Reverse osmosis membrane composition, structure and performance modification by bisulphite, iron(III), bromide and chlorite exposure

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Abstract

Reverse osmosis (RO) membrane exposure to bisulphite, chlorite, bromide and iron(III) was assessed in terms of membrane composition, structure and performance. Membrane composition was determined by Rutherford backscattering spectrometry (RBS) and membrane performance was assessed by water and chloride permeation, using a modified version of the solution-diffusion model. Iron(III) dosage in presence of bisulphite led to an autooxidation of the latter, probably generating free radicals which severely damaged the membrane. It comprised a significant raise in chloride passage (chloride permeation coefficient increased 5.3–5.1 fold compared to the virgin membrane under the conditions studied) rapidly. No major differences in terms of water permeability and membrane composition were observed. Nevertheless, an increase in the size of the network pores, and a raise in the fraction of aggregate pores of the polyamide (PA) layer were identified, but no amide bond cleavage was
observed. These structural changes were therefore, in accordance with the transport properties observed.

1. INTRODUCTION

Reverse osmosis (RO) membranes are commonly thin film composite (TFC) membranes consisting in a polyamide (PA) active layer (~ 50 – 250 nm thickness), supported by an asymmetric polysulphone support (~ 50 µm thickness) and a non-woven polyester fabric backing (~ 300 µm thickness) (Petersen, 1993). The partitioning-diffusion process which governs RO membranes water transport and solutes rejection takes place at the water-membrane interface (PA active layer) and across the membrane (Urama and Mariñas, 1997).

The PA pore size distribution of RO membranes has been reported as bimodal, comprised of smaller and larger pores (Kim et al., 2005). The later, referred as aggregate pores, have been related to void space between polymer aggregates (Coronell et al., 2008) and their size has been estimated in 1.0 – 1.6 nm in diameter (Saenz de Jubera et al., 2012). The smaller ones, named network pores, have been associated to the interstitial space between polymer branches within an aggregate (Coronell et al., 2008) and their diameter has been estimated in 0.4 – 0.8 nm (Saenz de Jubera et al., 2012). The ionization behaviour of functional groups in the PA active layer, carboxylic and amine, has been modelled by an acid-base equilibrium with the aqueous solution (Coronell et al., 2008). Ion probing experiments combined with Rutherford backscattering spectrometry (RBS) have enabled the quantification of the accessible deprotonated / protonated groups and thus, the determination of the associated acid-base parameters, providing insights into the pore size distribution, as well as other membrane properties like the total concentration of functional groups and the degree of crosslinking, as shown in the work of Coronell et al. (2009).
RO membranes are able to produce almost pure water in a reliable way, rejecting nearly all colloidal or dissolved matter from an aqueous solution (Fritzmann et al., 2007). RO energy consumption, which has decreased significantly during the last decades, is the lowest among seawater desalination technologies and is energetically advantageous for brackish water desalination as well (Fritzmann et al., 2007). RO membranes capabilities together with their maturity, have turned them into the best standard for desalination (Lin and Elimelech, 2015). Nevertheless, the sensitivity of TFC RO membranes toward certain compounds represents a main drawback nowadays. Indeed, the interaction of certain species with the PA active layer can encompass morphological and chemical changes in the latter, which can result into alterations of the RO membrane separation properties. These modifications can involve the permeate quality to be out of specification and thus, the need to prematurely replace RO membranes, with its associated cost.

It has been well reported in literature and it is recognised by membrane manufacturers that free chlorine damages TFC RO membranes performance. In particular, manufacturers have established maximum admissible concentrations to avoid membranes premature degradation (<0.1 mg/L of free chlorine, being 200-1000 mg/L·h the threshold above which eventual degradation may occur (Dow Water & Process Solutions, n.d.)) and recommend the use of a reducing agent to neutralise it. Sodium metabisulphite, which forms sodium bisulphite in water, has often been used because of its high cost-effectiveness when dechlorinating (Fritzmann et al., 2007). Nevertheless, few works have been devoted to determine bisulphite effects on RO membranes, particularly in presence of other substances naturally contained in the water to be treated or added during the treatment itself (e.g. coagulation/flocculation steps). (Nagai et al., 1994) reported the generation of oxidising agents when sodium bisulphite was dosed in presence of heavy metal ions, chloride ion and dissolved oxygen in a neutral pH solution, but their identification and their effects were not assessed. Sommariva et al. (2012) reported an increased salt passage in a seawater RO plant where sodium bisulphite was
overdosed in presence of heavy metal ions, but the impact was not quantitatively assessed. As a result, RO membrane degradation prevention may become complicated since, on one hand, a complete removal of oxidising agents is recommended (Suzuki et al., 2016) and bisulphite is commonly dosed for such purpose. On the other, some works indicate that an excess of bisulphite under certain circumstances can also lead to RO membrane degradation. Consequently, works systematically addressing bisulphite effects on RO active layer, in terms of composition and performance, when blended with chemicals likely to be present in the RO feed stream are needed.

