1. **Reverse osmosis membrane composition, structure and performance modification by**

2. **bisulphite, iron(III), bromide and chlorite exposure**

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12.

13. **Abstract**

14. Reverse osmosis (RO) membrane exposure to bisulphite, chlorite, bromide and iron(III) was

15. assessed in terms of membrane composition, structure and performance. Membrane

16. composition was determined by Rutherford backscattering spectrometry (RBS) and membrane

17. performance was assessed by water and chloride permeation, using a modified version of the

18. solution-diffusion model. Iron(III) dosage in presence of bisulphite led to an autooxidation of

19. the latter, probably generating free radicals which severely damaged the membrane. It

20. comprised a significant raise in chloride passage (chloride permeation coefficient increased

21. 5.3– 5.1 fold compared to the virgin membrane under the conditions studied) rapidly. No

22. major differences in terms of water permeability and membrane composition were observed.

23. Nevertheless, an increase in the size of the network pores, and a raise in the fraction of

24. aggregate pores of the polyamide (PA) layer were identified, but no amide bond cleavage was

25 observed. These structural changes were therefore, in accordance with the transport

26 properties observed.

27

1. INTRODUCTION

29 Reverse osmosis (RO) membranes are commonly thin film composite (TFC) membranes

30 consisting in a polyamide (PA) active layer (~ 50 – 250 nm thickness), supported by an

31 asymmetric polysulphone support (~ 50 μm thickness) and a non-woven polyester fabric

32 backing (~ 300 μm thickness) (Petersen, 1993). The partitioning-diffusion process which

33 governs RO membranes water transport and solutes rejection takes place at the water-

34 membrane interface (PA active layer) and across the membrane (Urama and Mariñas, 1997).

35 The PA pore size distribution of RO membranes has been reported as bimodal, comprised of

36 smaller and larger pores (Kim et al., 2005). The later, referred as aggregate pores, have been

37 related to void space between polymer aggregates (Coronell et al., 2008) and their size has

38 been estimated in 1.0 – 1.6 nm in diameter (Saenz de Jubera et al., 2012). The smaller ones,

39 named network pores, have been associated to the interstitial space between polymer

40 branches within an aggregate (Coronell et al., 2008) and their diameter has been estimated in

41 0.4 – 0.8 nm (Saenz de Jubera et al., 2012). The ionization behaviour of functional groups in

42 the PA active layer, carboxylic and amine, has been modelled by an acid-base equilibrium with

43 the aqueous solution (Coronell et al., 2008). Ion probing experiments combined with

44 Rutherford backscattering spectrometry (RBS) have enabled the quantification of the

45 accessible deprotonated / protonated groups and thus, the determination of the associated

46 acid-base parameters, providing insights into the pore size distribution, as well as other

47 membrane properties like the total concentration of functional groups and the degree of

48 crosslinking, as shown in the work of Coronell et al. (2009).

49   RO membranes are able to produce almost pure water in a reliable way, rejecting nearly all

50   colloidal or dissolved matter from an aqueous solution (Fritzmann et al., 2007). RO energy

51   consumption, which has decreased significantly during the last decades, is the lowest among

52   seawater desalination technologies and is energetically advantageous for brackish water

53   desalination as well (Fritzmann et al., 2007). RO membranes capabilities together with their

54   maturity, have turned them into the best standard for desalination (Lin and Elimelech, 2015).

55   Nevertheless, the sensitivity of TFC RO membranes toward certain compounds represents a

56   main drawback nowadays. Indeed, the interaction of certain species with the PA active layer

57   can encompass morphological and chemical changes in the latter, which can result into

58   alterations of the RO membrane separation properties. These modifications can involve the

59   permeate quality to be out of specification and thus, the need to prematurely replace RO

60   membranes, with its associated cost.

61   It has been well reported in literature and it is recognised by membrane manufacturers that

62   free chlorine damages TFC RO membranes performance. In particular, manufacturers have

63   established maximum admissible concentrations to avoid membranes premature degradation

64   (<0.1 mg/L of free chlorine, being 200-1000 mg/L·h the threshold above which eventual

65   degradation may occur (Dow Water & Process Solutions, n.d.)) and recommend the use of a

66   reducing agent to neutralise it. Sodium metabisulphite, which forms sodium bisulphite in

67   water, has often been used because of its high cost-effectiveness when dechlorinating

68   (Fritzmann et al., 2007). Nevertheless, few works have been devoted to determine bisulphite

69   effects on RO membranes, particularly in presence of other substances naturally contained in

70   the water to be treated or added during the treatment itself (e.g. coagulation/flocculation

71   steps). (Nagai et al., 1994) reported the generation of oxidising agents when sodium bisulphite

72   was dosed in presence of heavy metal ions, chloride ion and dissolved oxygen in a neutral pH

73   solution, but their identification and their effects were not assessed. Sommariva et al. (2012)

74   reported an increased salt passage in a seawater RO plant where sodium bisulphite was

75 overdosed in presence of heavy metal ions, but the impact was not quantitatively assessed. As

76 a result, RO membrane degradation prevention may become complicated since, on one hand,

77 a complete removal of oxidising agents is recommended (Suzuki et al., 2016) and bisulphite is

78 commonly dosed for such purpose. On the other, some works indicate that an excess of

79 bisulphite under certain circumstances can also lead to RO membrane degradation.

80 Consequently, works systematically addressing bisulphite effects on RO active layer, in terms

81 of composition and performance, when blended with chemicals likely to be present in the RO

82 feed stream are needed.

83 This work focused on the effects of bisulphite, alone and mixed with a secondary oxidant

84 (chlorite), an halide ion (bromide) and a transition metal based catalyst (iron(III)), not

85 previously addressed in literature. Exposed membranes composition was characterised by RBS

86 which provides average elements concentration on the PA active layer by penetrating 1-2 µm

87 on the membrane (PA and part of polysulphone layers) (Mi et al., 2007). Ion probing

88 experiments provided information on structural changes of the PA. These supported the

89 permeation results obtained, conducted with a monovalent ion (chloride) to track changes in

90 the network pores of the PA active layer.

91

92 **2. EXPERIMENTAL**

93 **2.1. Membrane exposure experiments**

94 Membrane coupons were cut randomly from different sheets and locations of a LE4040 (Dow

95 Filmtec Co.) spiral wound RO membrane module. They were soaked 6 times for at least 6h

96 each in nanopure water (Thermo Scientific Barnstead Dubuque) and were thoroughly rinsed

97 afterwards aiming at removing any potential remaining contamination from the manufacturing

98 process before being used. Nanopure water was used to prepare the chemical mixtures listed

99 in Table 1, which contained sodium bisulphite (Acrós Organics), ferric chloride hexahydrate

100   (BDH), sodium chlorite (Amresco) and sodium bromide (Fisher Chemical), as well as $5 \cdot 10^{-3}$ M

101   sodium hydrogen carbonate (Fisher BioReagents) and 10^{-3} M sodium chloride (Sigma Aldrich).

