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N-nitrosamine rejection by nanofiltration and reverse osmosis membranes: The importance of membrane characteristics

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Keywords

rejection, n, membrane, nanofiltration, characteristics, nitrosamine, reverse, osmosis, membranes, importance, GeoQuest

Disciplines

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Abstract

The influence of membrane characteristics on the rejection of eight N-nitrosamines was investigated using one nanofiltration (NF), one seawater reverse osmosis (SWRO) and six low pressure reverse osmosis (LPRO) membranes. The rejection of the two lowest molecular weight N-nitrosamines, namely N-nitrosodimethylamine (NDMA) and N-nitrosomethylethylamine (NMEA), varied in the range from 8–82% and 23–94%, respectively. In general, the rejection of NDMA and NMEA increased with decreasing membrane permeability. The impact of membrane characteristics became less important for higher molecular weight N-nitrosamines. Among the four LPRO membranes (i.e. ESPA2, LFC3, TFC-HR and 70LW) that are commonly used for water reclamation applications, similar rejections were obtained for NDMA (37–52%) and NMEA (69–82%). In addition, rejection values of NDMA and NMEA among two LPRO membranes (i.e. ESPA2 and 70LW) were almost identical when compared under variable permeate flux and feed temperature conditions. However, it is noteworthy that the ESPAB membrane could achieve very high rejection of NDMA (as high as 71%) despite having a similar permeability to the LPRO membranes. Results reported here suggest that membrane characteristics associated with permeability such as the pore size and thickness of the active skin layer can be a key factor determining N-nitrosamine rejection.

Keywords: Water recycling; N-nitrosamines; NDMA; reverse osmosis; nanofiltration.

1. Introduction

The occurrence of trace organic chemicals in reclaimed water has received significant scientific attention in recent years due to the practice of augmenting drinking water resources with reclaimed water by an increasing number of municipalities. These trace organic chemicals are numerous and although they have only been found in secondary treated effluent at very low concentrations (i.e. several tens of nanograms per litre or less) some might lead to adverse impacts on public health [1]. N-nitrosamines, which are an increasingly regulated group of disinfection by-products, are notable examples of these trace organic chemicals [1]. In recent years, extensive research has been conducted to elucidate the fate and formation of N-nitrosodimethylamine (NDMA) during water and wastewater treatment processes [2-3]. In addition to NDMA, N-nitrosomorpholine (NMOR) is also frequently found in treated wastewater, and NMOR concentration of as high as 12.7 µg/L has been detected in the wastewater from an industrial catchment [4]. Other N-nitrosamines that are often detected in treated effluent include N-nitrosomethylethylamine (NMEA), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP), N-nitrosodipropylamine (NDPA), N-nitrosodi-n-butylamine (NDBA) and N-Nitrosodiphenylamine (NDPhA) [5-6]. Most of these chemicals have been identified as probable human carcinogens [7-8]. For recycled water intended for augmenting drinking water resources, Australia has set guideline values for NDMA and NDEA at 10 ng/L and NMOR at 1 ng/L [9]. A notification level for NDMA, NDEA and NDPA has also been established at 10 ng/L by the California Department of Public Health [10].

In response to increasingly stringent regulations on reclaimed water quality, reverse osmosis (RO) treatment has been employed in most of the recent water reclamation systems intended for potable reuse [11]. Because the salinity of municipal wastewater is significantly lower than that of seawater, the so-called low pressure reverse osmosis (LPRO), and to a lesser extent nanofiltration (NF), membranes could also be considered for these applications. These membranes offer high separation performance but with a much lower applied pressure compared to seawater reverse osmosis (SWRO) membranes [12]. LPRO membranes have been reported to show high rejections of a wide range of trace organic chemicals [13-16]. Nevertheless, NDMA rejections by LPRO membranes observed at pilot- and full-scale plants are often low and highly variable [1].

70   Although most LPRO membranes available to date are able to achieve NaCl rejection of more

71   than 99% under similar recovery and flux conditions [17], there are no specific criteria for

72   selecting LPRO membranes in terms of the rejection of trace organic chemicals including N-

73   nitrosamines. Several laboratory-scale studies have investigated the rejection of N-

74   nitrosamines by several LPRO membranes in pure water matrices and reported NDMA

75   rejections to be in the range of 45 – 70% and the rejection of the other N-nitrosamines to be

76   over 75% [5, 18-19]. On the other hand, a recent laboratory-scale study carried out by Fujioka

77   et al. [20] demonstrated that LPRO membranes specifically designed for boron removal (such

78   as the ESPAB) may achieve as high as 80% NDMA rejection. These studies suggest that a

79   considerable variation in the rejection of N-nitrosamines exists amongst the LPRO

80   membranes. Operating conditions (such as feed pH, feed salt concentration, feed temperature

81   and permeate flux) can significantly influence the rejection of low molecular weight N-

82   nitrosamines including NDMA [5, 18]. Because the reported rejection values currently

83   available in the literature were obtained under different filtration conditions, it is unclear

84   whether the significant variation in the rejection of NDMA by LPRO membranes can also be

85   attributed to intrinsic differences in separation efficiency among the membranes.

86   The aim of this study was to evaluate the impact of membrane characteristics on N-

87   nitrosamine rejection. This investigation was carried out with eight NF and RO membranes,

88   with a specific focus on LPRO membranes used for water reclamation applications. The

89   rejection of N-nitrosamines was further examined under various permeate flux and feed

90   temperatures to elucidate the impact of operating conditions on the rejection of N-

91   nitrosamines and the underlying rejection mechanisms.

2. Materials and methods

2.1. RO membranes

94   Eight NF/RO membranes were selected for this study. They are thin film composite

95   membranes with a thin polyamide active skin layer on a porous polysulfone supporting layer.

96   The NF90 and ESPA1 membranes are typically used for brackish water treatment. The

97   ESPA2, LFC3, TFC-HR and 70LW are LPRO membranes which have been widely employed

98   for water reclamation applications [1, 21-23]. The ESPAB is another LPRO membrane which

99   is particularly designed to achieve a high rejection of boron during second pass seawater

100 desalination. A SWRO membrane (namely SWC5) was also used in this study. The nominal
101 salt rejection values of these membranes are summarised in Table 1. It is noteworthy that for
102 comparison purposes, the pure water permeability values of the different membranes were
103 measured under the same filtration condition (Table 1). Given the variety of membranes used
104 in this study, our filtration condition is not necessarily identical to the filtration protocol used
105 by each manufacturer to specify the performance of their membranes. Moreover, membrane
106 properties such as permeability are not always uniform in a membrane sheet. As a result, the
107 pure water permeability values reported in Table 1 may differ from what specified by the
108 manufacturer by up to 20%.