This work focused on the effects of bisulphite, alone and mixed with a secondary oxidant (chlorite), an halide ion (bromide) and a transition metal based catalyst (iron(III)), not previously addressed in literature. Exposed membranes composition was characterised by RBS which provides average elements concentration on the PA active layer by penetrating 1-2 µm on the membrane (PA and part of polysulphone layers) (Mi et al., 2007). Ion probing experiments provided information on structural changes of the PA. These supported the permeation results obtained, conducted with a monovalent ion (chloride) to track changes in the network pores of the PA active layer.

2. EXPERIMENTAL

2.1. Membrane exposure experiments

Membrane coupons were cut randomly from different sheets and locations of a LE4040 (Dow Filmtec Co.) spiral wound RO membrane module. They were soaked 6 times for at least 6h each in nanopure water (Thermo Scientific Barnstead Dubuque) and were thoroughly rinsed afterwards aiming at removing any potential remaining contamination from the manufacturing process before being used. Nanopure water was used to prepare the chemical mixtures listed in Table 1, which contained sodium bisulphite (Acrós Organics), ferric chloride hexahydrate
(BDH), sodium chlorite (Amresco) and sodium bromide (Fisher Chemical), as well as $5 \times 10^{-3}$ M sodium hydrogen carbonate (Fisher BioReagents) and $10^{-3}$ M sodium chloride (Sigma Aldrich). The iron(III) and chlorite concentrations selected (1.5 mg/L ($2.69 \times 10^{-5}$ M) and 37.5 mg/L ($5.56 \times 10^{-4}$ M) respectively), corresponded to 50 fold the average values that may be present in the feed stream of RO membranes from drinking water treatment plants equipped with coagulation and dioxichlorination. Bisulphite low dose (100 mg/L, $9.61 \times 10^{-4}$ M) was slightly below the stoichiometric concentration needed to reduce the chlorite, and the high dose (400 mg/L, $3.85 \times 10^{-3}$ M) was well above it. Bromide concentration (400 mg/L, $5.00 \times 10^{-3}$ M) was greater than typical values from surface waters (up to 1 mg/L) to evidence its effects. Bisulphite is a reducer widely implemented in water utilities equipped with RO membranes to prevent oxidising species from reaching the membranes. Nevertheless, studies on its impact on RO membranes, especially in presence of other compounds, are scarce in literature. Iron is often used in coagulation, which may be a pre-treatment step to RO membranes. As a result, iron traces may reach the membranes and catalyse the degradation of RO membranes as shown in previous works (Tessaro et al., 2005). Chlorite, a secondary oxidant generated when dosing chlorine dioxide (Odeh et al., 2002), could also degrade RO membranes (Zupanovich et al., 2012) but it has never been studied before. The co-existence of oxidising agents and halide ions, such as bromide, has also been claimed to induce RO membrane degradation (Kwon et al., 2011, Maugin, 2013, Valentino et al., 2015). As a result, the effects of bisulphite alone and mixed with the abovementioned chemicals have been studied in detail. pH was adjusted dosing sodium hydroxide and hydrochloric acid to 6.7, and no headspace was left. Ambar jars were used to avoid photodecomposition and were placed on a shaking table to ensure homogeneous mixture. Every day exposure solutions were replaced until the targeted exposure time was reached (generally 9 days, otherwise specified). Then, membrane coupons were soaked 3 times during 10 min each in a solution whose composition was the same as the
exposure one, but 1000 fold diluted in order to remove the compounds not bound to the membrane.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>[Fe (III)] (M)</th>
<th>[ClO$_2^-$] (M)</th>
<th>[Br$^-$] (M)</th>
<th>[NaHSO$_3^-$] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSO3_ex</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.85·10$^{-3}$</td>
</tr>
<tr>
<td>HSO3_ex-Fe</td>
<td>2.69·10$^{-5}$</td>
<td>0</td>
<td>0</td>
<td>3.85·10$^{-3}$</td>
</tr>
<tr>
<td>HSO3_ex-Fe-ClO$_2$</td>
<td>2.69·10$^{-5}$</td>
<td>5.56·10$^{-4}$</td>
<td>0</td>
<td>3.85·10$^{-3}$</td>
</tr>
<tr>
<td>HSO3_ex-Fe-ClO$_2$-4d</td>
<td>2.69·10$^{-5}$</td>
<td>5.56·10$^{-4}$</td>
<td>0</td>
<td>3.85·10$^{-3}$</td>
</tr>
<tr>
<td>HSO3_ex-ClO$_2$</td>
<td>0</td>
<td>5.56·10$^{-4}$</td>
<td>0</td>
<td>3.85·10$^{-3}$</td>
</tr>
<tr>
<td>HSO3_ex-ClO$_2$-Br</td>
<td>2.69·10$^{-5}$</td>
<td>5.56·10$^{-4}$</td>
<td>5.00·10$^{-3}$</td>
<td>3.85·10$^{-3}$</td>
</tr>
<tr>
<td>HSO3_Im</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>9.61·10$^{-4}$</td>
</tr>
<tr>
<td>HSO3_Im-Fe</td>
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<td>0</td>
<td>0</td>
<td>9.61·10$^{-4}$</td>
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<td>5.56·10$^{-4}$</td>
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</tr>
<tr>
<td>HSO3_Im-Fe-ClO$_2$-Br</td>
<td>2.69·10$^{-5}$</td>
<td>5.56·10$^{-4}$</td>
<td>5.00·10$^{-3}$</td>
<td>9.61·10$^{-4}$</td>
</tr>
</tbody>
</table>