102   The iron(III) and chlorite concentrations selected (1.5 mg/L ($2.69 \cdot 10^{-5}$ M) and 37.5 mg/L

103   ($5.56 \cdot 10^{-4}$ M) respectively), corresponded to 50 fold the average values that may be present in

104   the feed stream of RO membranes from drinking water treatment plants equipped with

105   coagulation and dioxichlorination. Bisulphite low dose (100 mg/L, $9.61 \cdot 10^{-4}$ M) was slightly

106   below the stoichiometric concentration needed to reduce the chlorite, and the high dose (400

107   mg/L, $3.85 \cdot 10^{-3}$ M) was well above it. Bromide concentration (400 mg/L, $5.00 \cdot 10^{-3}$ M) was

108   greater than typical values from surface waters (up to 1 mg/L) to evidence its effects.

109   Bisulphite is a reducer widely implemented in water utilities equipped with RO membranes to

110   prevent oxidising species from reaching the membranes. Nevertheless, studies on its impact

111   on RO membranes, especially in presence of other compounds, are scarce in literature. Iron is

112   often used in coagulation, which may be a pre-treatment step to RO membranes. As a result,

113   iron traces may reach the membranes and catalyse the degradation of RO membranes as

114   shown in previous works (Tessaro et al., 2005). Chlorite, a secondary oxidant generated when

115   dosing chlorine dioxide (Odeh et al., 2002), could also degrade RO membranes (Zupanovich et

116   al., 2012) but it has never been studied before. The co-existence of oxidising agents and halide

117   ions, such as bromide, has also been claimed to induce RO membrane degradation (Kwon et

118   al., 2011, Maugin, 2013, Valentino et al., 2015). As a result, the effects of bisulphite alone and

119   mixed with the abovementioned chemicals have been studied in detail.

120   pH was adjusted dosing sodium hydroxide and hydrochloric acid to 6.7, and no headspace was

121   left. Ambar jars were used to avoid photodecomposition and were placed on a shaking table to

122   ensure homogeneous mixture. Every day exposure solutions were replaced until the targeted

123   exposure time was reached (generally 9 days, otherwise specified). Then, membrane coupons

124   were soaked 3 times during 10 min each in a solution whose composition was the same as the

125   exposure one, but 1000 fold diluted in order to remove the compounds not bound to the

126   membrane.

127   Table 1. Iron(III), chlorite, bromide and bisulphite based exposure solutions assessed with their

128   corresponding concentrations.

Sample	[Fe (III)] (M)	[ClO$_2$$^-$] (M)	[Br$^-$] (M)	[NaHSO$_3$] (M)
HSO3_ex	0	0	0	$3.85 \cdot 10^{-3}$
HSO3_ex-Fe	$2.69 \cdot 10^{-5}$	0	0	$3.85 \cdot 10^{-3}$
HSO3_ex-Fe-ClO2, HSO3_ex-Fe-ClO2_4d HSO3_ex-Fe-ClO2_23d	$2.69 \cdot 10^{-5}$	$5.56 \cdot 10^{-4}$	0	$3.85 \cdot 10^{-3}$
HSO3_ex-ClO2	0	$5.56 \cdot 10^{-4}$	0	$3.85 \cdot 10^{-3}$
HSO3_ex-Fe-ClO2-Br	$2.69 \cdot 10^{-5}$	$5.56 \cdot 10^{-4}$	$5.00 \cdot 10^{-3}$	$3.85 \cdot 10^{-3}$
HSO3_lm	0	0	0	$9.61 \cdot 10^{-4}$
HSO3_lm-Fe	$2.69 \cdot 10^{-5}$	0	0	$9.61 \cdot 10^{-4}$
HSO3_lm-Fe-ClO2	$2.69 \cdot 10^{-5}$	$5.56 \cdot 10^{-4}$	0	$9.61 \cdot 10^{-4}$
HSO3_lm-ClO2	0	$5.56 \cdot 10^{-4}$	0	$9.61 \cdot 10^{-4}$
HSO3_lm-Fe-ClO2-Br	$2.69 \cdot 10^{-5}$	$5.56 \cdot 10^{-4}$	$5.00 \cdot 10^{-3}$	$9.61 \cdot 10^{-4}$

129

130   **2.2. Membrane permeation experiments**

131   Permeation experiments were conducted using a dead-end membrane apparatus (model

132   8050, Millipore Co.) connected to an analytical balance (BP211S, Sartorius Co.) logged into a

133   computer, as described in Saenz de Jubera et al. (2012). A 400 mg/L sodium chloride (Sigma

134   Aldrich) solution was used to assess the chloride passage. pH was adjusted to 6.7 ± 0.2 by

135   adding sodium hydroxide and hydrochloric acid. Chlorides were analysed by ion

136   chromatography (Dionex IC S-2000 with a Dionex ion Pac As 18 column) as detailed in Saenz de

137   Jubera et al. (2012).

138   Permeation data was fitted and interpreted using a modified version of the solution-diffusion

139   model (Wijmans and Baker, 1995) accounting for imperfections in the active layer (Urama and

140   Mariñas, 1997). The water and solute fluxes through the membrane at steady state can be

141   described by Eq. 1 and Eq. 2 respectively.

142

143 $$J_v = \frac{A}{(1-\alpha)} \cdot (\Delta p - \Delta \pi)$$ Eq. 1

144

145 $$J_s = J_v \cdot C_p = B \cdot (C_w - C_p) + \alpha \cdot J_v \cdot C_w$$ Eq. 2

146

147 J_v ($m^3/(m^2 \cdot d)$) and J_s ($mol/(m^2 \cdot d)$) represent the product water flux and the solute flux

148 respectively. A ($m^3/(m^2 \cdot d \cdot MPa)$) and B (m/d) correspond to the product water and solute

149 permeation coefficients and α is the fraction of the total product water flux corresponding to

150 advection through membrane imperfections. $\Delta p = (p_f - p_p)$ (MPa) and $\Delta \pi = (\pi_w - \pi_p)$ (MPa) are

151 the hydraulic and osmotic pressure differences across the membrane active layer, respectively.

152 C (M) is the solute concentration, and subscripts f, w, and p refer to bulk feed solution, feed

153 solution next to the membrane wall, and permeate, respectively. The methodology used for

154 data fitting was analogous to the one described in Saenz de Jubera et al. (2012).

