncharged and
84 low molecular weight compounds (e.g. boric acid); however, water permeability also
85 decreases. Heat treatment during the interfacial polymerisation process has the effect of
86 tightening the membrane structure and improving its salt rejection (Shintani et al., 2009). To
87 the best of our knowledge, there are still no RO membranes with a reported ability to remove
88 NDMA >90% (1.0-log).

89 This study aimed to achieve over 1.0-log removal of NDMA by modifying three commercial
90 and one prototype RO membrane using heat treatment. In addition to NDMA, this study
91 included five additional *N*-nitrosamines and five secondary amines to demonstrate the
92 separation performance and stability of heat-treated RO membranes for a range of feed
93 temperatures and permeate flux. Fouling propensity of heat-treated RO membranes was also
94 examined using treated wastewater. Lastly, the feasibility and implication of using high
95 rejection RO membranes for full-scale DPR schemes are discussed.

96 **2. Materials and methods**

97 *2.1. Chemicals*

98 Certified 100 mg/L solutions of six analytical grade *N*-nitrosamines (**Table S1**) – NDMA, *N*-
99 nitrosomethylethylamine (NMEA), *N*-nitrosopyrrolidine (NPYR), *N*-nitrosodiethylamine
100 (NDEA), *N*-nitrosopiperidine (NPIP) and *N*-nitrosomorpholine (NMOR) – were purchased
101 from Ultra Scientific (Kingstown, RI, USA). Five analytical grade secondary amines – DMA
102 hydrochloride, pyrrolidine (PYR), diethylamine (DEA), piperidine (PIP) and morpholine
103 (MOR) – selected as *N*-nitrosamine precursors were purchased from Tokyo Chemical
104 Industry (Tokyo, Japan). Physicochemical properties of these *N*-nitrosamines and secondary
105 amines are summarised in **Table 1**. The *N*-nitrosamines and secondary amines, all of which
106 have a Log *D* value of <2.0, are classified as hydrophilic compounds (Van der Bruggen et al.,

107 2006). pK_a values of *N*-nitrosamines are well below 8; thus, they are uncharged at pH 8. In
108 contrast, the secondary amines (except MOR) are all dissociated at pH 8 with pK_a values well
109 beyond 8. MOR is dissociated by ~75% at pH 8. Among the selected *N*-nitrosamines, NDMA
110 has the lowest minimum projection area, i.e., the area of the compound projected with the
111 minimum plane of its circular disk (**Fig. S2**). Stock solutions containing four or six
112 *N*-nitrosamines in methanol were prepared at 1 $\mu\text{g/mL}$ of each compound. Stock solutions of
113 each secondary amine were prepared at 100 mM in ultrapure water. All stock solutions were
114 stored at 4 °C in the dark. Analytical grade NaCl, CaCl₂ and NaHCO₃ were purchased from
115 Wako Pure Chemical Industries (Tokyo, Japan). Activated sludge effluent from a municipal
116 wastewater treatment plant in Japan was treated by ultrafiltration (UF) and used for fouling
117 experiments. Total organic carbon, pH and conductivity of the UF-treated wastewater was
118 6.5 mg/L, 6.5 and 1112 $\mu\text{S/cm}$, respectively.

119 **[Table 1]**

120 2.2. *Membranes and membrane treatment system*

121 Three commercial brackish water RO membranes – ESPA2, ESPAB and HYDRApro[®]501 –
122 and one prototype membrane were supplied as flat sheet samples by Hydranautics/Nitto
123 (Osaka, Japan). All of the RO membranes are thin-film composite polyamide. ESPA2 is
124 commonly used in water recycling applications (Fujioka et al., 2012a). ESPAB is employed
125 in the second stage of seawater desalination to achieve a high rejection of boron.
126 HYDRApro[®]501 (HYDRA) is an RO membrane that is designed for industrial process
127 applications. The prototype membrane (Prototype) is a proprietary RO membrane.

128 A bench-scale RO treatment system was comprised of a stainless steel membrane cell (Iwai
129 Pharma Tech, Tokyo, Japan), high-pressure pump (KP-12, FLOM, Tokyo, Japan), 2-L glass
130 reservoir with a stainless steel heat exchanging coil connected to a temperature control unit

131 (NCB-500, Tokyo Rikakikai, Tokyo, Japan) (**Fig. S3**). The membrane cell held a circular
132 flat-sheet membrane coupon with effective surface area of 36.3 cm².

133 2.3. *Experimental protocols*

134 2.3.1. Heat treatment

135 The RO membrane coupons were placed in 200 mL beakers and rinsed with copious amounts
136 of ultrapure water (18.0 MΩcm). Membranes were heat-treated by placing the beakers in a
137 temperature-controlled water bath (SWB-11A, AS ONE, Osaka, Japan) at 80 ± 1 °C for 4 h.
138 After heat treatment, the heat-treated RO membranes were rinsed with deionized water and
139 stored at 4 °C in the dark.

140 2.3.2. Separation evaluation

141 The performance of untreated and heat-treated RO membranes was evaluated in clean water.
142 RO membranes were first conditioned and stabilised with a deionized water at 1500 kPa.
143 Stock solutions of background electrolytes were dosed at 20 mM NaCl, 1 mM NaHCO₃,
144 1 mM CaCl₂ in the RO feed. *N*-nitrosamines were added to the RO feed at a concentration of
145 1000 ng/L. *N*-nitrosamines were evaluated separately from the secondary amines.
146 Concentrations of secondary amines in RO feed were adjusted at 50 µg/L. After conditioning,
147 the RO system was operated at 20 L/m²h permeate flux, which is typically employed in water
148 recycling applications (Fujioka et al., 2012a). The feed temperature was 20 °C. Following 1 h
149 of operation, RO feed and permeate samples were collected in 1.5 mL amber vials for the
150 analysis of *N*-nitrosamines and in 10 mL vials for the analysis of secondary amines. The *N*-
151 nitrosamines and secondary amines used in this study are very hydrophilic at pH 8; thus,
152 adsorption of these chemicals onto the membrane was unlikely to occur. In fact, previous
153 studies reported that the rejection of *N*-nitrosamines by RO membranes in clean water or
154 wastewater matrices reached a steady state condition within 1 h of filtration (Fujioka et al.,

155 2013a; Miyashita et al., 2009; Steinle-Darling et al., 2007). Thus, 1 h of filtration was
156 assumed to be sufficient to reach adsorption equilibrium.