2.2. Membrane permeation experiments

Permeation experiments were conducted using a dead-end membrane apparatus (model 8050, Millipore Co.) connected to an analytical balance (BP211S, Sartorius Co.) logged into a computer, as described in Saenz de Jubera et al. (2012). A 400 mg/L sodium chloride (Sigma Aldrich) solution was used to assess the chloride passage. pH was adjusted to 6.7 ± 0.2 by adding sodium hydroxide and hydrochloric acid. Chlorides were analysed by ion chromatography (Dionex IC S-2000 with a Dionex ion Pac As 18 column) as detailed in Saenz de Jubera et al. (2012).

Permeation data was fitted and interpreted using a modified version of the solution-diffusion model (Wijmans and Baker, 1995) accounting for imperfections in the active layer (Urama and Mariñas, 1997). The water and solute fluxes through the membrane at steady state can be described by Eq. 1 and Eq. 2 respectively.
\[ J_v = \frac{A}{(1-\alpha)} \cdot (\Delta p - \Delta \pi) \]  
\text{Eq. 1}

\[ J_s = J_v \cdot C_p = B \cdot (C_w - C_p) + \alpha \cdot J_v \cdot C_w \]  
\text{Eq. 2}

\[ J_v (m^3/(m^2\cdot d)) \] and \[ J_s (mol/(m^2\cdot d)) \] represent the product water flux and the solute flux respectively. \( A (m^3/(m^2\cdot d\cdot MPa)) \) and \( B (m/d) \) correspond to the product water and solute permeation coefficients and \( \alpha \) is the fraction of the total product water flux corresponding to advection through membrane imperfections. \( \Delta p = (p_f - p_p) \) (MPa) and \( \Delta \pi = (\pi_w - \pi_p) \) (MPa) are the hydraulic and osmotic pressure differences across the membrane active layer, respectively. \( C (M) \) is the solute concentration, and subscripts \( f, w, \) and \( p \) refer to bulk feed solution, feed solution next to the membrane wall, and permeate, respectively. The methodology used for data fitting was analogous to the one described in Saenz de Jubera et al. (2012).

RO membrane performance variability is a concern in membrane degradation studies; some works have encountered permeation discrepancies up to 20% between elements of the same membrane name (Tu et al., 2014). Four virgin membrane coupons were initially characterised obtaining low variability in terms of water and chloride permeation coefficients: \( A/A_0 \) and \( B/B_0 \) values did not differ more than 6% and B, 11% between them. Consequently, \( A/A_0 \) and \( B/B_0 \) values ranging from 0.94 to 1.10 and 0.9 to 1.1, respectively were considered as inherent variations of the membrane.

\[ \textbf{2.3. Membrane characterisation experiments} \]

Triplicate air-dried samples were analysed by Rutherford backscattering spectrometry (RBS). A 2-MeV He\(^+\) beam generated with a Van Graaf accelerator (High Voltage Engineering Corp) was used. The incident, exit and scattering angles of the He\(^+\) beam were 22.5\(^\circ\), 52.5\(^\circ\) and 150.0\(^\circ\),
and the data obtained was fitted using SIMNRA® software. This enabled characterising the composition of the membrane active layer, as described by Mi et al. (2007, 2006).