155 RO membrane performance variability is a concern in membrane degradation studies; some

156 works have encountered permeation discrepancies up to 20 % between elements of the same

157 membrane name (Tu et al., 2014). Four virgin membrane coupons were initially characterised

158 obtaining low variability in terms of water and chloride permeation coefficients: A parameter

159 did not differ more than 6 % and B, 11 % between them. Consequently, A/A_0 and B/B_0 values

160 ranging from 0.94 to 1.10 and 0.9 to 1.1, respectively were considered as inherent variations of

161 the membrane.

162

163 **2.3. Membrane characterisation experiments**

164 Triplicate air-dried samples were analysed by Rutherford backscattering spectrometry (RBS). A

165 2-MeV He+ beam generated with a Van Graaf accelerator (High Voltage Engineering Corp) was

166 used. The incident, exit and scattering angles of the He+ beam were 22.5°, 52.5° and 150.0°,

167 and the data obtained was fitted using SIMNRA® software. This enabled characterising the

168 composition of the membrane active layer, as described by Mi et al. (2007, 2006).

169 The RO membrane accessible carboxylic groups were determined by silver probing

170 experiments (AgNO$_3$ 99 %, Sigma-Aldrich), following the procedure described by Coronell et al.

171 (2009, 2008). Deprotonated accessible carboxylic groups were quantified in the pH range of

172 4.5 - 10.5 by assuming that they were in equilibrium with the ion probe solution and that their

173 concentration was equivalent to the Ag$^+$ one quantified by RBS means (Coronell et al., 2009,

174 2008). The concentration of Ag$^+$ in solution ranged from 10^{-3} to 10^{-6} M, being always below the

175 solubility limit, and pH was adjusted by adding nitric acid and sodium hydroxide. These

176 experiments were conducted in a dark room to avoid photochemical reactions.

177 Data obtained from RBS was fitted to Eq. 3, which describes a bimodal pore size distribution as

178 suggested by Kim et al. (2005) and Coronell et al. (2008), to determine the associated

179 membrane characteristics.

180 $$[R-COO^-] = C_{T,R-COOH} \cdot \sum_{i=1}^{n} \omega_i \cdot \frac{K_{a,i}}{[H^+]+K_{a,i}}$$ Eq. 3

181 [R-COO$^-$] (M) corresponds to the deprotonated accessible carboxylic groups, $C_{T,R-COOH}$ to the

182 total concentration of carboxylic groups, [H$^+$] the concentration of hydrogen ion in the ion

183 probe solution, ω_i the fraction of functional groups with acidic constant $K_{a,i}$, and n the number

184 of dissociation constants required to fit the data. As previously reported for other RO

185 membranes with fully aromatic PA active layer two dissociation constants (n = 2) resulted in

186 the most accurate representation of the experimental data (Coronell et al., 2009, 2008).

187 Those exposure conditions which involved iron uptake by the membrane required a cleaning

188 step before conducting the silver probing assays, aiming at removing the iron. Otherwise, iron

189 could prevent the interaction between some silver ions and the membrane carboxylic groups,

190 underestimating their concentration. For such purpose, these samples were immersed in a 2 %

191 citric acid monohydrate (Fischer Chemical) solution during three days, replacing the acid

192 solution every day and performing a final rinsing step with 1000 diluted citric acid solution.

193

194 **3. RESULTS**

195 **3.1. Bisulphite, iron(III), chlorite and bromide mixing effects**

196 Mixtures containing bisulphite, iron(III), chlorite and bromide were prepared as detailed in

197 Table 1. As can be seen, two main sets of experiments were carried out to elucidate bisulphite

198 effects on RO membranes composition and performance: one set of samples contained a

199 greater bisulphite molar concentration than the stoichiometrically needed to reduce the

200 chlorite dosed (2:1 according to Gordon et al., 1990) (samples HSO3_ex, HSO3_ex-Fe,

201 HSO3_ex-Fe-ClO2, HSO3_ex-ClO2, HSO3_ex-Fe-ClO2-Br), and the second set of samples with a

202 lower concentration than the stoichiometrically required (samples HSO3_lm, HSO3_lm-Fe,

203 HSO3_lm-Fe-ClO2, HSO3_lm-ClO2, HSO3_lm-Fe-ClO2-Br). The concentration of iron(III) was

204 well above its solubility at the working pH, 6.7, so that significant precipitation of hydroxo-

205 species may have occurred (Fábián and Gordon, 1991).

206 Table 2 shows the elemental composition of the exposed membranes, in atomic weight

207 percentage, obtained by RBS means. The Dow Filmtec LE4040 virgin membrane active layer

208 elemental composition quantified corresponded to a fully aromatic polyamide, with an

209 elemental repeating unit close to $C_{36}H_{24}N_6O_6$, as described by Coronell et al. (2009). It

210 contained trace amounts of chlorine whose presence was associated to the manufacturing

211 process, as reported elsewhere (Valentino et al., 2015, Raval et al., 2010).

212

213 Table 2. Virgin and exposed membranes elemental composition, in atomic weight percentage,

214 obtained by RBS analysis.

Sample	C (%)	H (%)	O (%)	N (%)	Cl (%)	Br (%)	Fe (%)
Virgin	41.23	44.14	7.58	6.96	0.09		
HSO3_ex	35.00	50.27	7.60	7.00	0.13		
HSO3_ex-Fe	35.33	48.51	8.13	7.50	0.11		0.42
HSO3_ex-Fe-ClO2,	34.00	50.16	7.87	07.73	0.11		0.13
HSO3_ex-ClO2	37.17	48.13	7.60	7.00	0.10		
HSO3_ex-Fe-ClO2-Br	35.00	49.66	7.90	7.00	0.10		0.34
HSO3_lm	33.50	52.81	6.73	6.87	0.09		
HSO3_lm-Fe	35.00	48.51	8.07	8.00	0.10		0.32
HSO3_lm-Fe-ClO2	33.00	50.13	9.00	6.83	0.51		0.53
HSO3_lm-ClO2	36.00	48.51	8.35	6.70	0.44		
HSO3_lm-Fe-ClO2-Br	33.17	48.42	8.13	6.00	0.15	3.72	0.41
HSO3_ex-Fe-ClO2_4d	37.67	48.86	6.67	6.60	0.11		0.09
HSO3_ex-Fe-ClO2_23d	38.00	47.36	7.53	6.73	0.10		0.28

215

3.1.1. Bisulphite as excess reactant

The most remarkable difference between the virgin membrane active layer composition and

the samples e exposed to an excess of bisulphite relative to chlorite (samples HSO3_ex,

HSO3_ex-Fe, HSO3_ex-Fe-ClO2, HSO3_ex-ClO2 and HSO3_ex-Fe-ClO2-Br from Table 1) (Table

2, Figure S.1) was the iron incorporation ($0.13 \pm 0.02 - 0.42 \pm 0.07$ % in atomic weight) from

those exposed to it (HSO3_ex-Fe, HSO3_ex-Fe-ClO2, and HSO3_ex-Fe-ClO2-Br). . Because

bisulphite was in excess compared to chlorite, no membrane chlorination occurred among

those samples exposed to chlorite (HSO3_ex-Fe-ClO2, HSO3_ex-ClO2 and HSO3_ex-Fe-ClO2-

Br). Also, a reducing environment was created, not enabling the bromide ion to be oxidised

and hence, to incorporate in the membrane active layer (HSO3_ex-Fe-ClO2-Br sample).