157 2.3.3. Fouling development

158 Fouling propensity of each RO membrane was evaluated by operating the system on a
159 secondary wastewater effluent. After conditioning the RO membrane, the deionized water
160 was replaced with UF-treated wastewater. Fouling development was accelerated by operating
161 the system at a high constant flux of 40 L/m²h with the feed temperature maintained at 20 °C.
162 Transmembrane pressure (TMP) was recorded.

163 2.4. Analytical techniques

164 2.4.1. *N*-nitrosamines

165 Concentrations of *N*-nitrosamines were determined by high-performance liquid
166 chromatography-photochemical reaction-chemiluminescence (HPLC-PR-CL). Details of this
167 technique are provided elsewhere (Fujioka et al., 2016; Kodamatani et al., 2016). The
168 analysis was performed with an eluent of 10 mM phosphate buffer and methanol (90:10 v/v)
169 and the sample injection volume was 200 µL. Clean water matrix samples and permeate
170 samples were analysed without any pretreatment. UF-filtered wastewater collected from the
171 RO feed was prefiltered with a 0.45-µm hydrophilic PTFE syringe filter (Filtstar, Starlab
172 Scientific, China) prior to the analysis.

173 2.4.2. Secondary amines

174 Concentrations of secondary amines were determined by HPLC-PR-CL after nitrosation
175 reaction of samples. Details of this technique are provided elsewhere (Kodamatani et al.,
176 2017). The nitrosation reaction was conducted by adding the sample solution (2.0 mL),
177 glacial acetic acid (100 µL, 0.8 M), and sodium nitrite (100 µL, 200 mM) to a 10-mL screw-
178 cap glass tube and then stored at 80 °C for 1 h. The solution was treated with sulfamic acid

179 (400 μ L, 1.5 M) and sodium carbonate solution (1.4 mL, 1 M) prior to the analysis by HPLC-
180 PR-CL. The sample injection volume was 20 μ L.

181 2.4.3. Zeta potential

182 The zeta potential of the RO membrane surface was measured at pH 8 in a 1 mM KCl
183 background electrolyte solution using a SurPASS electrokinetic analyser (Anton Paar GmbH,
184 Graz, Austria). The surface zeta potential was calculated from the measured streaming
185 potential of the membrane using the Fairbrother-Mastin method.

186 3. Results and discussion

187 3.1. NDMA Rejection

188 Rejection of NDMA by untreated and heat-treated RO membranes was >50% at 20 L/m²h
189 permeate flux. Among the untreated RO membranes, the Prototype revealed the highest
190 NDMA rejection (84%), followed by HYDRA (74%), ESPAB (62%) and ESPA2 (53%)
191 (**Fig. 1**). Although the Prototype membrane had the highest NDMA separation capability, the
192 TMP required to achieve 20 L/m²h permeate flux was as high as 1.54 MPa in contrast with
193 0.49, 0.65 and 1.29 MPa for the ESPA2, ESPAB and HYDRA membranes, respectively
194 (**Fig. S4**).

195 **[Fig. 1]**

196 Heat treatment applied to the RO membranes considerably enhanced their separation
197 performance. For example, NDMA rejection of the heat-treated ESPA2 membrane increased
198 from 53 to 62% (**Fig. 1**). Likewise, NDMA rejection by the heat-treated ESPAB and
199 HYDRA membranes increased by from 62 to 79% and from 74 to 88%, respectively. Finally,
200 the heat-treated Prototype membrane rejected 92% of the NDMA, achieving the primary
201 objective of this study (i.e. >90%). Enhanced performance from heat treatment was also

202 observed for the *N*-nitrosamines: NMEA, NPYR and NMOR (**Fig. S4**). Nevertheless, the
203 TMP required to achieve a 20 L/m²h permeate flux increased considerably—17% for ESPA2
204 and >40% for the other membranes (**Fig. S4**). The results indicate that heat treatment applied
205 to RO membranes can reduce the permeation of *N*-nitrosamines at the expense of membrane
206 permeability. The heat treatment of the RO membranes is believed to induce a change in the
207 polymer configuration where upon cooling the end result is a more compact structure of the
208 polyamide separations layer.

209 In contrast to *N*-nitrosamines, heat treatment resulted in a reduction in conductivity rejection.
210 Heat treatment applied to ESPA2 membrane reduced conductivity rejection from 99.0 to
211 98.8% (**Fig. 1**). Reduction in conductivity rejection after heat treatment was also apparent for
212 the other three RO membranes (i.e. ESPAB, HYDRA and Prototype). The permeation of ions
213 through an RO membrane is primarily governed by size exclusion and electrostatic repulsion
214 (Bellona et al., 2004). The loss of conductivity rejection by heat treatment may be due to
215 changes in the internal structure. Although a reduction in the negative charge on the
216 membrane surface was also expected to be a contributing factor to reduced conductivity
217 rejection, no definitive conclusions can be made from the charge data (zeta potential) because
218 the negative charge on the membrane surface increased, except for the ESPA2 membrane
219 (**Table 2**).