The RO membrane accessible carboxylic groups were determined by silver probing experiments (AgNO₃ 99 %, Sigma-Aldrich), following the procedure described by Coronell et al. (2009, 2008). Deprotonated accessible carboxylic groups were quantified in the pH range of 4.5 - 10.5 by assuming that they were in equilibrium with the ion probe solution and that their concentration was equivalent to the Ag⁺ one quantified by RBS means (Coronell et al., 2009, 2008). The concentration of Ag⁺ in solution ranged from 10⁻³ to 10⁻⁶ M, being always below the solubility limit, and pH was adjusted by adding nitric acid and sodium hydroxide. These experiments were conducted in a dark room to avoid photochemical reactions.

Data obtained from RBS was fitted to Eq. 3, which describes a bimodal pore size distribution as suggested by Kim et al. (2005) and Coronell et al. (2008), to determine the associated membrane characteristics.

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

\([R-COO^-] \text{ (M)}\) corresponds to the deprotonated accessible carboxylic groups, \(C_{T,R-COOH}\) to the total concentration of carboxylic groups, \([H^+]\) the concentration of hydrogen ion in the ion probe solution, \(\omega_i\) the fraction of functional groups with acidic constant \(K_{a,i}\) and \(n\) the number of dissociation constants required to fit the data. As previously reported for other RO membranes with fully aromatic PA active layer two dissociation constants (\(n = 2\)) resulted in the most accurate representation of the experimental data (Coronell et al., 2009, 2008).

Those exposure conditions which involved iron uptake by the membrane required a cleaning step before conducting the silver probing assays, aiming at removing the iron. Otherwise, iron could prevent the interaction between some silver ions and the membrane carboxylic groups, underestimating their concentration. For such purpose, these samples were immersed in a 2 %...
citric acid monohydrate (Fischer Chemical) solution during three days, replacing the acid solution every day and performing a final rinsing step with 1000 diluted citric acid solution.

3. RESULTS

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

Mixtures containing bisulphite, iron(III), chlorite and bromide were prepared as detailed in Table 1. As can be seen, two main sets of experiments were carried out to elucidate bisulphite effects on RO membranes composition and performance: one set of samples contained a greater bisulphite molar concentration than the stoichiometrically needed to reduce the chlorite dosed (2:1 according to Gordon et al., 1990) (samples HSO3_ex, HSO3_ex-Fe, HSO3_ex-Fe-ClO2, HSO3_ex-ClO2, HSO3_ex-Fe-ClO2-Br), and the second set of samples with a lower concentration than the stoichiometrically required (samples HSO3_lm, HSO3_lm-Fe, HSO3_lm-Fe-ClO2, HSO3_lm-ClO2, HSO3_lm-Fe-ClO2-Br). The concentration of iron(III) was well above its solubility at the working pH, 6.7, so that significant precipitation of hydroxo-species may have occurred (Fábián and Gordon, 1991).

Table 2 shows the elemental composition of the exposed membranes, in atomic weight percentage, obtained by RBS means. The Dow Filmtec LE4040 virgin membrane active layer elemental composition quantified corresponded to a fully aromatic polyamide, with an elemental repeating unit close to $C_{36}H_{24}N_6O_6$ as described by Coronell et al. (2009). It contained trace amounts of chlorine whose presence was associated to the manufacturing process, as reported elsewhere (Valentino et al., 2015, Raval et al., 2010).

Table 2. Virgin and exposed membranes elemental composition, in atomic weight percentage, obtained by RBS analysis.
The most remarkable difference between the virgin membrane active layer composition and the samples exposed to an excess of bisulphite relative to chlorite (samples HSO3\textsubscript{ex}, HSO3\textsubscript{ex-Fe}, HSO3\textsubscript{ex-Fe-CIO2}, HSO3\textsubscript{ex-Fe-CIO2-Br} from Table 1) (Table 2, Figure S.1) was the iron incorporation (0.13 ± 0.02 – 0.42 ± 0.07 % in atomic weight) from those exposed to it (HSO3\textsubscript{ex-Fe}, HSO3\textsubscript{ex-Fe-CIO2}, and HSO3\textsubscript{ex-Fe-CIO2-Br}). Because bisulphite was in excess compared to chlorite, no membrane chlorination occurred among those samples exposed to chlorite (HSO3\textsubscript{ex-Fe-CIO2}, HSO3\textsubscript{ex-CIO2} and HSO3\textsubscript{ex-Fe-CIO2-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\textsubscript{ex-Fe-CIO2-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\textsubscript{0} = 1.46 m/(MPa·d)).