The water and chloride permeation coefficients (from Eq. 1 and Eq. 2) of the exposed samples

are depicted in Figure 1. From a water permeability perspective, no major changes were

found, with most of the samples presenting a similar water permeability coefficient to the

virgin membrane one ($A_0 = 1.46$ m/(MPa·d)).

Nevertheless, chloride passage was affected to different extents (Figure 1, Figure 2). Nine days

of 400 mg/L ($3.85 \cdot 10^{-3}$ M) sodium bisulphite exposure (HSO3_ex sample) resulted in almost

doubling the chloride permeation coefficient (B/B_0 1.8, being $B_0 = 1.2 \cdot 10^{-2}$ m/d). In the case of

233   chlorite and bisulphite dosage, because bisulphite was in excess compared to chlorite, after

234   reducing the chlorite some may be left, leading to an increased chloride passage (HSO3_ex-

235   ClO2 sample) compared to a virgin membrane (B/B_0 1.2), but to a lesser extent than the

236   bisulphite blank sample (HSO3_ex sample). When dosing iron(III) in presence of bisulphite at

237   the working pH, a remarkable raise in chloride passage was experienced (HSO3_ex-Fe,

238   HSO3_ex-Fe-ClO2 samples), achieving chloride permeation coefficients (B/B_0) of 5.3 – 4.0 fold

239   the virgin membrane one. In the case of bisulphite, chlorite, iron(III) and bromide (HSO3_ex-

240   Fe-ClO2-Br sample) exposure, the chloride permeation coefficient relative to the virgin

241   membrane one (B/B_0) was 2.2.

3.1.2. Bisulphite as limiting reactant

243   A second set of samples with bisulphite concentration lower than the stoichiometrically

244   required to reduce chlorite was studied (HSO3_lm, HSO3_lm-Fe, HSO3_lm-Fe-ClO2, HSO3_lm-

245   ClO2, HSO3_lm-Fe-ClO2-Br samples from Table 1). In this case, there were some differences in

246   terms of composition in comparison with the virgin membrane, particularly those exposed to

247   iron(III) (HSO3_lm-Fe, HSO3_lm-Fe-ClO2 samples), to bromide (HSO3_lm-Fe-ClO2-Br sample)

248   and to chlorite (HSO3_lm-Fe-ClO2, HSO3_lm-ClO2, samples) together with bisulphite, as shown

249   in Table 2 and Figure S.2. In the case of membranes exposed to iron containing solutions, iron

250   incorporation occurred, presenting similar values to the previous set of samples: 0.32 ± 0.03 –

251   0.53 ± 0.03 % in atomic weight. Those membranes soaked in chlorite and bisulphite (HSO3_lm-

252   Fe-ClO2, HSO3_lm-ClO2, samples) presented an increased chlorine concentration in the active

253   layer compared to the virgin membrane. In the case of the bromide containing solution

254   (HSO3_lm-Fe-ClO2-Br sample: bromide, bisulphite, chlorite and iron(III)) large amounts of

255   bromine were uptaken by the membrane, achieving 3.72 ± 0.14 % of the atomic weight of the

256   active layer. Because chlorite was in excess compared to bisulphite, bromide ion could be

257   oxidised and hence, be incorporated into the membrane.

258 In terms of water permeability, bisulphite (HSO3_lm) and bisulphite and iron (HSO3_lm-Fe)

259 exposed membranes performance was similar to the virgin membrane, presenting A/A_0 values

260 of 1.02 and 1.09 respectively. On the contrary, the water permeability coefficient of the

261 membrane exposed to bromide, bisulphite, chlorite and iron(III) (HSO3_lm-Fe-ClO2-Br sample)

262 dropped by half approximately (A/A_0 0.51); the one soaked in bisulphite, chlorite and iron(III)

263 (HSO3_lm-Fe-ClO2 sample), increased 1.23 fold; and the one exposed to chlorite and

264 bisulphite (HSO3_lm-ClO2 sample), 1.13 times (Figure 3). Interestingly, those samples

265 presenting greater water permeability were those which showed increased chlorine content,

266 which is in accordance with previous works (Maugin, 2013, (Do et al., 2012)).

267 Chloride passage assessment of this set of samples (Figure 3 and Figure 4) also indicated the

268 degradation caused by bisulphite (3.9 fold increase in terms of chloride permeation coefficient,

269 HSO3_lm sample) and the synergistic effect in presence of iron(III) (HSO3_lm-Fe, HSO3_lm-Fe-

270 ClO2 samples) under the conditions assessed. When comparing these last two samples,

271 HSO3_lm-Fe presented a 5.1 fold increase in chloride permeation coefficient whereas

272 HSO3_lm-Fe-ClO2, 1.8. This could be attributed to the presence of chlorite in the later

273 scenario, which would consume bisulphite (limited) and hence, damage the membrane to a

274 lesser extent. In the equivalent conditions of the previous set of data (HSO3_ex-Fe-ClO2

275 sample), where bisulphite was in excess, chloride permeation coefficient increase was 4.0 fold

276 the virgin membrane one, and 5.3 when chlorite was not dosed (HSO3_ex-Fe sample) which

277 would support this hypothesis.

278 HSO3_lm-ClO2 sample reinforced the synergistic effects of iron(III) and bisulphite, since the

279 chloride permeation coefficient was virtually the same as the virgin membrane (Figure 3) when

280 iron(III) was not dosed. Bromide, chlorite, iron(III) and bisulphite exposure (HSO3_lm-Fe-ClO2-

281 Br sample) also turned out into a 2.9 fold increase in chloride permeability coefficient (Figure

282 3).

283

3.2. Bisulphite, iron(III) and chlorite time dependence effects

285 Bisulphite in excess, iron and chlorite exposure time effects were determined by

286 characterising the composition and performance of membranes soaked into such mixture for 4

287 (HSO3_ex-Fe-ClO2_4d sample) and 23 (HSO3_ex-Fe-ClO2_23d sample) days. Similarly to the

288 previous results, the main difference compared to the virgin membrane composition was the

289 incorporation of iron, being higher at longer exposure times (Table 2). In terms of water and

290 chloride permeation coefficients (Figure A.3) no significant differences were found among the

291 samples, suggesting that the degradation (only experienced in terms of chloride passage) was

292 a fast process, causing a severe effect at low exposure times and not significantly increasing

293 afterwards.