109 **Table 1**: Properties of the membranes used in this study (salt rejection values were specified
110 by the manufacturers).

Membrane	Membrane type	Manufacturer	NaCl rejection [%]	MgSO$_4$ rejection [%]	Pure water permeability [f] [L/m^{2}hbar at 20°C]	Contact angle [g] [°]
NF90	NF	Dow/Filmtec	-	> 97[e]	12.6 (±0.2)	69
ESPA1	LPRO	Hydranautics	99.3[a]	-	8.1 (±0.3)	61
ESPA2	LPRO	Hydranautics	99.6[a]	-	5.2 (±0.2)	53
LFC3	LPRO	Hydranautics	99.7[a]	-	2.9 (±0.3)	35
TFC-HR	LPRO	KMS	99.6[b]	-	2.8 (±0.3)	52
70LW(TML)	LPRO	Toray	99.7[c]	-	2.5 (±0.2)	41
ESPAB	LPRO	Hydranautics	99.3[a]	-	4.3 (±0.5)	47
SWC5	SWRO	Hydranautics	99.8[d]	-	1.9 (±0.1)	61

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

112 [b] Filtration condition: 2,000 ppm NaCl, 1.55 MPa, 25 °C and pH 7.5.

113 [c] Filtration condition: 2,000 ppm NaCl, 1.55 MPa, 25 °C and pH 7.0.

114 [d] Filtration condition: 32,000 ppm NaCl, 5.5 MPa, 25 °C and pH 6.5 - 7.0.

115 [e] Filtration condition: 2,000 ppm $MgSO_4$, 0.48 MPa, 25 °C and pH 8.
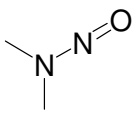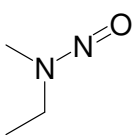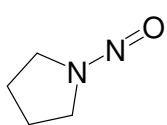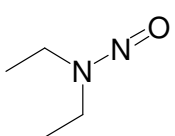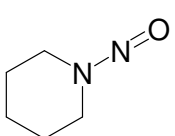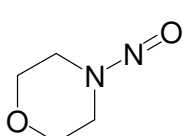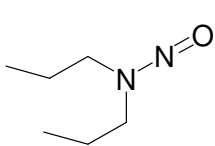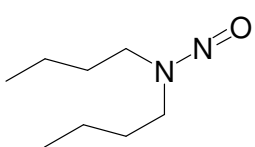
116 [f] Determined with Milli-Q water at 1,000 kPa and 20 °C feed temperature. Errors represent
117 the standard deviation of two replicates.

118 **2.2.** *[g] Measured with a Rame-Hart Goniometer (Model 250, Rame-Hart,*
119 *Netcong, NJ, USA) using the standard sessile drop* **Chemicals**

120 Eight N-nitrosamines with molecular weight in the range from 74 to 158 g/mol were used in
121 this study. Their molecular structures and molecular weights are summarised in Table 2. They
122 were of analytical grade and were purchased from Sigma-Aldrich (St Louis, MO, USA). A
123 stock solution was prepared in pure methanol at 10 mg/L of each N-nitrosamine. Eight
124 deuterated N-nitrosamines used as surrogates include N-nitrosodimethylamine-D6, N-
125 nitrosomethylethylamine-D3, N-nitrosopyrrolidine-D8, N-nitrosodiethylamine-D10, N-
126 nitrosopiperidine-D10, N-nitrosomorpholine-D8, N-nitrosodipropylamine-D14 and N-
127 nitrosodi-n-butylamine-D9. These deuterated chemicals were supplied by CDN isotopes
128 (Pointe-Claire, Quebec, Canada). A surrogate stock solution was also prepared in pure
129 methanol at 100 µg/L of each deuterated N-nitrosamine. The stock solutions were always kept
130 at -18 ºC in the dark and were used within 1 month of preparation. Chemicals selected for
131 background electrolytes (NaCl, $CaCl_2$ and $NaHCO_3$) were also of analytical grade and were
132 supplied by Ajax Finechem (Taren Point, NSW, Australia).

133 **Table 2:** Physicochemical properties of the selected N-nitrosamines.

Compound	Structure	Molecular formula	Molecular weight [g/mol]	Low K_{ow}[a] [-]	Dipole moment[b] [Debye]

NDMA		$C_2H_6N_2O$	74.05	-0.64	3.71
NMEA		$C_2H_8N_2O$	88.06	-0.15	3.71
NPYR		$C_4H_8N_2O$	100.06	0.23	3.74
NDEA		$C_4H_{10}N_2O$	102.08	0.34	3.72
NPIP		$C_5H_{10}N_2O$	114.08	0.74	3.73
NMOR		$C_4H_8N_2O_2$	116.06	-1.39	2.68
NDPA		$C_6H_{14}N_2O$	130.11	1.35	3.77
NDBA		$C_8H_{18}N_2O$	158.14	2.31	3.82

134   [a] GSI chemical properties database (GSI ENVIRONMENTAL INC), http://www.gsi-
135   net.com/en/publications/gsi-chemical-database.html.

2.3. [b] Millsian 2.1 software (Millsian INC).

Membrane filtration system

138   A bench-scale cross flow filtration system was used for this investigation (Figure 1). The

139   system mainly comprises a stainless steel reservoir, high pressure pump (Hydra-Cell, Wanner

140   Engineering Inc., Minneapolis, MN, USA), stainless steel membrane cell, and bypass and

141   back-pressure valves (Swagelok, Solon, OH, USA). The membrane cell holds a 4 cm × 10 cm

142   flat-sheet membrane with a channel height of 2 mm. During the system operation, the

143   permeate flow and retentate flow were continuously monitored with a digital flow meter

144   (FlowCal, GJC Instruments Ltd, Cheshire, UK) and rotameter, respectively. The feed solution

145   temperature was controlled with a chiller/heater unit (Neslab RTE 7, Thermo Scientific Inc.,

146   Waltham, MA, USA) using a cooling coil installed in the feed reservoir. The feed reservoir

147   and pipe work between the reservoir and membrane cell was fully covered with insulation

148   materials to maintain a constant feed temperature during filtration.