220 [Table 2]

221 Heat treatment reduced the pure water permeability of the ESPA2, ESPAB, HYDRA and
222 Prototype RO membranes by 21%, 33%, 35% and 31%, respectively (**Table 2**), indicating
223 that RO membranes could lose 20–35% of their water permeability by heat treatment in
224 exchange for improved rejection. Among eight RO membranes tested in this study, a high
225 correlation ($R^2 = 0.998$) between pure water permeability and NDMA rejection was observed

226 (Fig. 2). The trade-off between permeability and separation performance is often reported in
227 literature (Bernstein et al., 2011; Geise et al., 2011; Werber et al., 2016b; Zhang and Geise,
228 2016). In contrast, conductivity rejection revealed no correlation with pure water
229 permeability. Providing detailed mechanisms to explain the correlations between
230 *N*-nitrosamine rejection and conductivity rejection requires characterisation of their
231 membrane properties (e.g. free-volume, hole-size and surface charge) (Dražević et al., 2014;
232 Freger, 2015) and will be the scope of future studies.

233 [Fig. 2]

234 3.2. Separation performance

235 The separation capability of the heat-treated Prototype membrane was further evaluated by
236 comparison with the ESPA2 membrane. The ESPA2 membrane was selected as a reference
237 because it is widely used in potable reuse (Fujioka et al., 2012a) and thus, served as a
238 comparison with the best membrane for separations (i.e. heat-treated Prototype). For both RO
239 membranes, rejection of the six *N*-nitrosamines increased with increasing minimum
240 projection area (Fig. 3). This confirmed that size exclusion is the dominant mechanism for
241 the removal of *N*-nitrosamines. In contrast to the uncharged *N*-nitrosamines, secondary
242 amines, which are *N*-nitrosamine precursors, are mostly present in the form of charged species
243 at pH 8. As a result of electrostatic repulsion interaction in addition to the size exclusion
244 mechanism, their rejection was very high (>98%) for both RO membranes (Fig. 4). DMA, the
245 smallest compound tested, revealed high rejection—98.2% for ESPA2 and 98.9% for the
246 heat-treated Prototype membrane. In addition, heat treatment enhanced the rejection of three
247 secondary amines (MOR, PYR and PIP) to near-complete removal levels (i.e. >99.9%).
248 Overall, the separation capacity of the heat-treated Prototype membrane for secondary amines
249 was greater than the ESPA2 membrane.

250 [Fig. 3]

251 [Fig. 4]

252 A seasonal change in feed temperature could alter the separation performance; thus, stability
253 in the separation performance of the untreated ESPA2 and heat-treated Prototype membrane
254 under conditions of variable feed temperature was evaluated. The variation in *N*-nitrosamine
255 rejection was significant for the ESPA2 membrane. An increase in feed temperature from 10
256 to 30 °C led to a considerable drop in NDMA rejection from 59 to 39% (**Fig. 5**). In contrast,
257 far less impact of feed temperature was observed with the heat-treated Prototype membrane
258 as NDMA rejection only dropped from 94 to 90% when the temperature increased from 10 to
259 30 °C, The rejection of the other *N*-nitrosamines remained almost constant across the 10–
260 40 °C range.

261 [Fig. 5]

262 The impact of varying the permeate flux on *N*-nitrosamine rejection was also evaluated.
263 Similar to the case of feed temperature above, the rejection of *N*-nitrosamines by the heat-
264 treated Prototype membrane remained high (**Fig. 6**). A reduction in permeate flux from 20 to
265 10 L/m²h resulted in a decrease in NDMA rejection by ESPA2 membrane from 53 to 42%,
266 while NDMA rejection by the heat-treated Prototype membrane decreased from 92 to 88%.
267 Impacts of varied permeate flux were less significant for the other three *N*-nitrosamines (**Fig.**
268 **6**). The results here indicate that the heat-treated Prototype membrane is resilient to changes
269 in operating conditions, which is important to achieve a stable operation. Although permeate
270 flux is usually unchanged during RO system operation, there could be a large variation in
271 permeate flux inside a vessel of a three-stage RO where permeate flux at later stages is
272 typically very low (Hoek et al., 2008). A multiple-stage configuration is commonly utilized in
273 water recycling to achieve a recovery near 85% (Fujioka et al., 2012a). Thus, if the

274 membrane were to be implemented at a full scale, the high stable rejection under variable
275 permeate flux would be advantageous in maintaining high NDMA rejection throughout the
276 RO train.

277 **[Fig. 6]**

278 *3.3. Fouling propensity*

279 The fouling propensity of the ESPA2 and heat-treated Prototype membranes was evaluated
280 with a UF-treated wastewater effluent. Initial TMPs for the ESPA2 and Prototype membrane
281 were 0.77 and 3.9 MPa, respectively. Operation of the membranes at a high permeate flux
282 resulted in progressive fouling of the ESPA2 membrane. Permeability dropped to 87% of the
283 initial level after 23 h (**Fig. 7**). In contrast, the permeability of the heat-treated Prototype
284 membrane remained at 98% of the initial level between 0.5–23 h. The mechanism of the
285 improved fouling resistance by heat treatment has not been determined and will be the scope
286 of future studies.

287 **[Fig. 7]**

288 *3.4. Outlook for high rejection RO membranes*

289 One of the drawbacks of high rejection RO membranes is low permeability. Lower
290 membrane permeability equates to higher TMP to produce comparable permeate flux at the
291 expense of high energy cost. Nevertheless, greater NDMA removal capability by RO could
292 potentially lead to less energy utilization by the UV-based AOP. UV/AOP requires
293 $\sim 1,000 \text{ mJ/cm}^2$ to provide a 1.2-log reduction for NDMA (Sharpless et al., 2003) and the
294 energy requirement is about 10 times greater than a typical UV dose for a 4-log removal of
295 *Cryptosporidium* (USEPA, 2006). Energy consumption of AOP could be cut in half if 0.6-log
296 removal credits for NDMA were given to the RO process with only 0.6-log removal needed
297 for NDMA by the UV/AOP. Nevertheless, because the increase in feed pressure requires a

298 greater capital investment in RO feed pumps and greater energy consumption, the impact of a
299 reduction in energy consumption by AOP on the overall energy requirement still remains
300 unknown. Thus, a feasibility investigation is vital to the development of a new RO system
301 configuration with high rejection RO membranes and high pressure pumps. More importantly,
302 the development of a high rejection RO membrane with high permeability is needed to
303 improve the security of recycled water in potable reuse and make potable water reuse more
304 cost-effective.