Nevertheless, chloride passage was affected to different extents (Figure 1, Figure 2). Nine days of 400 mg/L (3.85·10\textsuperscript{-3} M) sodium bisulphite exposure (HSO3\textsubscript{ex} sample) resulted in almost doubling the chloride permeation coefficient (B/B\textsubscript{0} 1.8, being B\textsubscript{0} = 1.2·10\textsuperscript{-2} m/d). In the case of...
chlorite and bisulphite dosage, because bisulphite was in excess compared to chlorite, after reducing the chlorite some may be left, leading to an increased chloride passage (HSO3_ex-CIO2 sample) compared to a virgin membrane (B/B0 1.2), but to a lesser extent than the bisulphite blank sample (HSO3_ex sample). When dosing iron(III) in presence of bisulphite at the working pH, a remarkable raise in chloride passage was experienced (HSO3_ex-Fe, HSO3_ex-Fe-CIO2 samples), achieving chloride permeation coefficients (B/B0) of 5.3 – 4.0 fold the virgin membrane one. In the case of bisulphite, chlorite, iron(III) and bromide (HSO3_ex-Fe-CIO2-Br sample) exposure, the chloride permeation coefficient relative to the virgin membrane one (B/B0) was 2.2.

3.1.2. Bisulphite as limiting reactant

A second set of samples with bisulphite concentration lower than the stoichiometrically required to reduce chlorite was studied (HSO3_lm, HSO3_lm-Fe, HSO3_lm-Fe-CIO2, HSO3_lm-CIO2, HSO3_lm-Fe-CIO2-Br samples from Table 1). In this case, there were some differences in terms of composition in comparison with the virgin membrane, particularly those exposed to iron(III) (HSO3_lm-Fe, HSO3_lm-Fe-CIO2 samples), to bromide (HSO3_lm-Fe-CIO2-Br sample) and to chlorite (HSO3_lm-Fe-CIO2, HSO3_lm-CIO2, samples) together with bisulphite, as shown in Table 2 and Figure S.2. In the case of membranes exposed to iron containing solutions, iron incorporation occurred, presenting similar values to the previous set of samples: 0.32 ± 0.03 – 0.53 ± 0.03 % in atomic weight. Those membranes soaked in chloride and bisulphite (HSO3_lm-Fe-CIO2, HSO3_lm-CIO2, samples) presented an increased chlorine concentration in the active layer compared to the virgin membrane. In the case of the bromide containing solution (HSO3_lm-Fe-CIO2-Br sample: bromide, bisulphite, chlorite and iron(III)) large amounts of bromine were uptaken by the membrane, achieving 3.72 ± 0.14 % of the atomic weight of the active layer. Because chlorite was in excess compared to bisulphite, bromide ion could be oxidised and hence, be incorporated into the membrane.
In terms of water permeability, bisulphite (HSO$_3$-lm) and bisulphite and iron (HSO$_3$-lm-Fe) exposed membranes performance was similar to the virgin membrane, presenting A/A$_0$ values of 1.02 and 1.09 respectively. On the contrary, the water permeability coefficient of the membrane exposed to bromide, bisulphite, chlorite and iron(III) (HSO$_3$-lm-Fe-ClO$_2$-Br sample) dropped by half approximately (A/A$_0$ 0.51); the one soaked in bisulphite, chlorite and iron(III) (HSO$_3$-lm-Fe-ClO$_2$ sample), increased 1.23 fold; and the one exposed to chlorite and bisulphite (HSO$_3$-lm-ClO$_2$ sample), 1.13 times (Figure 3). Interestingly, those samples presenting greater water permeability were those which showed increased chlorine content, which is in accordance with previous works (Maugin, 2013, (Do et al., 2012)).

Chloride passage assessment of this set of samples (Figure 3 and Figure 4) also indicated the degradation caused by bisulphite (3.9 fold increase in terms of chloride permeation coefficient, HSO$_3$-lm sample) and the synergistic effect in presence of iron(III) (HSO$_3$-lm-Fe, HSO$_3$-lm-Fe-ClO$_2$ samples) under the conditions assessed. When comparing these last two samples, HSO$_3$-lm-Fe presented a 5.1 fold increase in chloride permeation coefficient whereas HSO$_3$-lm-Fe-ClO$_2$, 1.8. This could be attributed to the presence of chlorite in the later scenario, which would consume bisulphite (limited) and hence, damage the membrane to a lesser extent. In the equivalent conditions of the previous set of data (HSO$_3$_ex-Fe-ClO$_2$ sample), where bisulphite was in excess, chloride permeation coefficient increase was 4.0 fold the virgin membrane one, and 5.3 when chlorite was not dosed (HSO$_3$_ex-Fe sample) which would support this hypothesis.

