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Reverse osmosis membranes oxidation by hypochlorite and chlorine dioxide: spectroscopic techniques vs. Fujiwara test

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ABSTRACT

The aim of this work was the study of degradation of a commercial polyamide membrane by two commonly employed oxidants for disinfection in seawater desalination, hypochlorite, and chlorine dioxide. A conventional reverse osmosis (RO) membrane is a thin film composite membrane composed of three different layers, a polyester support web, a microporous polysulfone interlayer, and a thin cross-linked polyamide barrier layer on the top surface, which is the active layer of the RO membrane. The degree of membrane degradation in seawater was evaluated in terms of decline in membrane performance calculated from permeability and salt rejection. In order to establish a relationship between the hydraulic properties and spectroscopic data, infrared and X-ray photoemission techniques (ATR-FTIR and XPS) were employed. The obtained results were compared with the Fujiwara test which is usually performed in membrane autopsies to check the degradation of polyamides with halogens. The chemical degradation of the surface active layer was analyzed using infrared spectroscopy (ATR-FTIR) by monitoring the changes in the characteristic infrared bands of the polyamide. It is possible to calculate the transmittance bands ratio between peak at 1540 cm^{-1} (due to amide II) and peak at 1585 cm^{-1} (due to the polysulfone layer) in order to get the comparison of the degraded membranes with a virgin membrane. The amide II band was selected to evaluate the degradation process, because it is the first band that reduces its transmittance value when the degradation process begins. Once the ratio is obtained for the degraded membrane and considering the value obtained from the virgin membrane as the reference point, a new index is calculated named as degradation index. The higher the parameter is, the greater the chemical attacks the polyamide layer. X-ray spectroscopy (XPS) measures the elemental composition and the chemical state of the elements that exist in the surface of a solid. Evaluation of the binding energy is possible to determine if the halogens are attached to the polyamide structure. It was concluded in this work that both spectroscopic techniques ATR-FTIR and XPS could detect the membrane degradation process earlier than Fujiwara test.

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Keywords: Polyamide membrane; Reverse osmosis; Fujiwara test; XPS; ATR-FTIR

1. Introduction

Polyamide composite membranes are most commonly used in the reverse osmosis (RO) process. These membranes consist of three different layers with different functions. The active layer is a cross-linked aromatic polyamide film and its function is to remove salts and dissolve organic molecules. The interlayer consists of a microporous polysulfone thick film above which the active layer is placed. The other layer is a polyester support which brings the necessary mechanical properties [1].

The active layer is produced by interfacial polymerization of m-phenylendiamine (MPD) and trimesoyl chloride (TMC). The chemical structure is shown in Fig. 1. Since its development by Cadotte in 1981 [2], these membranes have increased spectacularly their salt rejection and permeate flux due to improvements in the manufacture process of the membrane and improvements in module designs. However, nowadays, the chemical composition of the active layer remains the same because a polymer with better properties has not been developed to the moment. A strategy used by several membrane manufacturers involves the coating or grafting with hydrophilic polymers in order to avoid the fouling and increasing the permeability. As a consequence of the interfacial polymerization process, rough surfaces are obtained that allow getting enhanced permeability and salt rejection. This roughness can be observed and quantified with atomic force spectroscopy [3,4].

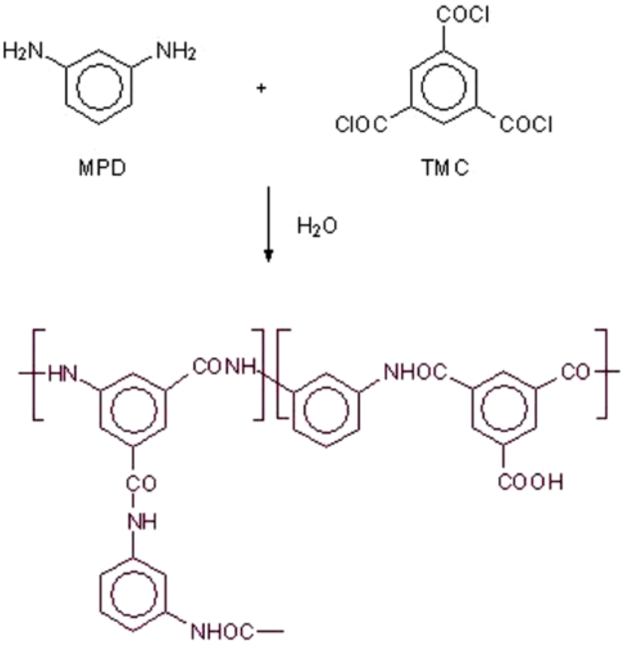

Fig. 1. Synthesis of the fully aromatic polyamide active layer.