149
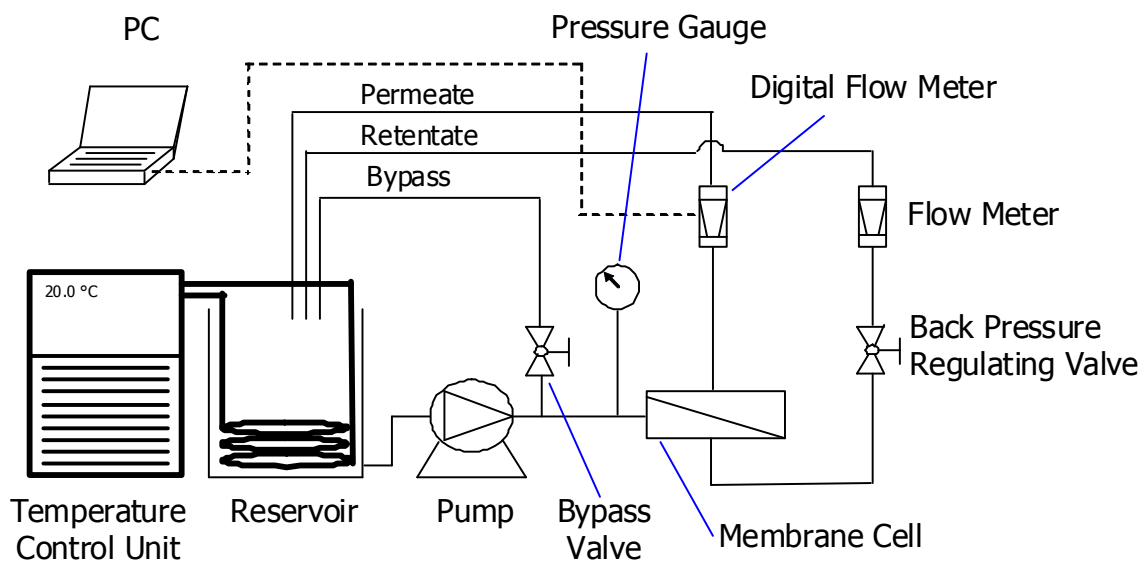
150   **Figure 1**

2.4. Filtration experiments

Prior to the experiment, each membrane sample was rinsed with a few litres of Milli-Q water to remove any water soluble preservatives on surface. Each filtration experiment started with a compaction step where the membrane was compacted at 1,800 kPa for at least 1 h using Milli-Q water feed. The cross-flow velocity was maintained at 0.42 m/s during the experiment. Unless otherwise stated, the feed temperature was maintained at 20±0.1 °C. After the permeate flux stabilised, the feed pressure was adjusted to 1,000 kPa and pure water permeability was measured using the feed pressure. The feed solution was then conditioned at 20 mM NaCl, 1mM $CaCl_2$ and 1 mM $NaHCO_3$ by adding the stock solution of background electrolytes. A similar composition of background electrolytes simulating treated wastewater effluent has been reported in previous studies [5, 24]. The stock solution of N-nitrosamines was spiked into the feed to make up an initial concentration of 250 ng/L of each target compound. The system was then operated at 20 L/m²h permeate flux, which is typically used for water reclamation applications [1]. Following at least 1 h of operation, 200 mL of feed and permeate samples were taken for analysis. Immediately following each sampling, the surrogate stock solution was dosed into each feed and permeate sample to make up 50 ng/L of each N-nitrosamine surrogate. For the experiments using variable permeate flux, the permeate fluxes was first set at 40 or 60 L/m²h and was stepwise decreased down to 5 L/m²h. Experiments with variable feed temperature started with low temperature (10 or 14 °C) and the feed temperature was stepwise increased up to 40 °C. In each experiment, the filtration system was operated for at least 1 h prior to any samplings to stabilise N-nitrosamine rejections. Conductivity and pH were both measured using an Orion 4-Star Plus pH/conductivity meter (Thermo scientific, USA).

2.5. N-nitrosamine analytical methods

N-nitrosamine concentrations in the permeate and feed samples were determined using a previously developed analytical method consisting of solid phase extraction (SPE), gas chromatography and determination using a mass spectrometer detector (GC/MS) [25]. Only a brief summary of the procedure is described here. Supelclean™ Coconut Charcoal SPE cartridge (2 g) purchased from Supelco (St Louis, MO, USA) was used for the SPE process. The extraction of N-nitrosamines to a SPE cartridge was performed at a flow rate of less than 5 mL/min. After drying the SPE cartridge with a gentle high purity nitrogen gas stream, the

182   SPE cartridges were eluted using 12 mL dichloromethane. The eluent was then added with 50

183   µL of toluene, and concentrated to 1 mL with a Turbovap LV (Caliper Life Sciences,

184   Hopkinton, MA, USA) under a gentle nitrogen gas stream. The concentration of N-

185   nitrosamines was quantified using an Agilent 7890A gas chromatograph coupled with an

186   Agilent 7000B triple quadrupole mass spectrometer using electron ionisation. The

187   quantitative detection limits of this analytical technique are 5 ng/L for NDMA, NDEA and

188   NDPA and 10 ng/L for NMEA, NPYR, NPIP, NMOR and NDBA.

189   *2.6. Transport model description*

190   A numerous number of previous studies reported in the literature have been carried out based

191   on the irreversible thermodynamics model [26]. Kedem and Katchalsky described water (J_v)

192   and solute (J_s) flux through an NF/RO membrane with the following equations [27]:

193
$$J_v = L_p\left(\Delta P - \sigma\Delta\pi\right) \tag{1}$$

194
$$J_s = P_s\Delta x\frac{d}{dx}C + \left(1-\sigma\right)CJ_v \tag{2}$$

195   where L_p is pure water permeability; ΔP is pressure difference between the feed and permeate

196   sides; σ is reflection coefficient; $\Delta\pi$ is osmotic pressure difference between the feed and

197   permeate sides; P_s is solute permeability coefficient; Δx is membrane thickness; x is position

198   in a pore from inlet; and C is solute concentration. The reflection coefficient (σ) represents

199   the fraction of solute reflected by the membrane in convective flow [28]. Equation 2 is

200   integrated with boundary limits ($x = 0$, $C = C_p$ and $x = \Delta x$, $C = C_m$) and is described with the

201   following Spiegler-Kedem equations [29]:

202
$$R_{real} = 1 - \frac{C_p}{C_m} = \frac{\sigma\left(1-F\right)}{\left(1-\sigma F\right)} \tag{3}$$

203
$$F = \exp\left(-\frac{\left(1-\sigma\right)}{P_s}J_v\right) \tag{4}$$

204   where C_p and C_m are permeate and membrane concentration, respectively. Because solute

205   concentration in the feed (C_b) can be obtained from experiments, the real rejection (R_{real}) is

206   calculated using the observed rejection ($R_{obs}=1-C_p/C_b$) as follows [30]:

207
$$R_{real} = \frac{R_{obs} \exp\left(\dfrac{J_v}{k}\right)}{1 + R_{obs}\left[\exp\left(\dfrac{J_v}{k}\right) - 1\right]}$$
(5)

208   where k is mass transfer coefficient. The value of k is calculated by the Sherwood number

209   (Sh) using the following Grover equation [31]:

210
$$Sh = \frac{d_h k}{D} = 0.664\,\text{Re}^{0.5}\,Sc^{0.33}\left(\frac{d_h}{L}\right)^{0.33}$$
(6)

211   where Reynolds number (Re) = ($d_h u/v$), Schmidt number (Sc) = (v/D), d_h = hydraulic

212   diameter, u = feed velocity, v = kinetic viscosity and D = diffusion coefficient. Further details

213   of the calculation are also available elsewhere [18].

3. Results and discussion

214

3.1. *N-nitrosamine rejection by NF/RO membranes*

215

216   3.1.1. N-nitrosamine rejection

217   The rejection of low molecular weight N-nitrosamines (i.e. NDMA and NMEA) by the eight

218   NF/RO membranes used in this study varied significantly in the range from 8 – 82% and 23 –

219   94%, respectively (Figure 2). The type of membrane was less significant for other N-

220   nitrosamines with higher molecular weights. NDPA and NDBA, which are the two largest N-

221   nitrosamines selected in this study, were rejected by approximately 70% by the NF90 and

222   over 90% by any of the RO membranes. A small but discernible variation in the rejection of

223   N-nitrosamines was observed among the four LPRO membranes (i.e. ESPA2, LFC3, TFC-

224   HR and 70LW) which have been widely used for water reclamation applications. For

225   example, NDMA rejection by these membranes ranged from 37% to 52%. The variation was

226   less apparent for NMEA (69-82%) followed by NPYR (84-94%) and NDEA (86-95%), and

227   was negligible for all the other N-nitrosamines. The results reported here suggest that the

228   rejections of N-nitrosamines by LPRO membranes commonly used for water recycling

229   applications under an identical filtration condition may differ from one another by about 15%

230   despite the similarity in their nominal NaCl rejection values (Table 1). In other words, the

3

231   nominal salt rejection value specified by the manufacturers may be not an appropriate

232   criterion to accurately predict the rejection of low molecular weight N-nitrosamines by LPRO

233   membranes. It is noteworthy that a model aquatic solution was used in this study. The

234   presence of effluent organic matter in treated effluent can lead to membrane fouling, which

235   may exert a small influence on the rejection of N-nitrosamines and inorganic salts by NF/RO

236   membranes [20].
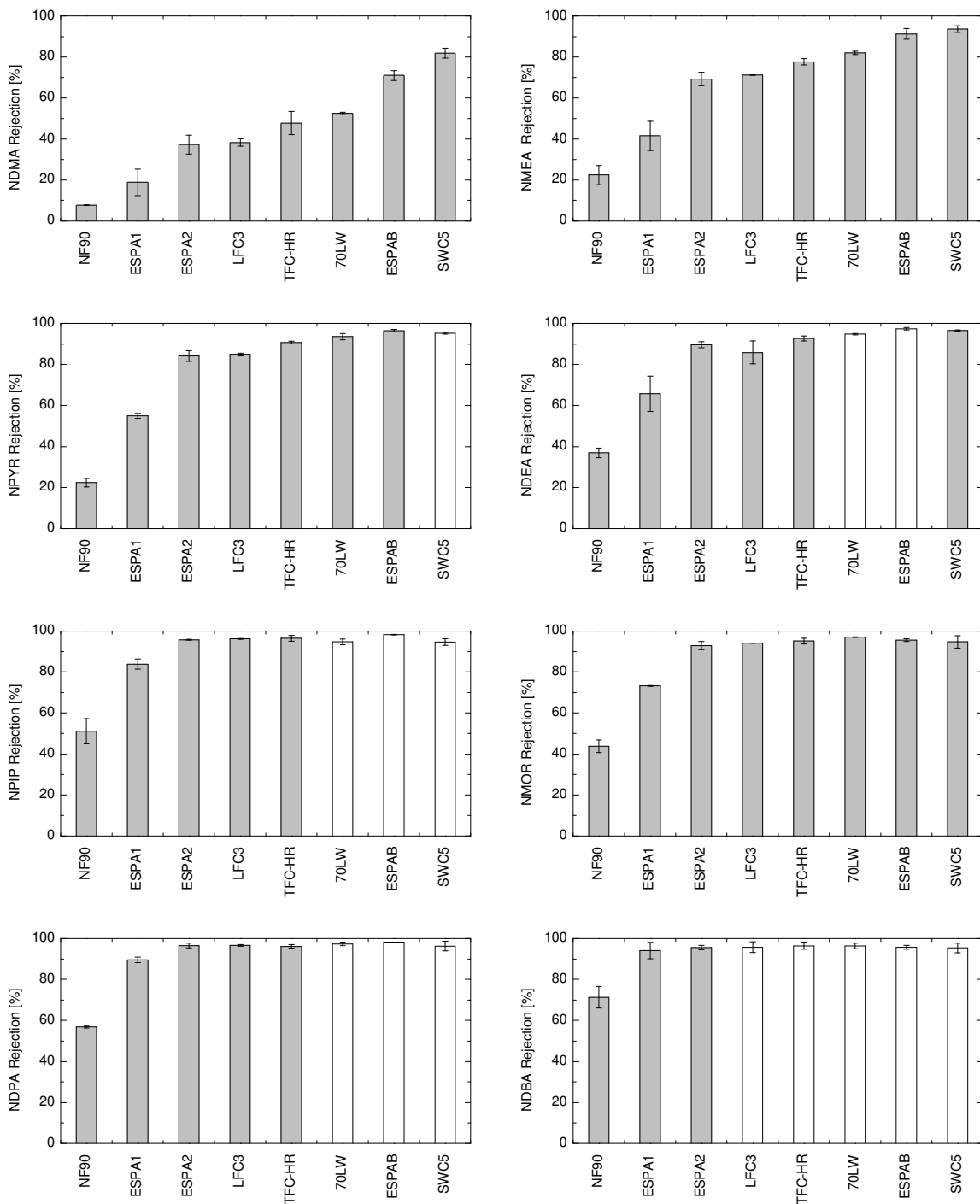
237
238 In general, the rejection of N-nitrosamines by a given membrane increased in the increasing
239 order of their molecular weight (Figure 2). In addition to molecular weight, other solute
240 properties such as charge, hydrophobicity and dipole moment can be also important factors
241 determining solute rejections [32-35]. Van der Bruggen et al. [32] investigated the rejection
242 of various organic compounds using NF membranes and reported that, for compounds with