294

3.3. Bisulphite, iron(III) and chlorite structural effects

296 Membrane performance degradation due to oxidising species has often been related to

297 halogen uptake and/or polyamide bond cleavage ((Do et al., 2012), (Powell et al., 2015),

298 (Valentino et al., 2015)), involving polymer deformation and polymer depolymerisation,

299 respectively (Kwon et al., 2011). RBS analysis and the combination of ion probing experiments

300 and RBS analysis enabled the characterisation of the membranes composition and structure,

301 respectively, providing further insights into the degradation processes.

302 Silver probing experiments consisted in determining the titration curve of the accessible

303 deprotonated carboxylic groups in the membrane. For such purpose, it was assumed that silver

304 ions ionically bound to the deprotonated carboxylic groups as described in (Coronell et al.,

305 2008), so that by quantifying the silver concentration in the active layer at different pHs, it was

306 possible to determine the ionisation behaviour of the carboxylic groups. Figure 5 presents the

307 concentration of accessible deprotonated carboxylic groups of the active layer, being higher at

308   greater pHs. The ionisation behaviour of the active layer functional groups was modelled by an

309   acid-base equilibrium, with two dissociation constants (Coronell et al., 2008), pka_1 and pka_2,

310   which is consistent with a bimodal pore size distribution. A larger pore presents a lower

311   dielectric constant surrounding the functional group, and thus, the energy needed for

312   ionisation is greater, leading to a lower pka (Coronell et al., 2008). As a result, ion probing

313   assays provide information about the membrane active layer pore size distribution, and hence,

314   by comparing the virgin and the exposed RO membranes, insights into the structural changes

315   suffered by the degraded membrane.

316

317   The RBS characterisation of the virgin membrane used (Dow Filmtec Co., LE4040) had not been

318   published before, neither in terms of chemical composition nor in pores size distribution. Its

319   composition (Table 2) was relatively similar to other brackish water RO membranes previously

320   reported (Coronell et al., 2010).Nevertheless, its carboxylic content was lower (0.31 M versus

321   0.64 M from (Coronell et al., 2010) and its pore size distribution differed. Apparently, it

322   presented smaller network and aggregate pores (greater pka_1 and pka_2), but a larger fraction of

323   aggregate pores (ω_2) (Figure 5 and (Coronell et al., 2010)).).

324

325   The composition of the sample exposed to bisulphite, iron(III) and chlorite during 23 days

326   (HSO3_ex-Fe-ClO2_23d) was similar to the virgin membrane one, mainly differing in the iron

327   uptaken by the exposed sample (0.28 ± 0.04 % in atomic weight). No chlorine incorporation

328   was experienced, which is consistent with sample HSO3_ex-Fe-ClO2 and may be due to the

329   excess of bisulphite compared to chlorite, as previously discussed.

330   Before conducting the silver probing assays of the membrane exposed to bisulphite, iron and

331   chlorite for 23 days (HSO3_ex-Fe-ClO2_23d sample), its uptaken iron was diminished (from

332   0.28 ± 0.04 % to 0.07 ± 0.03 % in atomic weight) by a 2% citric acid soaking during 72h. This

333   step aimed at removing the iron to enable the ionic binding between silver ions and all the

334   accessible deprotonated carboxylic groups.

335   Silver probing experiments (Figure 5) showed that the total number of carboxylic groups did

336   not differ (p = 0.05) between the virgin membrane and the membrane exposed to bisulphite,

337   iron(III) and chlorite (HSO3_ex-Fe-ClO2_23d sample) (0.31 ± 0.01 M vs. 0.29 ± 0.01 M), which is

338   in accordance with the constant concentration of oxygen to nitrogen ratio (O:N) reported from

339   the samples analysed. This means that the exposure conditions did not cause amide bond

340   cleavage, which would have led to more carboxylic and amine groups. However, an increase in

341   the fraction of aggregate pores (associated to the acid-base equilibrium pKa_1) could be

342   appreciated, since ω_1 from Eq. 3 increased, particularly from 0.28 of the virgin membrane to

343   0.41 of the exposed membrane (HSO3_ex-Fe-ClO2_23d sample) (Figure 5). Also, the decrease

344   of pKa_2 (from 8.73 to 8.20) indicated that network pores increased in size. Therefore, the

345   exposure to bisulphite, iron(III) and chlorite modified the membrane pore size distribution,

346   increasing the size of the network pores and the fraction of the aggregate ones. The two

347   phenomena explain the increased chloride passage quantified in the permeation experiments.

348   RO membranes PA active layers are highly crosslinked and thus, the nonhydrated radius is the

349   ionic dimension of interest to determine the accessibility of ions (Coronell et al., 2008). As a

350   result, iron(III) due to its ionic radius (0.063 – 0.092 nm according to (Shannon, 1976)) is able

351   to access to the network pores. Iron(III) reacts with bisulphite during the autooxidation of the

352   later, generating metal sulphito complexes and free radicals among others. It is hypothesized

353   that some of the compounds generated, larger in size, deform the network pores, increasing

354   their diameter or even transforming them into aggregate pores. This would be in accordance

355   with the modifications in the pore size distribution observed and the chloride permeation

356   results.

357

4. DISCUSSION

Both sets of data provided consistent results. Considering chloride passage effects, it can be concluded that in presence of bisulphite alone, some degradation occurred in the tested conditions (HSO3_ex, HSO3_lm samples), involving a chloride passage of 6.5 ± 0.6 % and 9.8 ± 0.5 % respectively. When combined with iron(III) (HSO3_ex-Fe, HSO3_lm-Fesamples), chloride permeation coefficient increased 5.3 – 5.1 fold the virgin membrane one (B/B$_0$), achieving values up to 15 % of chloride passage. When dosing chlorite below the stoichiometrically required dose compared to bisulphite and in presence of iron(III) (HSO3_ex-Fe-ClO2 sample), significant degradation occurred (B/B$_0$ 4.0); whereas in excess (HSO3_lm-Fe-ClO2 sample) the effects were more limited (B/B$_0$ 1.8). This may be due to the oxidation of bisulphite by chlorite, hence limiting the bisulphite capable of reacting with iron and thus, the membrane degradation extent. When bisulphite and chlorite were present (HSO3_ex-ClO2, HSO3_lm-ClO2 samples), but without iron(III) dosage, the effect depended on the stoichiometric amount dosed: when bisulphite was limiting, no significant degradation in terms of chloride passage was suffered. But some chlorination (Figure S.1) and a slight increase in water flux occurred. When bisulphite was in excess, there was a certain increase in chloride passage (B/B$_0$ 1.2), but to a lower extent than bisulphite alone. In this case, chlorination and increased water passage were not experienced (Figure S.2). Bisulphite both in excess and limiting, when iron(III) was not dosed, the extent of the impact on chloride passage was much lower than when present, evidencing its catalytic effect.