HSO$_3$-lm-ClO$_2$ sample reinforced the synergistic effects of iron(III) and bisulphite, since the chloride permeation coefficient was virtually the same as the virgin membrane (Figure 3) when iron(III) was not dosed. Bromide, chlorite, iron(III) and bisulphite exposure (HSO$_3$-lm-Fe-ClO$_2$-Br sample) also turned out into a 2.9 fold increase in chloride permeability coefficient (Figure 3).
3.2. Bisulphite, iron(III) and chlorite time dependence effects

Bisulphite in excess, iron and chlorite exposure time effects were determined by characterising the composition and performance of membranes soaked into such mixture for 4 (HSO₃_ex-Fe-CIO₂_4d sample) and 23 (HSO₃_ex-Fe-CIO₂_23d sample) days. Similarly to the previous results, the main difference compared to the virgin membrane composition was the incorporation of iron, being higher at longer exposure times (Table 2). In terms of water and chloride permeation coefficients (Figure A.3) no significant differences were found among the samples, suggesting that the degradation (only experienced in terms of chloride passage) was a fast process, causing a severe effect at low exposure times and not significantly increasing afterwards.

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

Membrane performance degradation due to oxidising species has often been related to halogen uptake and/or polyamide bond cleavage ((Do et al., 2012), (Powell et al., 2015), (Valentino et al., 2015)), involving polymer deformation and polymer depolymerisation, respectively (Kwon et al., 2011). RBS analysis and the combination of ion probing experiments and RBS analysis enabled the characterisation of the membranes composition and structure, respectively, providing further insights into the degradation processes.

Silver probing experiments consisted in determining the titration curve of the accessible deprotonated carboxylic groups in the membrane. For such purpose, it was assumed that silver ions ionically bound to the deprotonated carboxylic groups as described in (Coronell et al., 2008), so that by quantifying the silver concentration in the active layer at different pHs, it was possible to determine the ionisation behaviour of the carboxylic groups. Figure 5 presents the concentration of accessible deprotonated carboxylic groups of the active layer, being higher at
greater pHs. The ionisation behaviour of the active layer functional groups was modelled by an acid-base equilibrium, with two dissociation constants (Coronell et al., 2008), pka\textsubscript{1} and pka\textsubscript{2}, which is consistent with a bimodal pore size distribution. A larger pore presents a lower dielectric constant surrounding the functional group, and thus, the energy needed for ionisation is greater, leading to a lower pka (Coronell et al., 2008). As a result, ion probing assays provide information about the membrane active layer pore size distribution, and hence, by comparing the virgin and the exposed RO membranes, insights into the structural changes suffered by the degraded membrane.

The RBS characterisation of the virgin membrane used (Dow Filmtec Co., LE4040) had not been published before, neither in terms of chemical composition nor in pores size distribution. Its composition (Table 2) was relatively similar to other brackish water RO membranes previously reported (Coronell et al., 2010). Nevertheless, its carboxylic content was lower (0.31 M versus 0.64 M from (Coronell et al., 2010) and its pore size distribution differed. Apparently, it presented smaller network and aggregate pores (greater pka\textsubscript{1} and pka\textsubscript{2}), but a larger fraction of aggregate pores (ω\textsubscript{2}) (Figure 5 and (Coronell et al., 2010)).

The composition of the sample exposed to bisulphite, iron(III) and chlorite during 23 days (HSO3\textsubscript{ex}-Fe-CIO2\textsubscript{23d}) was similar to the virgin membrane one, mainly differing in the iron uptake by the exposed sample (0.28 ± 0.04 % in atomic weight). No chlorine incorporation was experienced, which is consistent with sample HSO3\textsubscript{ex}-Fe-CIO2 and may be due to the excess of bisulphite compared to chlorite, as previously discussed.

Before conducting the silver probing assays of the membrane exposed to bisulphite, iron and chlorite for 23 days (HSO3\textsubscript{ex}-Fe-CIO2\textsubscript{23d sample}, its uptake iron was diminished (from
0.28 ± 0.04 % to 0.07 ± 0.03 % in atomic weight) by a 2% citric acid soaking during 72h. This step aimed at removing the iron to enable the ionic binding between silver ions and all the accessible deprotonated carboxylic groups.