305 **4. Conclusions**

306 Heat treatment was applied to three commercial and one prototype RO membrane to develop
307 a high rejection membrane with over 1.0-log NDMA removal. Among four untreated and
308 four heat-treated RO membranes, the heat-treated Prototype membrane was able to achieve a
309 1.1-log (92%) removal of NDMA. Nevertheless, permeability was considerably reduced by
310 heat treatment. DMA, an NDMA precursor, was well rejected by the heat-treated Prototype
311 membrane (>98%), and near complete rejection of high molecular weight secondary amines
312 (i.e., MOR, PYR and PIP) was achieved. In addition, rejection by the heat-treated Prototype
313 membrane remained stable under conditions of changing feed temperature and permeate flux.
314 When operated on UF-treated wastewater, permeability of the membrane remained high
315 (98%), as compared to the ESPA2 membrane (87%). Despite the very low permeability of the
316 heat-treated Prototype membrane, the results indicate that its enhanced ability to reject *N*-
317 nitrosamines could contribute to improved security of recycled water in potable water reuse.
318 Further development of highly selective RO membranes with high permeability is still needed
319 to ensure the feasibility of using these membranes at full scale.

320 **5. Acknowledgements**

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Table 1 – Physicochemical properties of the selected *N*-nitrosamines and secondary amines.

Compound	Molecular formula	Molecular weight [Da]	Log <i>D</i> at pH 8 ^a	pK _a ^a	Minimum projection area ^a [Å]
<i>N</i> -Nitrosamines					
NDMA	C ₂ H ₆ N ₂ O	74.1	0.04	3.5	19.5
NMEA	C ₂ H ₈ N ₂ O	88.1	0.40	3.4	21.9
NPYR	C ₄ H ₈ N ₂ O	100.1	0.44	3.3	25.0
NDEA	C ₄ H ₁₀ N ₂ O	102.1	0.75	3.3	25.4
NPIP	C ₅ H ₁₀ N ₂ O	114.1	0.89	3.3	27.2
NMOR	C ₄ H ₈ N ₂ O ₂	116.1	-0.18	3.1	25.2
Secondary amines					
DMA	C ₂ H ₇ N	45.1	-2.64	10.5	15.8
PYR	C ₄ H ₉ N	71.1	-2.80	11.4	22.5
DEA	C ₄ H ₁₁ N	73.1	-1.98	10.6	20.3
PIP	C ₅ H ₁₁ N	85.2	-1.69	10.4	25.6
MOR	C ₄ H ₉ NO	87.1	-1.03	8.5	21.5

^a Chemicalize (<http://www.chemicalize.org>).

Table 2 – Properties of the selected RO membranes.

Membrane	Treatment	Pure water permeability* [L/m ² hbar]	Conductivity rejection* [%]	Zeta potential at pH 7.9** [mV]
ESPA2	untreated	6.3 ± 0.2	99.0 ± 0.0	-51 ± 11
	heat-treated	5.0 ± 0.2	98.8 ± 0.3	-44 ± 8
ESPAB	untreated	4.3 ± 0.1	98.5 ± 0.1	-28 ± 3
	heat-treated	2.9 ± 0.04	97.3 ± 0.1	-35 ± 2
HYDRA	untreated	1.9 ± 0.03	99.3 ± 0.03	-18 ± 1
	heat-treated	1.2 ± 0.03	98.9 ± 0.2	-21 ± 2
Prototype	untreated	1.5 ± 0.02	99.8 ± 0.02	-33 ± 4
	heat-treated	1.0 ± 0.04	99.5 ± 0.1	-37 ± 2

*Pure water permeability and conductivity rejection were obtained from two replicates.

**Zeta potential was obtained from three replicates.

FIGURES

Fig. 1 – Rejection of NDMA and conductivity by untreated and heat-treated RO membranes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed temperature = 20.0 ± 0.1 °C, permeate flux = 20 L/m²h). Error bars show the range of two replicate experiments.

Fig. 2 – Correlation between NDMA rejection and pure water permeability of eight RO membranes. Error bars show the range of two replicate experiments.

Fig. 3 – Correlation between minimum projected area and the rejection of *N*-nitrosamine by (a) untreated ESPA2 and (b) heat-treated Prototype membranes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, permeate flux = 20 L/m²h, feed temperature = 20.0 ± 0.1 °C). Error bars show the range of two replicate experiments.

Fig. 4 – Correlation between minimum projected area and the rejection of secondary amines by (a) untreated ESPA2 and (b) heat-treated Prototype membranes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, permeate flux = 20 L/m²h, feed temperature = 20.0 ± 0.1 °C). Solid symbol indicates that the permeate concentration was below the instrumental detection limit. Error bars show the range of two replicate experiments.

Fig. 5 – Effects of feed temperature on *N*-nitrosamine rejection by (a) untreated ESPA2 and (b) heat-treated Prototype membranes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, permeate flux = 20 L/m²h).

Fig. 6 – Effects of permeate flux on *N*-nitrosamine rejection by (a) untreated ESPA2 and (b) heat-treated Prototype membranes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed temperature = 20.0 ± 0.1 °C).

Fig. 7 – RO treatment using a UF-filtered wastewater by (a) untreated ESPA2 and (b) heat-treated Prototype membranes (permeate flux = 40 L/m²h, feed temperature = 20.0 ± 0.1 °C). The initial TMP for ESPA2 and heat-treated Prototype membranes were 0.77 and 3.9 MPa, respectively.