Several authors (Ziajka et al., 1994, Bal Reddy and van Eldik, 1992, Brandt et al., 1994) described an autooxidation process of bisulphite catalysed by iron(III) where free radicals are generated. 1:1, 1:2 and 1:3 sulphito complexes can be formed, depending on the total S(IV) concentration used (Kraft and Van Eldik, 1989a), being SO_4^{2-} and $S_2O_6^{-}$ the main oxidation

382 products (Kraft and Van Eldik, 1989b). The transition metal-sulphito complexes decompose

383 spontaneously and the sulphite radical, $SO_3^{\cdot-}$, and the reduced form of the metal are produced

384 (Brandt et al., 1994). In absence of oxygen, SO_4^{2-} and $S_2O_6^{2-}$ are generated; when oxygen is

385 present, peroxomonosulphate radical, $SO_5^{\cdot-}$, a strong oxidant, is also formed, which can react

386 with HSO_3^- or Fe(II) to produce HSO_5^- (Brandt et al., 1994). Greater Fe(III) and S(IV)

387 concentrations result in a higher formation rate of $SO_3^{\cdot-}$ (Brandt et al., 1994). The ratio of Fe(III),

388 Fe(II) and S(IV) versus oxygen is important in the overall decay of the iron(III)-sulphite

389 complexes (Brandt et al., 1994), varying the oxidation pathway with the ratio bisulphite/iron

390 (Ziajka et al., 1994).

391 The free radicals generated in the bisulphite autooxidation catalysed by iron(III) species could

392 be the responsible for the increase in chloride passage experienced. Because of the free radical

393 nature, the process could be sensitive to time (i.e. from bisulphite mixing point to membranes

394 location), so that some full scale plants may have not been affected by this process. In addition

395 to this, due to their radical nature, membrane autopsies would not probably enable the

396 identification of the origin of the degradation. Martin and Li (1996) concluded that the kinetics

397 of the catalysis of bisulphite oxidation by aqueous iron(III) strongly depended on pH and ionic

398 strength, and that the reaction mechanism was very complex in itself. Furthermore, in natural

399 water, radicals, intermediates and heavy metal ions could react with natural organic matter

400 (NOM), $SO_4^{\cdot-}$ radicals could be scavenged by some anions like hydrogen carbonate and

401 carbonate (Li et al., 2015), or some species could react with oxygen, not leading to the

402 detrimental effects on RO membranes observed in this work. Nevertheless, Sommariva et al.

403 (2012) reported the same phenomena in a seawater RO plant where sodium bisulphite was

404 overdosed in presence of heavy metal ions. The plant suffered an increased salt passage and

405 no halogens were detected in the membrane surface. The dosage of a chelating agent,

406 ethylenediaminetetraacetic acid (EDTA), which complexed with iron(III), prevented the

407 membrane degradation from occurring, evidencing the catalysing effect of the heavy metal

408   ions. Also, unintentionally, Gabelich et al. (2002) experienced a significant increase in salt

409   passage in RO membranes when bisulphite was dosed to water pre-treated with $FeCl_3$ (4.0 -

410   5.0 mg/L). Gabelich et al. (2002) attributed this decay in performance to residual iron(III)

411   catalysing a chlorine-amide reaction on the membrane surface (despite having quenched

412   residual chlorine and obtaining negative results on free chlorine residuals in feed water);

413   nevertheless, based on the results obtained in this work, it could be attributed to the

414   bisulphite and iron(III) synergistic effects.

415

416   The reactivity of bisulphite with bromine-based species has been reported in literature (Khan

417   et al., 2003) and the autocatalytic nature of bisulphite with bromine based species too (Wang

418   et al., 2012). Li et al. (2015) studied the formation of bromate when Co(II) reacted with

419   peroxymonosulphate by means of the sulphate radical, $SO_4^{\cdot-}$, with Br^- and $Br_2^{\cdot}$ as intermediates.

420   It was noted that $SO_4^{\cdot-}$ could oxidise Br^- to $Br^{\cdot}$, generating bromine, hypobromous acid, OBr^- and

421   ultimately bromate. Similar reactions involving the formation of bromine active species could

422   be envisaged, which could explain the large amount of bromine uptaken by the membrane

423   when bisulphite, iron(III), bromide and chlorite in excess were studied (HSO3_lm-Fe-ClO2-Br

424   sample). No increase in chlorine content was noticed in the RO active layer, which would be in

425   accordance with the greater affinity for bromine than chlorine reported (Kwon et al., 2011).

426   Besides bromination, a large decrease in water passage was experienced, which could be due

427   to the collapse of the polymer chains caused by the high bromine uptake, breaking the PA

428   membrane bonds (Maugin, 2013) or the hydrogen bonds (Kwon et al., 2011). Chloride

429   permeation coefficient increased (B/B_0 2.9), involving 12.0 ± 0.8 % chloride passage, under the

430   tested conditions. (Suzuki et al., 2016) recently characterised the performance and the

431   physicochemical properties of a RO membrane used in a seawater desalination plant during

432   three years. Sodium bisulphite was dosed to quench the free chlorine added upstream aiming

433 at controlling membrane biofouling. The assessed membrane presented an increased chloride

434 (B/B_0 3.2) and water (A/A_0 0.67) permeation coefficients and bromine was incorporated in its

435 active layer. The authors attributed the increased solute passage mainly to the bromine uptake

436 and the reduced water permeability both to bromination and reduction of the polyvinyl

437 alcohol (PVA) coating coverage. Despite the fact that the conditions that led to membrane

438 bromination may be different in both works, the effects experienced are consistent.

439 When bisulphite was in excess (sample HSO3_ex-Fe-ClO2-Br: bisulphite, iron(III), chlorite and

440 bromide), because of the reducing environment generated, no bromine and chlorine were

441 uptaken by the PA. Under these conditions, water permeability coefficient did not differ from

442 the virgin membrane one, but chloride one raised (B/B_0 2.2), involving 7.7 ± 0.2 % chloride

443 passage.

444

445 Further studies to determine the reactions and compounds involved in the degrading

446 mechanisms identified in this study should be explored to better understand and control them.