243 similar molecular weights, charged and hydrophilic compounds could be better rejected than
244 hydrophobic compounds. This is because the apparent size of charged and hydrophilic
245 compounds becomes larger due to hydration once they are in an aqueous solution. On the
246 other hand, adsorption followed by diffusion could be a considerable transport mechanism for
247 hydrophobic compounds to permeate NF/RO membranes [32, 34]. It has also been reported
248 that compounds with higher dipole moments could have a lower rejection in comparison to
249 another compound of similar molecular size but with a lower dipole moment [33, 35].
250 Nevertheless, the eight N-nitrosamines investigated here are neutral, quite hydrophilic and
251 have very similar dipole moment (Table 2) and thus molecule weight (rather than charge,
252 hydrophobicity, and dipole moment) appears to be the most important parameter when
253 evaluating the rejection of N-nitrosamines by NF/RO membranes.

254 3.1.2.   Impact of membrane permeability
255 The separation performance of NF/RO membranes can be evaluated by pure water
256 permeability and solute rejection. A comparison between these parameters revealed that the
257 rejection of NDMA and NMEA was inversely proportional to membrane permeability
258 (Figure 3). For example, the SWC5 membrane revealed a high NDMA rejection (82%) but
259 low permeability (1.9 L/m^{2}hbar), while the NF90 membrane revealed a high permeability (13
260 L/m^{2}hbar) but negligible rejection (8%). Permeability and N-nitrosamine rejection values
261 obtained using the LPRO membranes were both within these limits of the SWC5 and NF90
262 membranes. Importantly, among the LPRO membranes the ESPAB membrane revealed a
263 remarkably higher rejection of NDMA (71%) and NMEA (91%) despite of its relatively high
264 permeability (4.3 L/m^{2}hbar). In fact, the exclusion of the ESPAB membrane data improved
265 the correlation of the rejections and permeability significantly, changing the coefficient of
266 determination (R^2) of the linear regression between NDMA or NMEA rejection and the
267 membrane permeability from 0.61 to 0.70 and from 0.86 to 0.95, respectively. The
268 underlying reason for this notably better performance of the ESPAB with respect to NDMA
269 and NMEA rejection observed here is currently unknown and is the subject for a future study.

270 In the surface force-pore flow model, membrane permeability (L_p) increases with increasing
271 membrane pore size (r_p) and with decreasing the thickness of the membrane active layer (Δx)
272 as described with the Hagen-Poiseuille equation [36-37].

273
$$L_p = \frac{r_p^2 A_k}{8\mu\Delta x} \qquad\qquad (7)$$

274 where A_k is membrane porosity; and μ is viscosity of water. Because the changes in
275 membrane pore size and the thickness of the membrane active layer also affect solute
276 rejection [37], it can be hypothesized that the variation in NDMA and NMEA rejection by
277 these NF/RO membranes is associated with the difference in the properties (i.e. r_p and Δx) of
278 these membranes.
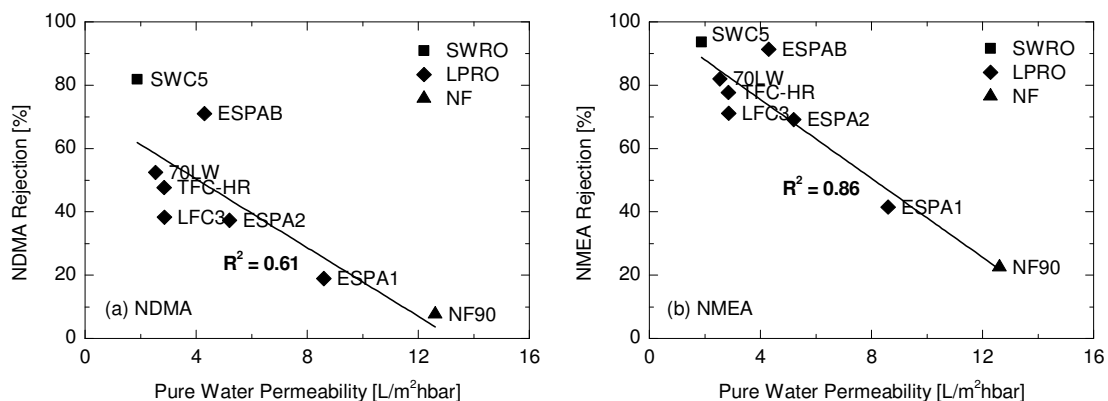
279 *3.2.*
280 *Effects of filtration conditions*

281 3.2.1. Permeate flux

282 In general, solute rejection increases when water permeate flux increases, because water flux
283 increases with applied feed pressure while the applied pressure has only a negligible impact
284 on solute flux [38]. As expected, an increase in permeate flux led to the increased rejection of
285 conductivity and N-nitrosamines (Figure 4). For the 70LW membrane, permeate flux of 60
286 L/m²h was excluded from the experiment due to the feed pressure limitation of the filtration
287 setup. For both membranes, the impact of the changes in permeate flux on N-nitrosamine
288 rejection was stronger in lower ranges (e.g. 5-10 L/m²h). In addition, the rejection of low
289 molecular weight N-nitrosamines was significantly affected by the changes in permeate flux.
290 For instance, NDMA rejection by the ESPA2 dropped from 53 to 36% when permeate flux
291 decreased from 42 to 10 L/m²h. The rejection trends observed in this investigation are
292 consistent with a previous study using the LPRO TFC-HR membrane [18]. In addition, the
293 difference in N-nitrosamine rejection value between the ESPA2 and 70LW membranes was

7

observed to be small (<11%) when compared at both 10 and 42 L/m^{2}h permeate flux (Figure
295　5).