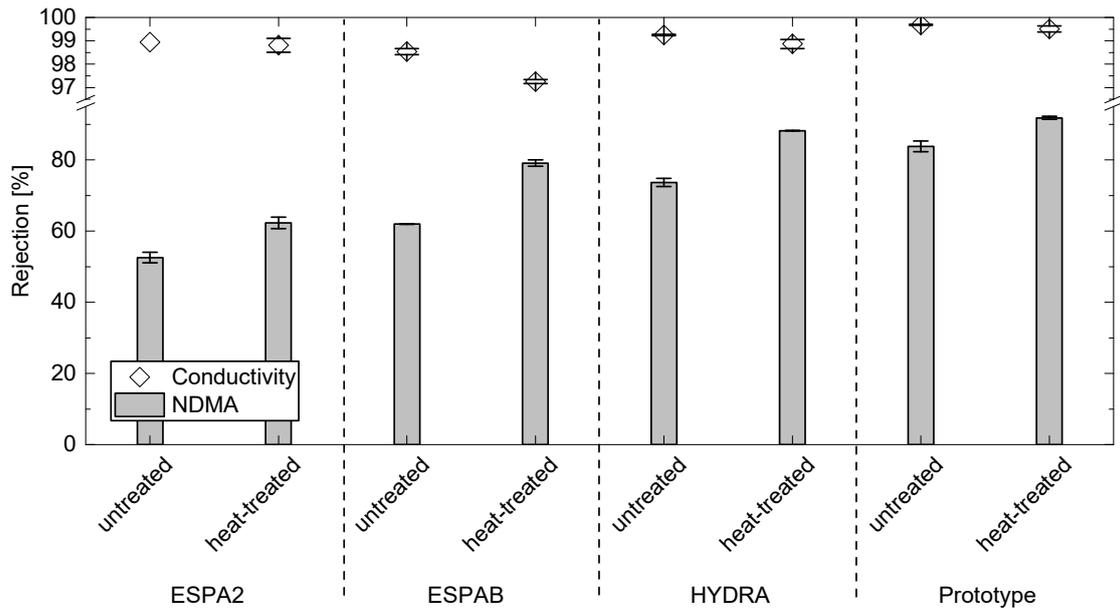


Fig. 1

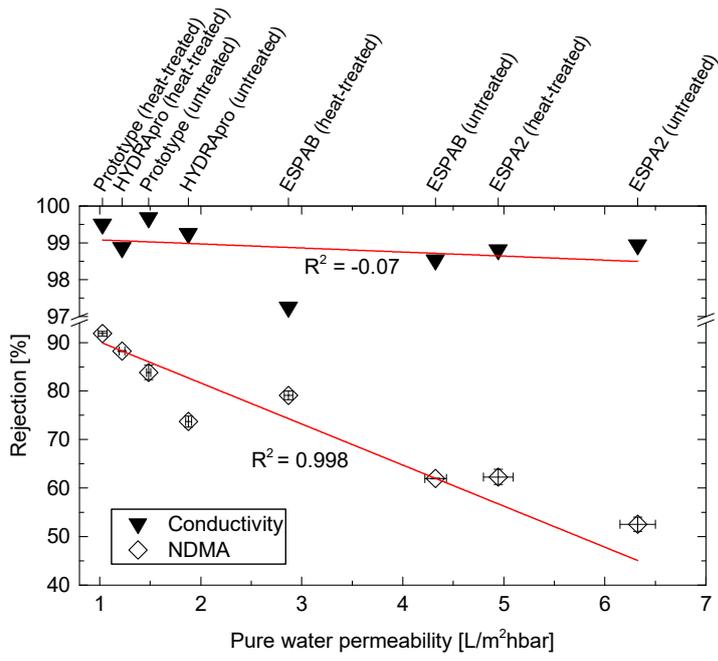


Fig. 2

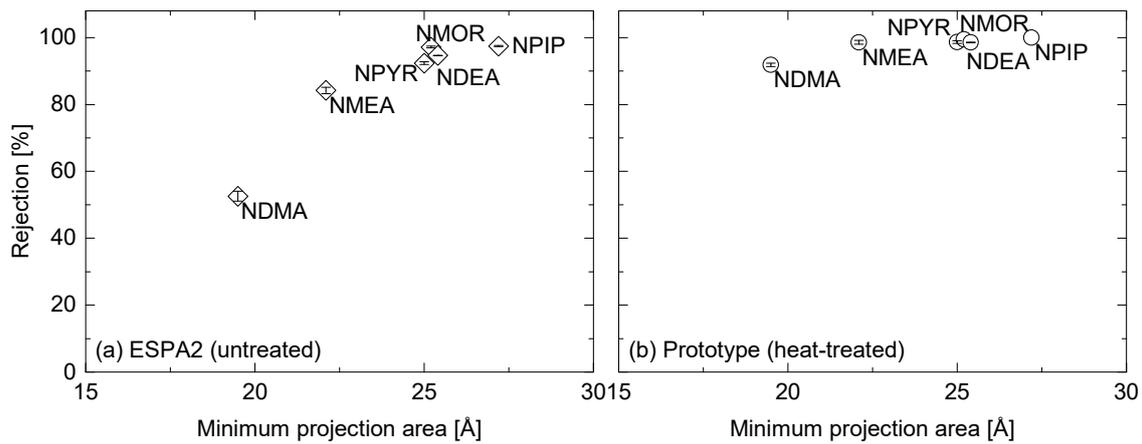


Fig. 3

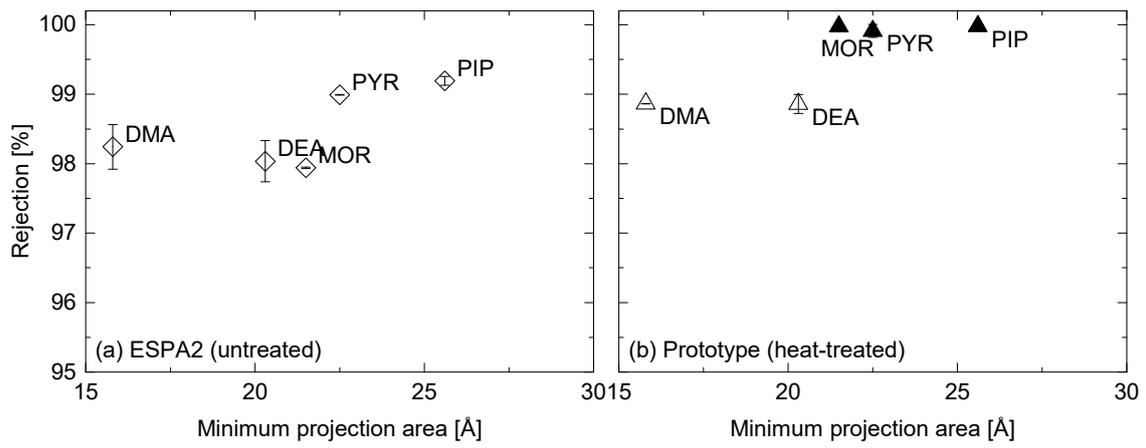


Fig. 4

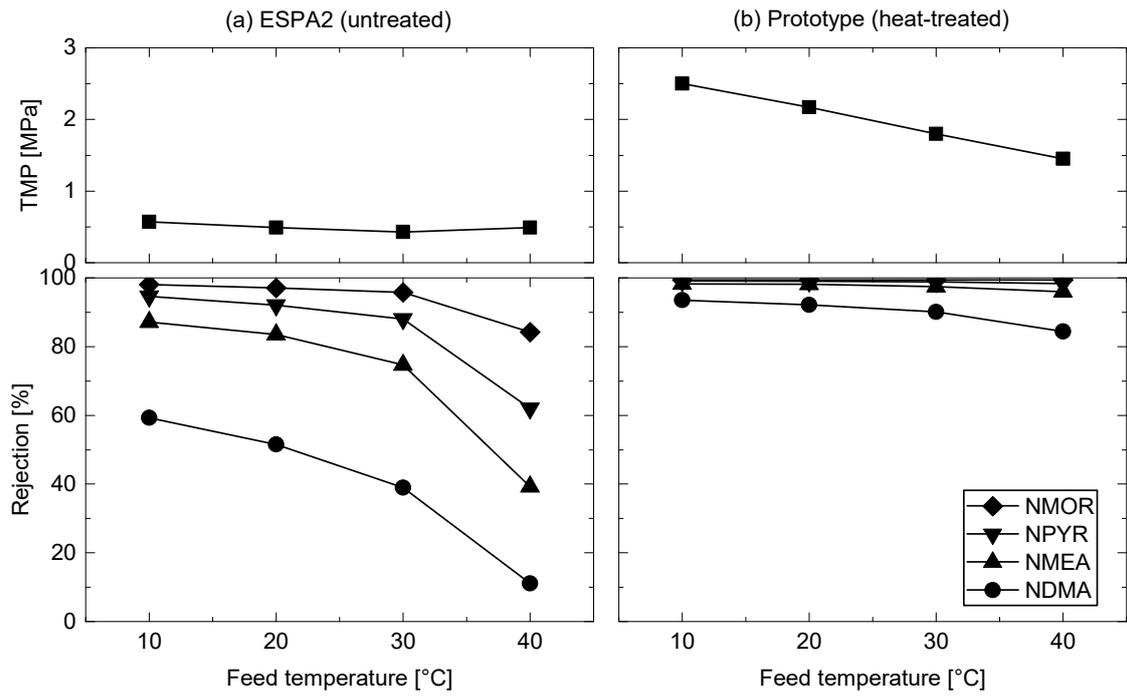


Fig. 5

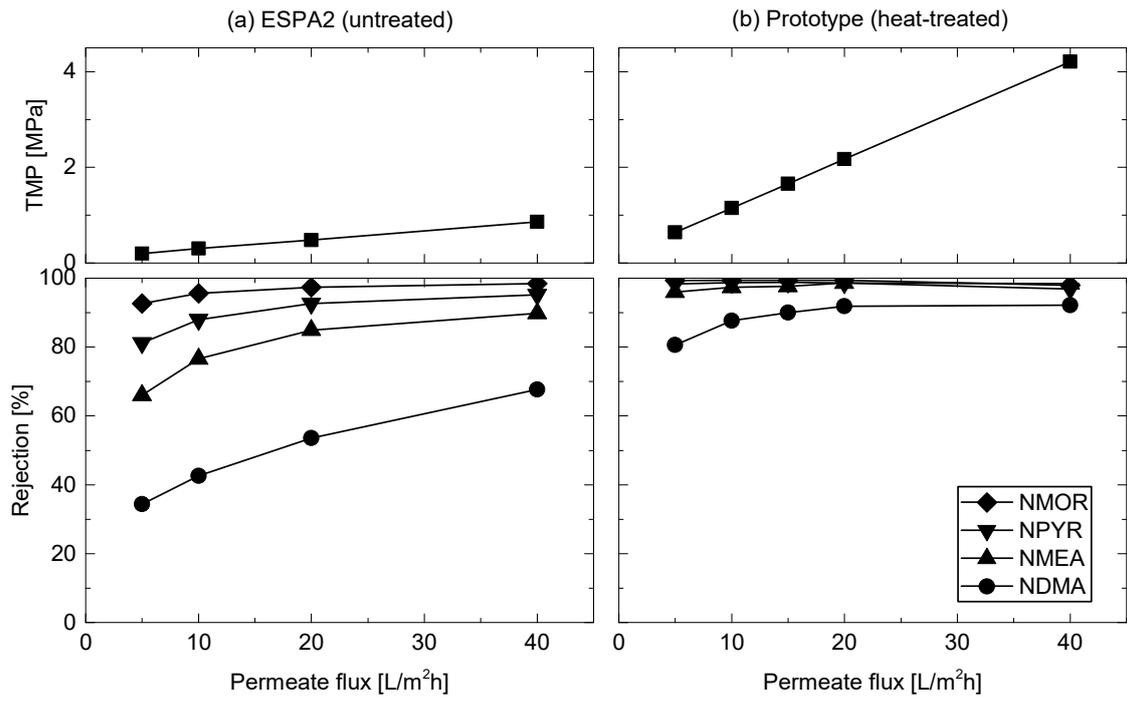


Fig. 6

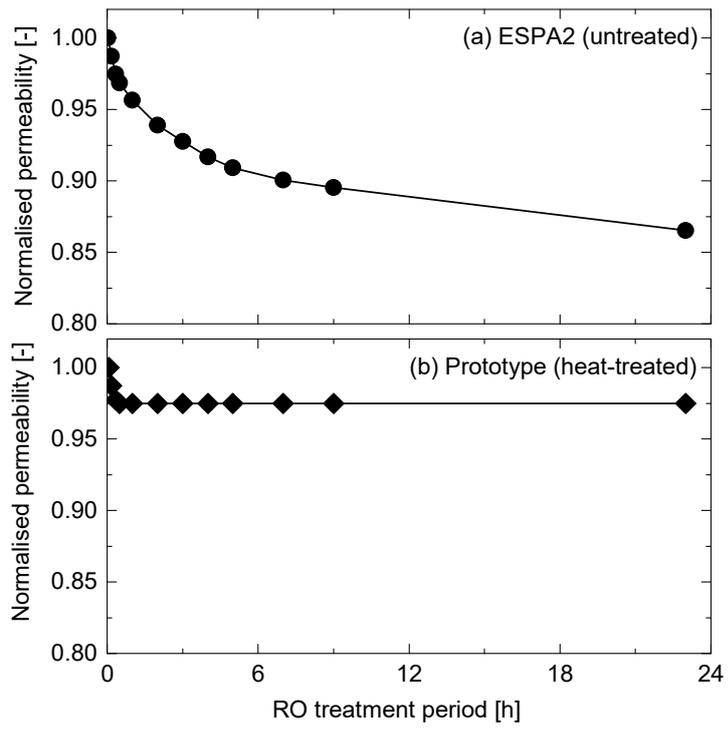


Fig. 7

1 **High rejection reverse osmosis membrane for**
2 **removal of *N*-nitrosamines and their precursors**

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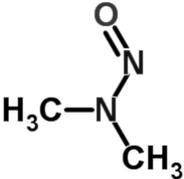