447

448 **5. CONCLUSIONS**

449 • Bisulphite exposure caused an increased chloride passage (B/B_0 1.8 – 3.9), but no major

450 changes in terms of membrane composition were identified. The effect of chlorite and

451 bisulphite blended depended on their relative proportion, being more pronounced those

452 effects associated to the compound with greater stoichiometric molar concentration.

453 • The mixture of bisulphite and iron(III) resulted in a severe increase in chloride permeation

454 coefficient (B/B_0 5.3 – 5.1). It is hypothesized that an autooxidation of bisulphite catalysed

455 by iron(III) occurred, generating highly reactive species which interacted with the

456 membrane, negatively affecting its performance (increased chloride passage).

457 • When dosing bisulphite, iron(III) and chlorite, there was always an increase in chloride

458   passage (B/B$_0$ 4.0 – 1.8), but the extent varied according to the bisulphite and chlorite

459   molar ratios. The process was fast, affecting the membrane during the initial exposure

460   and not increasing significantly afterwards. It was shown by silver probing experiments

461   coupled with RBS analysis that scission of the amide bond from the PA active layer did not

462   occur, but the size of the network pores increased and the proportion of aggregate pores

463   raised. These two effects explain the increase in chloride passage experienced. .

464 • When bisulphite, iron(III), chlorite and bromide were mixed the effects differed, again

465   depending on the relative quantity of bisulphite and chlorite. In both cases the chloride

466   passage increased (B/B$_0$ 2.2 – 2.9). In excess of chlorite, significant bromination of the

467   membrane took place. It is thought that free radicals generated when bisulphite was

468   limiting oxidised bromide, which was uptaken by the PA. Besides bromination, a large

469   decrease in water passage was experienced. When bisulphite was in excess, because of

470   the reducing environment generated, no bromine and chlorine were uptaken by the PA,

471   and the water permeability coefficient did not differ from the virgin membrane one.

472 Taking into account the results obtained, water treatment facilities should carefully control

473 iron(III) and bisulphite dosages upstream RO membranes in order to minimise their effects.

474 The increase in chloride passage provoked when blended, under the tested conditions, may

475 lead to a chloride passage well above the process specifications, requiring premature

476 replacement of the RO membranes. Finally, the bisulphite dosage required upstream RO

477 membranes should be determined in each case in order to avoid over/under dosing which

478 could cause an undesired membrane performance as well.

479

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486

487 **References**

488 Bal Reddy, K., van Eldik, R., 1992. Kinetics and mechanism of the sulfite-induced autoxidation
489   of Fe(II) in acidic aqueous solution. Atmos. Environ. Part A. Gen. Top. 26, 661–665.
490   doi:10.1016/0960-1686(92)90177-M

491 Brandt, C., Fábián, I., van Eldik, R., 1994. Kinetics and Mechanism of the Iron(III)-catalyzed
492   Autoxidation of Sulfur(IV) Oxides in Aqueous Solution. Evidence for the Redox Cycling of
493   Iron in the Presence of Oxygen and Modeling of the Overall Reaction Mechanism. Inorg.
494   Chem. 33, 687–701. doi:10.1021/ic00082a012

495 Coronell, O., González, M.. I., Mariñas, B.J., Cahill, D.G., 2010. Ionization Behavior,
496   Stoichiometry of Association, and Accessibility of Functional Groups in the Active Layers
497   of Reverse Osmosis and Nanofiltration Membranes. Environ. Sci. Technol. 44, 6808–6814.
498   doi:10.1021/es100891r

499 Coronell, O., Mariñas, B.J., Cahill, D.G., 2009. Accessibility and ion exchange stoichiometry of
500   ionized carboxylic groups in the active layer of FT30 reverse osmosis membrane. Environ.
501   Sci. Technol. 43, 5042–5048. doi:10.1021/es803595f

502 Coronell, O., Mariñas, B.J., Zhang, X., Cahill, D.G., 2008. Quantification of functional groups and
503   modeling of their ionization behavior in the active layer of FT30 reverse osmosis
504   membrane. Environ. Sci. Technol. 42, 5260–5266. doi:10.1021/es8002712

505 Do, V.T., Tang, C.Y., Reinhard, M., Leckie, J.O., 2012. Effects of hypochlorous acid exposure on
506   the rejection of salt , polyethylene glycols , boron and arsenic (V) by nanofiltration and
507   reverse osmosis membranes. Water Res. 46, 5217–5223.
508   doi:10.1016/j.watres.2012.06.044

509 Dow Water & Process Solutions, n.d. FILMTEC^{TM} Reverse Osmosis Membranes Technical
510   Manual.

511 Fábián, I., Gordon, G., 1991. Kinetics and Mechanism of the Complex Formation of the Chlorite
512   Ion and Iron (III) in Aqueous Solution. Inorg. Chem. 30, 3994–3999.

513 Fritzmann, C., Löwenberg, J., Wintgens, T., Melin, T., 2007. State-of-the-art of reverse osmosis
514   desalination. Desalination 216, 1–76.

515   Gabelich, C.J., Yun, T.I., Coffey, B.M., Suffet, I.H.M., 2002. Effects of aluminum sulfate and
516   ferric chloride coagulant residuals on polyamide membrane performance. Desalination
517   150, 15–30. doi:10.1016/S0011-9164(02)00926-8

518   Gordon, G., Slootmaekers, B., Tachiyashiki, S., Wood III, D.W., 1990. Minimizing Chlorite Ion
519   and Chlorate Ion in Water Treated With Chlorine Dioxide. J. Am. Water Work. Assoc. 82,
520   160–165.

521   Khan, K.M., Maharvi, G.M., Hayat, S., Zia-Ullah, Choudhary, M.I., Atta-ur-Rahman, 2003. An
522   expedient esterification of aromatic carboxylic acids using sodium bromate and sodium
523   hydrogen sulfite. Tetrahedron 59, 5549–5554. doi:10.1016/S0040-4020(03)00812-3

524   Kim, S.H., Kwak, S.Y., Suzuki, T., 2005. Positron annihilation spectroscopic evidence to
525   demonstrate the flux-enhancement mechanism in morphology-controlled thin-film-
526   composite (TFC) membrane. Environ. Sci. Technol. 39, 1764–1770.
527   doi:10.1021/es049453k

528   Kraft, J., Van Eldik, R., 1989a. Kinetics and Mechanism of the Iron(III)-Catalyzed Autoxidation of
529   Sulfur(IV) Oxides in Aqueous Solution. 1. Formation of Transient Iron(III)-Sulfur(IV)
530   Complexes. Inorg. Chem. 28, 2297–2305.