Silver probing experiments (Figure 5) showed that the total number of carboxylic groups did not differ (p = 0.05) between the virgin membrane and the membrane exposed to bisulphite, iron(III) and chlorite (HSO3_ex-Fe-ClO2_23d sample) (0.31 ± 0.01 M vs. 0.29 ± 0.01 M), which is in accordance with the constant concentration of oxygen to nitrogen ratio (O:N) reported from the samples analysed. This means that the exposure conditions did not cause amide bond cleavage, which would have led to more carboxylic and amine groups. However, an increase in the fraction of aggregate pores (associated to the acid-base equilibrium pKa1) could be appreciated, since ω1 from Eq. 3 increased, particularly from 0.28 of the virgin membrane to 0.41 of the exposed membrane (HSO3_ex-Fe-ClO2_23d sample) (Figure 5). Also, the decrease of pKa2 (from 8.73 to 8.20) indicated that network pores increased in size. Therefore, the exposure to bisulphite, iron(III) and chlorite modified the membrane pore size distribution, increasing the size of the network pores and the fraction of the aggregate ones. The two phenomena explain the increased chloride passage quantified in the permeation experiments.

RO membranes PA active layers are highly crosslinked and thus, the nonhydrated radius is the ionic dimension of interest to determine the accessibility of ions (Coronell et al., 2008). As a result, iron(III) due to its ionic radius (0.063 – 0.092 nm according to (Shannon, 1976)) is able to access to the network pores. Iron(III) reacts with bisulphite during the autooxidation of the later, generating metal sulphito complexes and free radicals among others. It is hypothesized that some of the compounds generated, larger in size, deform the network pores, increasing their diameter or even transforming them into aggregate pores. This would be in accordance with the modifications in the pore size distribution observed and the chloride permeation results.
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 $6.5 \pm 0.6\%$ and $9.8 \pm 0.5\%$ respectively. When combined with iron(III) (HSO3_ex-Fe, HSO3_lm-F samples), 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 $S_2O_6^{2-}$ the main oxidation products.
products (Kraft and Van Eldik, 1989b). The transition metal-sulphite complexes decompose spontaneously and the sulphite radical, \( \text{SO}_3^- \), and the reduced form of the metal are produced (Brandt et al., 1994). In absence of oxygen, \( \text{SO}_4^{2-} \) and \( \text{S}_2\text{O}_6^{2-} \) are generated; when oxygen is present, peroxomonosulphate radical, \( \text{SO}_5^- \), a strong oxidant, is also formed, which can react with \( \text{HSO}_3^- \) or \( \text{Fe(II)} \) to produce \( \text{HSO}_5^- \) (Brandt et al., 1994). Greater \( \text{Fe(III)} \) and \( \text{S(IV)} \) concentrations result in a higher formation rate of \( \text{SO}_3^- \) (Brandt et al., 1994). The ratio of \( \text{Fe(III)} \), \( \text{Fe(II)} \) and \( \text{S(IV)} \) versus oxygen is important in the overall decay of the iron(III)-sulphite complexes (Brandt et al., 1994), varying the oxidation pathway with the ratio bisulphite/iron (Ziajka et al., 1994).

The free radicals generated in the bisulphite autooxidation catalysed by iron(III) species could be the responsible for the increase in chloride passage experienced. Because of the free radical nature, the process could be sensitive to time (i.e. from bisulphite mixing point to membranes location), so that some full scale plants may have not been affected by this process. In addition to this, due to their radical nature, membrane autopsies would not probably enable the identification of the origin of the degradation. Martin and Li (1996) concluded that the kinetics of the catalysis of bisulphite oxidation by aqueous iron(III) strongly depended on pH and ionic strength, and that the reaction mechanism was very complex in itself. Furthermore, in natural water, radicals, intermediates and heavy metal ions could react with natural organic matter (NOM), \( \text{SO}_4^- \) radicals could be scavenged by some anions like hydrogen carbonate and carbonate (Li et al., 2015), or some species could react with oxygen, not leading to the detrimental effects on RO membranes observed in this work. Nevertheless, Sommariva et al. (2012) reported the same phenomena in a seawater RO plant where sodium bisulphite was overdosed in presence of heavy metal ions. The plant suffered an increased salt passage and no halogens were detected in the membrane surface. The dosage of a chelating agent, ethylenediaminetetraacetic acid (EDTA), which complexed with iron(III), prevented the membrane degradation from occurring, evidencing the catalysing effect of the heavy metal...
ions. Also, unintentionally, Gabelich et al. (2002) experienced a significant increase in salt passage in RO membranes when bisulphite was dosed to water pre-treated with FeCl₃ (4.0 - 5.0 mg/L). Gabelich et al. (2002) attributed this decay in performance to residual iron(III) catalysing a chlorine-amide reaction on the membrane surface (despite having quenched residual chlorine and obtaining negative results on free chlorine residuals in feed water); nevertheless, based on the results obtained in this work, it could be attributed to the bisulphite and iron(III) synergistic effects.