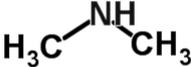
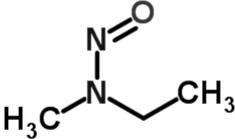
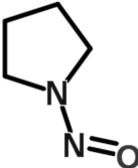
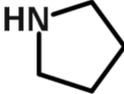
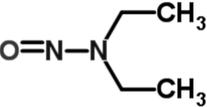
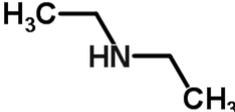
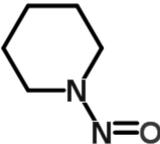
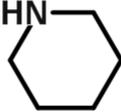
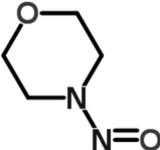
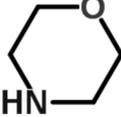
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12 **SUPPLEMENTARY MATERIAL**

13 _____
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Table S1 – Structure of the selected *N*-nitrosamines and secondary amines.

N-nitrosamines	Structure ^a	Secondary amine	Structure ^a
NDMA		DMA	
NMEA			
NPYR		PYR	
NDEA		DEA	
NPIP		PIP	
NMOR		MOR	

^aChemspider (<http://www.chemspider.com/>).

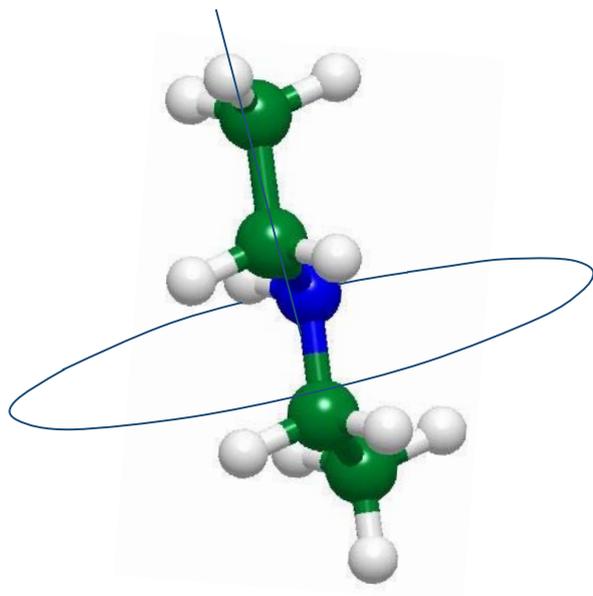


Fig. S2 – Schematic figure of minimum projection area. The line perpendicular to the circular disk represents the centre axis of the minimum projection area.