531   Kraft, J., Van Eldik, R., 1989b. Kinetics and mechanism of the iron(III)-catalyzed autoxidation of
532   sulfur(IV) oxides in aqueous solution. 2. Decomposition of transient iron(III)-sulfur(IV)
533   complexes. Inorg. Chem. 28, 2306–2312. doi:10.1021/ic00311a011

534   Kwon, Y., Joksimovic, R., Kim, I., Leckie, J., 2011. Effect of bromide on the chlorination of a
535   polyamide membrane. Desalination 280, 80–86. doi:10.1016/j.desal.2011.06.046

536   Li, Z., Chen, Z., Xiang, Y., Ling, L., Fang, J., Shang, C., Dionysiou, D.D., 2015. Bromate formation
537   in bromide-containing water through the cobalt-mediated activation of
538   peroxymonosulfate. Water Res. 83, 132–140. doi:10.1016/j.watres.2015.06.019

539   Lin, S., Elimelech, M., 2015. Staged reverse osmosis operation: Configurations, energy
540   efficiency and application potential. Desalination 366, 9–14.

541   Martin, R.R., Li, J., 1996. Secondary ion mass spectroscopy (SIMS) and kinetics of the catalysis
542   of bisulphite oxidation by aqueous iron. Can. J. Chem. 74, 2217–2220. doi:10.1139/v96-
543   249

544   Maugin, T., 2013. Fate of reverse osmosis (RO) membranes during oxidation by disinfectants
545   used in water treatment: impact on membrane structure and performances.

546   Mi, B., Cahill, D.G., Marinas, B.J., 2007. Physico-chemical integrity of nanofiltration/reverse
547   osmosis membranes during characterization by Rutherford backscattering spectrometry.
548   J. Memb. Sci. 291, 77–85. doi:10.1016/j.memsci.2006.12.052

549   Mi, B., Coronell, O., Marinas, B., Watanabe, F., Cahill, D., Petrov, I., 2006. Physico-chemical
550   characterization of NF/RO membrane active layers by Rutherford backscattering
551   spectrometry. J. Memb. Sci. 282, 71–81. doi:10.1016/j.memsci.2006.05.015

552   Nagai, M., Iwahashi, H., Hayashi, Y., Ogino, Y., 1994. The behavior of an oxidizing/reducing
553   agent in seawater. Desalination 96, 291–301. doi:10.1016/0011-9164(94)85180-8

554   Odeh, I.N., Francisco, J.S., Margerum, D.W., 2002. New Pathways for Chlorine Dioxide
555   Decomposition in Basic Solution. Inorg. Chem. 41, 6500–6506. doi:10.1021/ic0204676

556   Petersen, R.J., 1993. Composite reverse osmosis and nanofiltration membranes. J. Memb. Sci.
557   83, 81–150. doi:10.1016/0376-7388(93)80014-O

558   Powell, J., Luh, J., Coronell, O., 2015. Amide Link Scission in the Polyamide Active Layers of
559   Thin-Film Composite Membranes upon Exposure to Free Chlorine: Kinetics and
560   Mechanisms. Environ. Sci. Technol. 1, 151012104531007. doi:10.1021/acs.est.5b02110

561   Raval, H.D., Trivedi, J.J., Joshi, S.V., Devmurari, C.V., 2010. Flux enhancement of thin film
562   composite RO membrane by controlled chlorine treatment. Desalination 250, 945–949.
563   doi:10.1016/j.desal.2009.05.005

564   Saenz de Jubera, A.M., Gao, Y., Moore, J.S., Cahill, D.G., Mariñas, B.J., 2012. Enhancing the
565   Performance of Nano fi ltration Membranes by Modifying the Active Layer with Aramide
566   Dendrimers. Environ. Sci. Technol. 46, 9592–9599.

567   Shannon, R.D., 1976. Revised effective ionic radii and systematic studies of interatomic
568   distances in halides and chalcogenides. Acta Crystallogr. Sect. A 32, 751–767.
569   doi:10.1107/S0567739476001551

570   Sommariva, C., Attenborough, A., Poggi, F., Al-Mahdi, A.A.M., Hori, T., Tokunaga, T.K., Ito, Y.,
571   Maeda, Y., 2012. Matching Hollow-Fiber With Spiral-Wound Membranes : Process
572   Compatibility and Optimization. IDA J. 40–44.

573   Suzuki, T., Tanaka, R., Tahara, M., Isamu, Y., Niinae, M., Lin, L., Wang, J., Luh, J., Coronell, O.,
574   2016. Relationship between performance deterioration of a polyamide reverse osmosis
575   membrane used in a seawater desalination plant and changes in its physicochemical
576   properties. Water Res. 100, 326–336.

577   Tessaro, I.C., da Silva, J.B. a, Wada, K., 2005. Investigation of some aspects related to the
578   degradation of polyamide membranes: Aqueous chlorine oxidation catalyzed by
579   aluminum and sodium laurel sulfate oxidation during cleaning. Desalination 181, 275–
580   282. doi:10.1016/j.desal.2005.04.008

581   Tu, K.L., Chivas, A.R., Nghiem, L.D., 2014. Effects of chemical preservation on flux and solute
582   rejection by reverse osmosis membranes. J. Memb. Sci. 472, 202–209.
583   doi:10.1016/j.memsci.2014.08.052

584   Urama, R.I., Mariñas, B.J., 1997. Mechanistic interpretation of solute permeation through a
585   fully aromatic polyamide reverse osmosis membrane. J. Memb. Sci. 123, 267–280.
586   doi:10.1016/S0376-7388(96)00230-X

587   Valentino, L., Renkens, T., Maugin, T., Croué, J.-P., Mariñas, B.J., 2015. Changes in
588   Physicochemical and Transport Properties of a Reverse Osmosis Membrane Exposed to
589   Chloraminated Seawater. Environ. Sci. Technol. 49, 2301–2309. doi:10.1021/es504495j

590   Wang, Z., Gao, Q., Pan, C., Zhao, Y., Horváth, A.K., 2012. Bisulfite-driven Autocatalysis in the
591   Bromate-Thiosulfate Reaction in a Slightly Acidic Medium. Inorg. Chem. 51, 12062–
592   12064. doi:10.1021/ic302019k

593   Wijmans, J.G., Baker, R.W., 1995. The solution-diffusion model: A review. J. Memb. Sci. 107, 1–
594   21. doi:10.1016/0376-7388(95)00102-I

595   Ziajka, J., Beer, F., Warneck, P., 1994. Iron-catalysed oxidation of bisulphite aqueous solution:
596   evidence for a free radical chain mechanism. Atmos. Environ. 28, 2549–2552.

597   Zupanovich, J., Bishop, D., Doak, A., Duff, M., 2012. Microbiological control in thin film
598   composite membrane systems using a high purity chlorine dioxide solution, in:
599   AWWA/AMTA Membrane Technology Conference and Exposition 2012.

600