(a) ESPA2

(b) 70LW
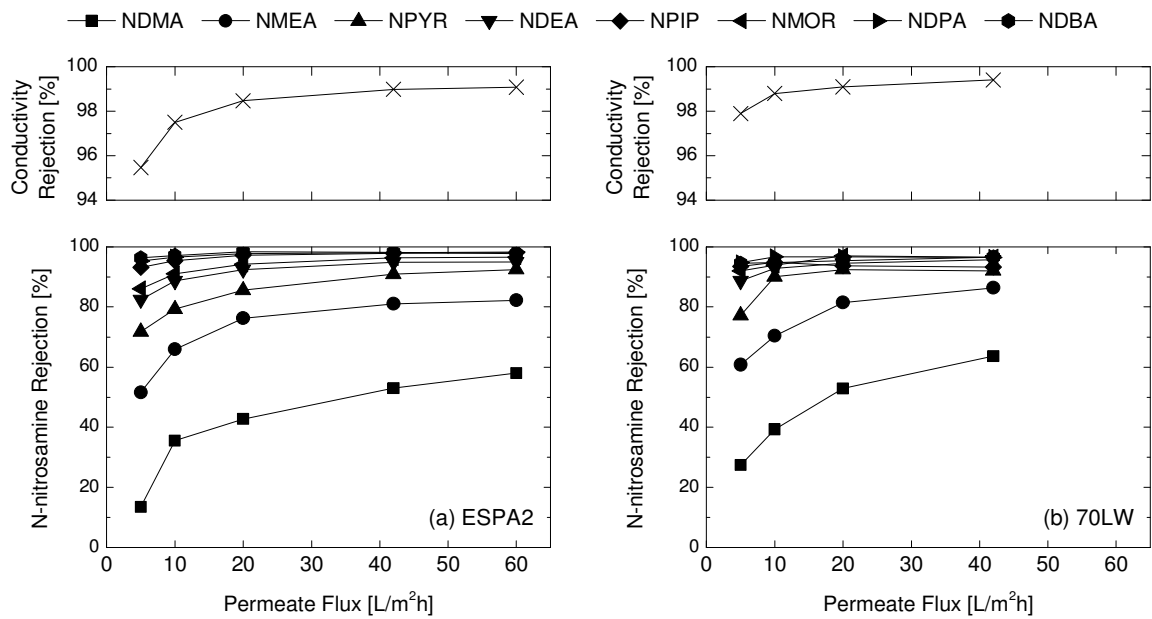
296
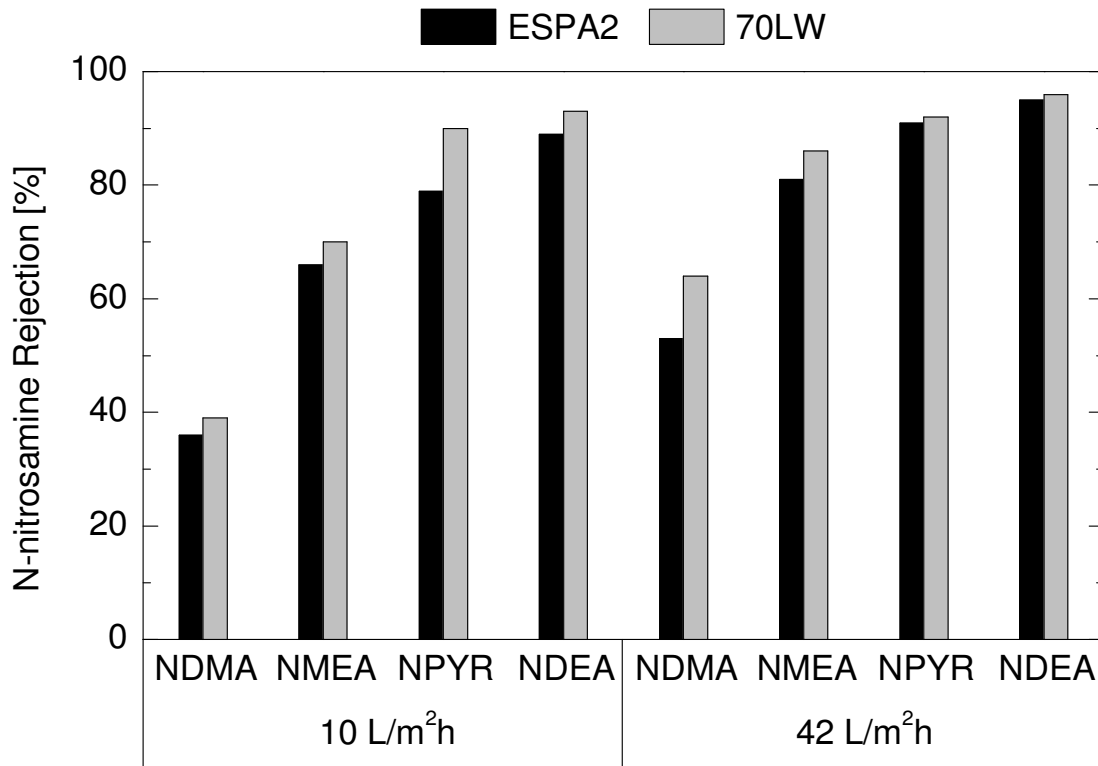
297

298　The real rejection of N-nitrosamines by the ESPA2 and 70LW membranes was well
299　described by the irreversible thermodynamic model (Figure 6). For the 70LW membrane,