The reactivity of bisulphite with bromine-based species has been reported in literature (Khan et al., 2003) and the autocatalytic nature of bisulphite with bromine based species too (Wang et al., 2012). Li et al. (2015) studied the formation of bromate when Co(II) reacted with peroxymonosulphate by means of the sulphate radical, SO₄⁺, with Br⁻ and Br₂⁻ as intermediates. It was noted that SO₄⁺ could oxidise Br⁻ to Br⁺, generating bromine, hypobromous acid, OBr⁻ and ultimately bromate. Similar reactions involving the formation of bromine active species could be envisaged, which could explain the large amount of bromine uptaken by the membrane when bisulphite, iron(III), bromide and chlorite in excess were studied (HSO₃⁻-Fe-ClO₂-Br sample). No increase in chlorine content was noticed in the RO active layer, which would be in accordance with the greater affinity for bromine than chlorine reported (Kwon et al., 2011). Besides bromination, a large decrease in water passage was experienced, which could be due to the collapse of the polymer chains caused by the high bromine uptake, breaking the PA membrane bonds (Maugin, 2013) or the hydrogen bonds (Kwon et al., 2011). Chloride permeation coefficient increased (B/B₀ 2.9), involving 12.0 ± 0.8 % chloride passage, under the tested conditions. (Suzuki et al., 2016) recently characterised the performance and the physicochemical properties of a RO membrane used in a seawater desalination plant during three years. Sodium bisulphite was dosed to quench the free chlorine added upstream aiming
at controlling membrane biofouling. The assessed membrane presented an increased chloride (B/B₀ 3.2) and water (A/A₀ 0.67) permeation coefficients and bromine was incorporated in its active layer. The authors attributed the increased solute passage mainly to the bromine uptake and the reduced water permeability both to bromination and reduction of the polyvinyl alcohol (PVA) coating coverage. Despite the fact that the conditions that led to membrane bromination may be different in both works, the effects experienced are consistent.

When bisulphite was in excess (sample HSO₃_ex-Fe-ClO₂-Br: bisulphite, iron(III), chlorite and bromide), because of the reducing environment generated, no bromine and chlorine were uptaken by the PA. Under these conditions, water permeability coefficient did not differ from the virgin membrane one, but chloride one raised (B/B₀ 2.2), involving 7.7 ± 0.2 % chloride passage.

Further studies to determine the reactions and compounds involved in the degrading mechanisms identified in this study should be explored to better understand and control them.

5. CONCLUSIONS

- Bisulphite exposure caused an increased chloride passage (B/B₀ 1.8 – 3.9), but no major changes in terms of membrane composition were identified. The effect of chlorite and bisulphite blended depended on their relative proportion, being more pronounced those effects associated to the compound with greater stoichiometric molar concentration.

- The mixture of bisulphite and iron(III) resulted in a severe increase in chloride permeation coefficient (B/B₀ 5.3 – 5.1). It is hypothesized that an autooxidation of bisulphite catalysed by iron(III) occurred, generating highly reactive species which interacted with the membrane, negatively affecting its performance (increased chloride passage).
• When dosing bisulphite, iron(III) and chlorite, there was always an increase in chloride passage \((B/B_0 4.0 – 1.8)\), but the extent varied according to the bisulphite and chlorite molar ratios. The process was fast, affecting the membrane during the initial exposure and not increasing significantly afterwards. It was shown by silver probing experiments coupled with RBS analysis that scission of the amide bond from the PA active layer did not occur, but the size of the network pores increased and the proportion of aggregate pores raised. These two effects explain the increase in chloride passage experienced.

• When bisulphite, iron(III), chlorite and bromide were mixed the effects differed, again depending on the relative quantity of bisulphite and chlorite. In both cases the chloride passage increased \((B/B_0 2.2 – 2.9)\). In excess of chlorite, significant bromination of the membrane took place. It is thought that free radicals generated when bisulphite was limiting oxidised bromide, which was uptaken by the PA. Besides bromination, a large decrease in water passage was experienced. When bisulphite was in excess, because of the reducing environment generated, no bromine and chlorine were uptaken by the PA, and the water permeability coefficient did not differ from the virgin membrane one.

Taking into account the results obtained, water treatment facilities should carefully control iron(III) and bisulphite dosages upstream RO membranes in order to minimise their effects. The increase in chloride passage provoked when blended, under the tested conditions, may lead to a chloride passage well above the process specifications, requiring premature replacement of the RO membranes. Finally, the bisulphite dosage required upstream RO membranes should be determined in each case in order to avoid over/under dosing which could cause an undesired membrane performance as well.

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