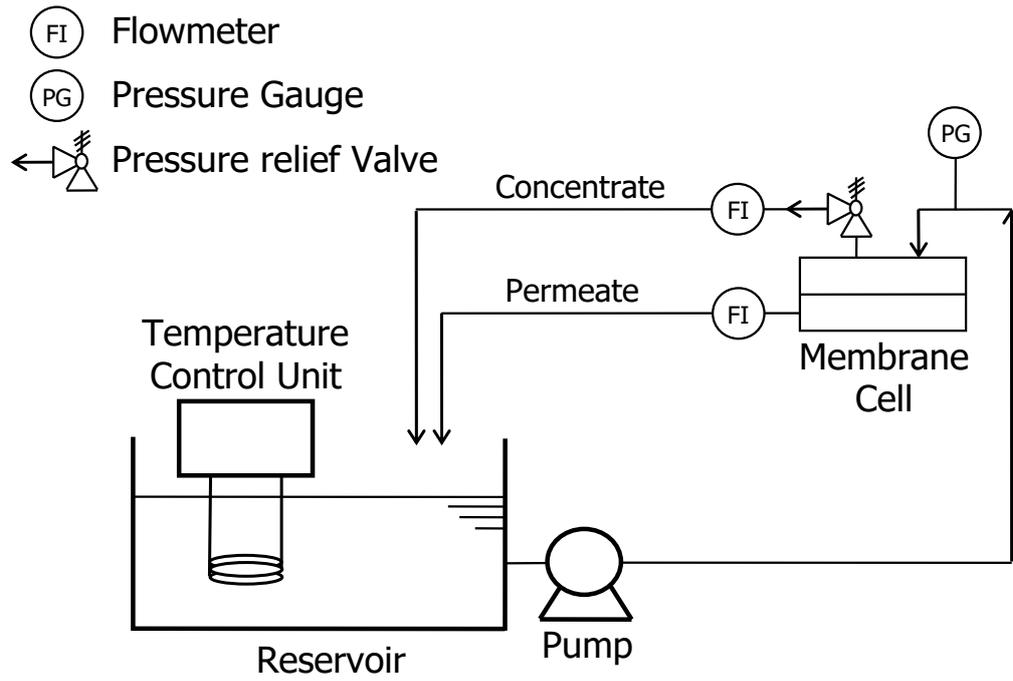


Fig. S3 – Schematic diagram of the cross-flow RO filtration system.

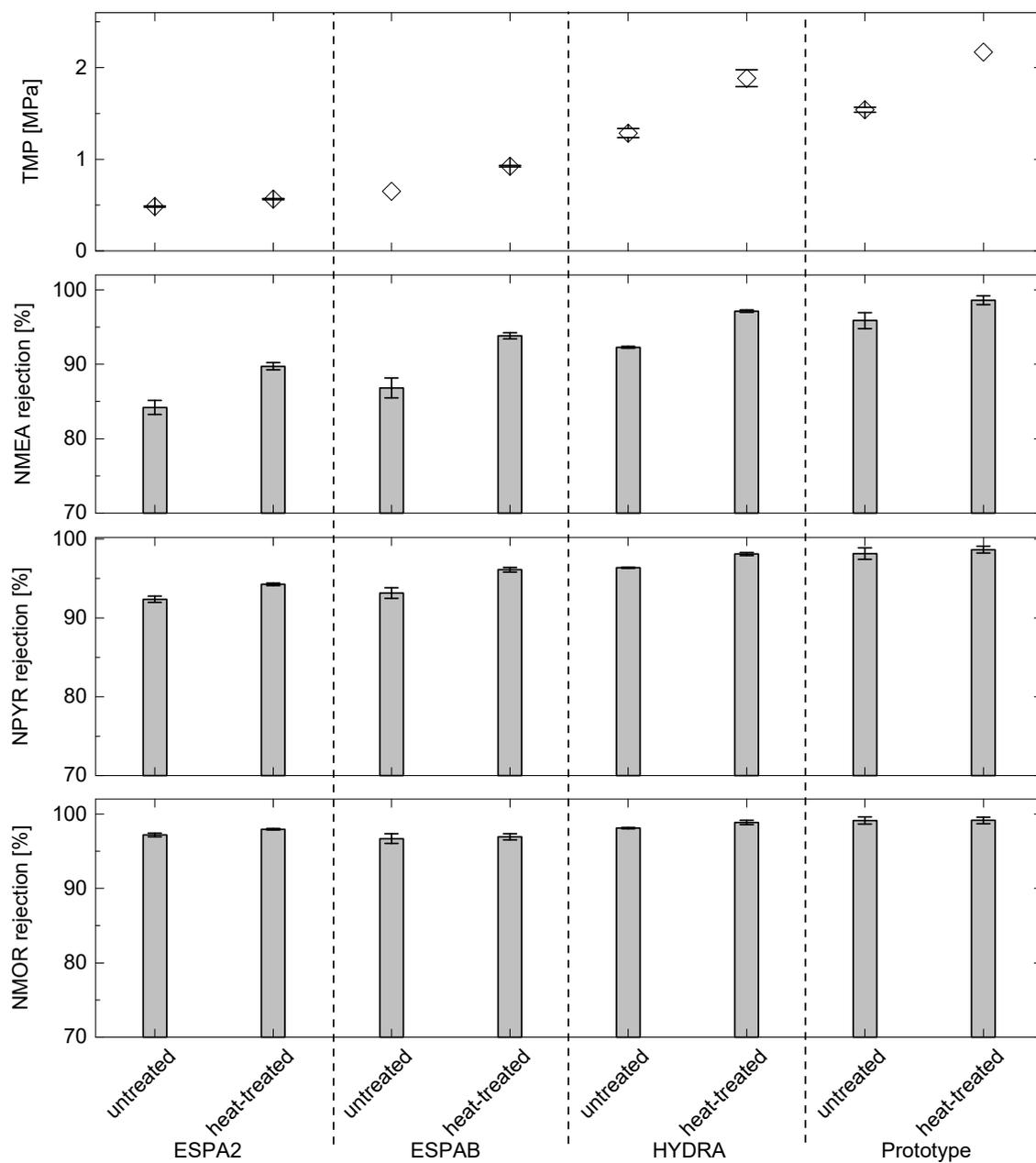


Fig. S4 – TMP and rejection of NMEA, NPYR and NMOR by untreated and heat-treated RO membranes (20 mM NaCl, 1 mM NaHCO₃, 1 mM CaCl₂, feed temperature = 20.0 ± 0.1 °C, permeate flux = 20 L/m²h).