300 NPYR, NPIP, NMOR, NDPA and NDBA were excluded from the modelling because some
301 of their permeate concentrations were below their analytical detection limits. The reflection
302 coefficient (σ) of all N-nitrosamines was generally high (>0.9) (Table 3) which is consistent
303 with a previous study using the TFC-HR membrane [18]. These observations suggest that
304 these LPRO membranes may be comparable in terms of N-nitrosamine rejection even in
305 different permeate flux conditions.
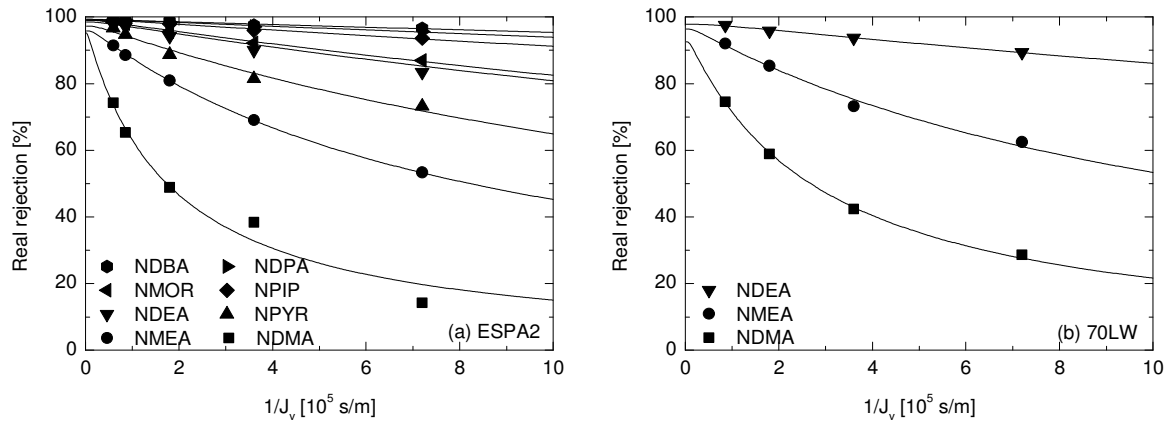
306
307 **Table 3:** Transport parameters of N-nitrosamines through the ESPA2, 70LW and TFC-HR
308 [18] membranes of the irreversible thermodynamics model.

N-nitrosamine	k [m/s]	σ [-]			P [m/s]		
		ESPA2	70LW	TFC-HR	ESPA2	70LW	TFC-HR
NDMA	2.26×10^{-5}	0.953	0.926	0.949	5.35×10^{-6}	3.32×10^{-6}	4.15×10^{-6}
NMEA	1.99×10^{-5}	0.958	0.963	0.968	1.14×10^{-6}	8.24×10^{-7}	1.07×10^{-6}
NPYR	1.99×10^{-5}	0.973	-	0.989	5.12×10^{-7}	-	6.74×10^{-7}
NDEA	1.99×10^{-5}	0.985	0.978	0.998	2.26×10^{-7}	1.47×10^{-7}	2.49×10^{-7}
NPIP	2.09×10^{-5}	0.993	-	-	9.25×10^{-8}	-	-
NMOR	2.18×10^{-5}	0.991	-	0.988	2.06×10^{-7}	-	1.99×10^{-7}

NDPA	2.02×10^{-5}	0.992	-	-	6.02×10^{-8}	-	-
NDBA	1.99×10^{-5}	0.990	-	0.983	4.33×10^{-8}	-	1.01×10^{-7}

309

310   3.2.2.   Feed temperature

311   An increase in feed temperature resulted in the decreased rejection of conductivity and N-

312   nitrosamines (Figure 7). For example, an increase in the feed temperature from 20 to 40 °C

313   led to a decrease in NDMA rejection by the ESPA2 and 70LW membrane from 41 to 15%

314   and from 52 to 22%, respectively. In response to the feed temperature increase, NMEA and

315   NPYR rejections also dropped significantly. The impact of feed temperature was less

316   pronounced with increasing their molecular weight, and the rejection of high molecular

317   weight N-nitrosamines (i.e. NDPA and NDBA) equally remained almost constant and high

318   (>94%) within the ranges of feed temperature tested here (Figure 7). When feed temperature

319   increases, the pore size within an active skin layer of membranes can enlarge slightly [39]

320   and the permeability coefficient of solutes also increases [28, 30], both of which cause more

321   solute passage through membranes. Thus, these combination effects may have decreased the

322   rejection of N-nitrosamines against the increase in feed temperature. Between the two LPRO

323   membranes, the difference in the rejection vales of NDMA, NMEA, NPYR and NDEA was

324   always less than 13% at the feed temperature of both 20 and 40 °C (Figure 8). The

325   observations reported here indicate that the impact of feed temperature on the rejection of N-

326   nitrosamines is similar among the LPRO membranes tested.

327

328
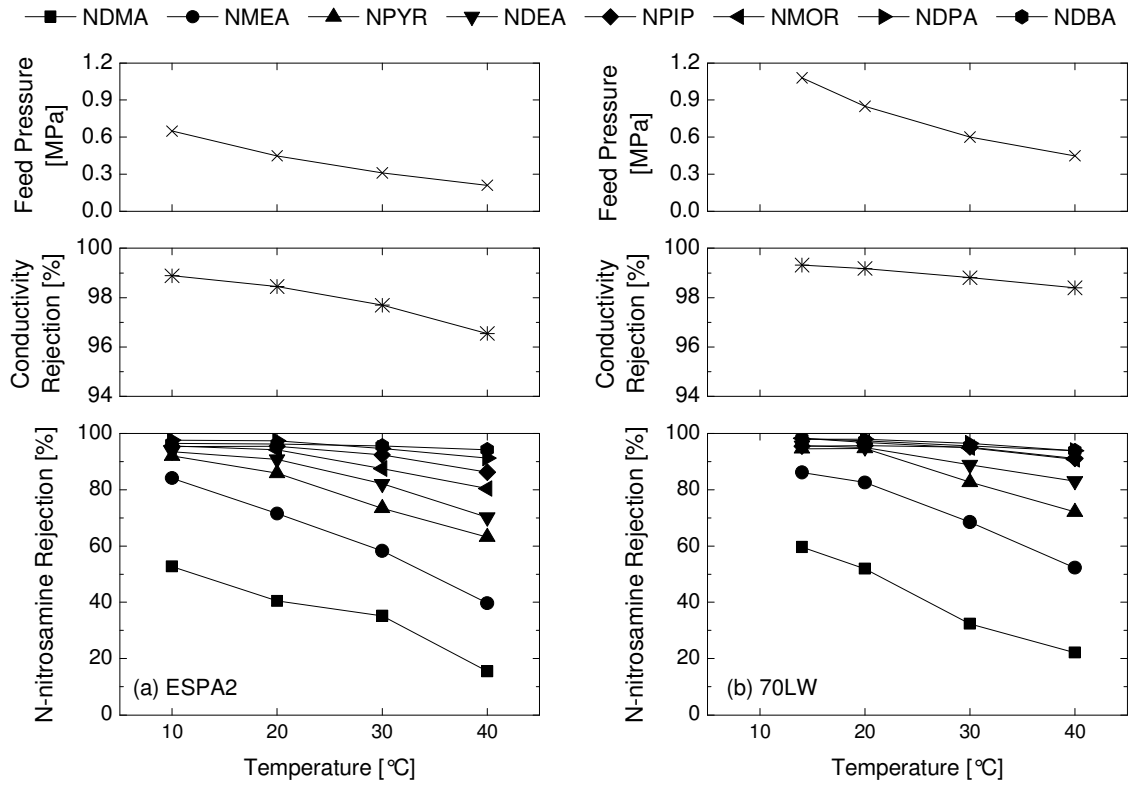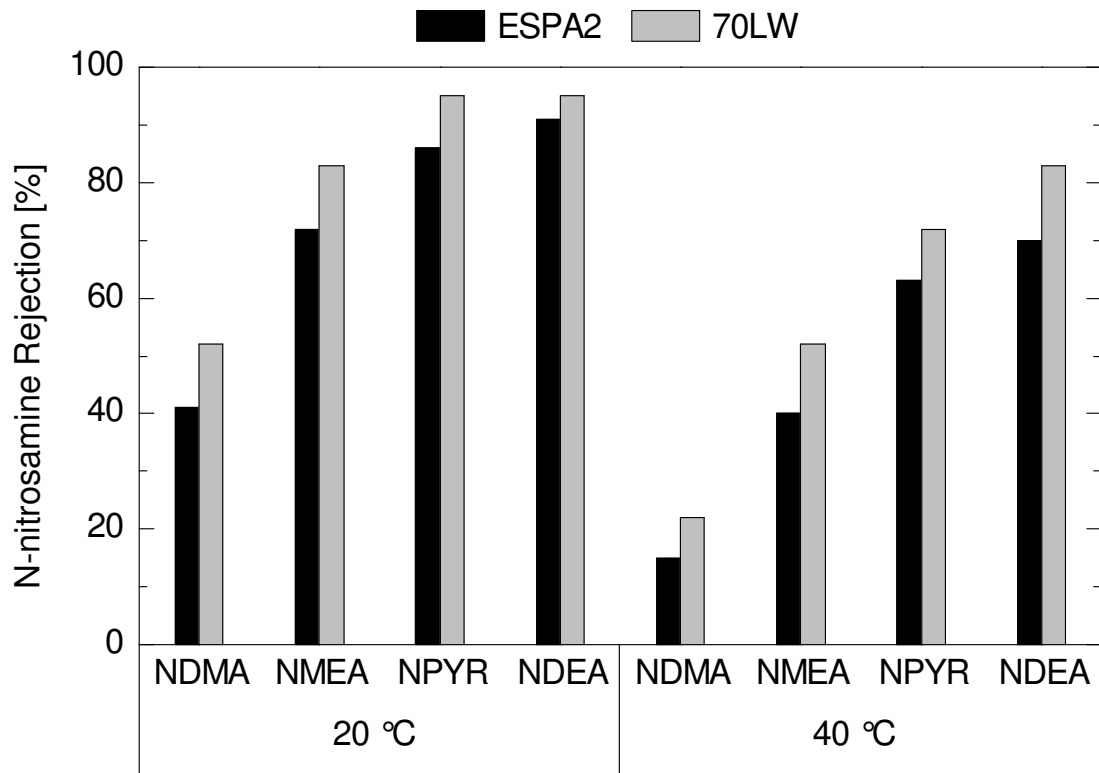
4. Conclusions

The rejection of NDMA by NF/RO membranes varied significantly in the range of 8-82% depending on the membrane and operating conditions. The impact of membrane characteristics was less apparent for higher molecular weight N-nitrosamines and the rejection of NPYR, NMOR, NDPA and NDBA were over 90% by any of the tested RO membranes. Using these NF/RO membranes, a correlation was found between membrane permeability and the rejection of low molecular weight N-nitrosamines (i.e. NDMA and NMEA). The variation in NDMA and NMEA rejections among the LPRO membranes frequently used for water reclamation applications (i.e. ESPA2, LFC3, TFC-HR and 70LW) was relatively small, at 37-52% and 69-82%, respectively. However, a high rejection of NDMA (71%) and NMEA (91%) was obtained with the ESPAB membrane which is also an LPRO membrane but is specifically designed for the removal of boron. Results reported here suggest the potential of using boron removal LPRO membranes (i.e. ESPAB) for wastewater recycling applications where NDMA concentration in the final water is a critical parameter under water quality regulations. Similar rejection behaviours of N-nitrosamines were obtained with two different LPRO membranes (i.e. ESPA2 and 70LW) when compared with variable permeate flux and feed temperature conditions. In particular, the rejection of low molecular weight N-nitrosamines such as NDMA and NMEA decreased significantly when the permeate flux decreased or the feed temperature increased. In practice, some variations in permeate flux and temperature are inevitable. Thus, the impact of permeate flux and solute temperature on the rejection of N-nitrosamines reported here has an important implication to full-scale operation of NF/RO systems for water reclamation applications. Results reported here also suggest that membrane properties associated with membrane permeability such as the pore size and thickness of the active skin layer might determine N-nitrosamine rejection. Thus, further work is necessary to elucidate the impact of physicochemical properties of NF/RO membranes on N-nitrosamine rejection.

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6. Nomenclatures

362   C_b concentration in the feed (ng/L)

363   C_m membrane concentration (ng/L)

364   C_p permeate concentration (ng/L)

365   d_h hydraulic diameter (m)

366   D diffusion coefficient (m^2/s)

367   J_s solute flux (m/s)

368   J_v water flux, permeate flux (m/s)

369   k mass transfer coefficient (m/s)

370   L the length of the membrane (m)

371   L_p pure water permeability (L/m^{2}h)

372   P_s solute permeability coefficient (m/s)

373   Re Reynolds number (-)

374   R_{obs} observed rejection (-)

375   R_{real} real rejection (-)

376   Sc Schmidt number (-)

377   Sh Sherwood number (-)

378   u feed velocity (m/s)

379   ΔP Pressure difference between the feed and permeate sides (Pa)

380   x position in a pore from inlet (m)

381   Δx membrane thickness (m)

382   σ reflection coefficient (-)

383    $\Delta \pi$ osmotic pressure difference between the feed and permeate sides (Pa)

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