The ideal situation for RO membranes would be the separation of salts from water, but seawater contains so many impurities that must be previously removed by specific pretreatments to preserve the hydraulic properties of the membranes. These impurities could be present dissolved, suspended, or in a colloidal state. The most common impurities found in water are zooplacton, phytoplacton, bacteria, virus, humic acids, fulvic acids, carbohydrates, other hydrocarbonated compounds, and other organic molecules coming from the degradation of biological processes [5]. All these compounds produce fouling in the RO membranes, because they are specifically designed for separating dissolved salts but not suspended solids.

Optimized water pretreatment is essential in order to reduce the amount of suspended solids, colloidal, organic, and biological matter. This is the reason why the design and the behavior of the particular pretreatment become critical to operate properly a desalination plant.

Chlorine has been widely used as a disinfection chemical in water pretreatment; however, it is known with certainty that the reaction of chlorine with natural organic matter (NOM) produces its undesirable chlorination [6]. Nowadays, the use of chlorine dioxide (ClO_2) as a disinfection chemical is increasing taking advantage of its ability to oxidize the NOM with little chlorination, while improving water taste and odor control [7]. Dabrowska et al. reported that the most commonly found by-products in water disinfection with ClO_2 are formaldehyde, acetaldehyde, glyoxal, and methylglyoxal [8,9].

The chlorination effect was tested in polyamide membranes by Glater et al. [10] employing chlorine and ClO_2 with similar results. Most polyamide RO membranes manufacturers recommend not to exceed 0.1 mg/L of available free chlorine in feed water in order to prevent damage to the membranes.

Several mechanisms have been proposed which explain the degradation produced by chlorine in RO membranes involving a sequence of two stages. First, a polymer deformation is produced (N-chlorination and/or ring chlorination) followed by a polymer depolymerization [10–13]. The last published scheme degradation, to the authors' knowledge, is the one proposed by Kang et al. which is shown in Fig. 2 [13].

Oxidation is the worst problem that RO membranes can suffer because it causes an irreversible degradation of the active layer which inevitably leads to the membrane replacement. Fujiwara test is conventionally used to check if the membrane is affected by chlorine exposure; however, Antony et al. pointed out ATR-FTIR spectroscopy as a useful tool that can detect oxidation in RO membranes in the presence of hypochlorite more efficiently than the Fujiwara test [14].

Originally, Fujiwara test was based on a spectrophotometric analysis which could detect halogenated organic substances with the absorbance at 530 nm and even quantify them at concentration levels as low as 1 μg [15].

Traditionally, a three step mechanism has been widely accepted to explain the Fujiwara reaction. The chromophore responsible for the red color was assigned to the product in the second step. The mechanism is shown in Fig. 3 [16].

However, a different mechanism was proposed by Uno et al. [17] to describe the reaction in 1981. This mechanism was based on a nuclear magnetic resonance study, where the red colored specie was assigned to the product in the fourth step. The new mechanism is shown in Fig. 4.

Nevertheless, in the area of membrane autopsy, Fujiwara test is performed as a qualitative test indicative of membrane exposure to chlorine. One of the targets of this work was to confirm that the Fujiwara test detected the oxidation only when it is in an advanced stage.

Furthermore, the water matrix composition has a high influence on the degradation processes object of this study; in particular, it is known that bromide ions are present in seawater at a concentration of 65 mg/L and react rapidly with hypochlorous acid to form hypobromous acid [18]. Consequently, it should be taken into consideration that the presence of chlorine-based oxidants in seawater could lead to the oxidation of bromide ions into bromine which is a significant candidate to take part in the degradation of the

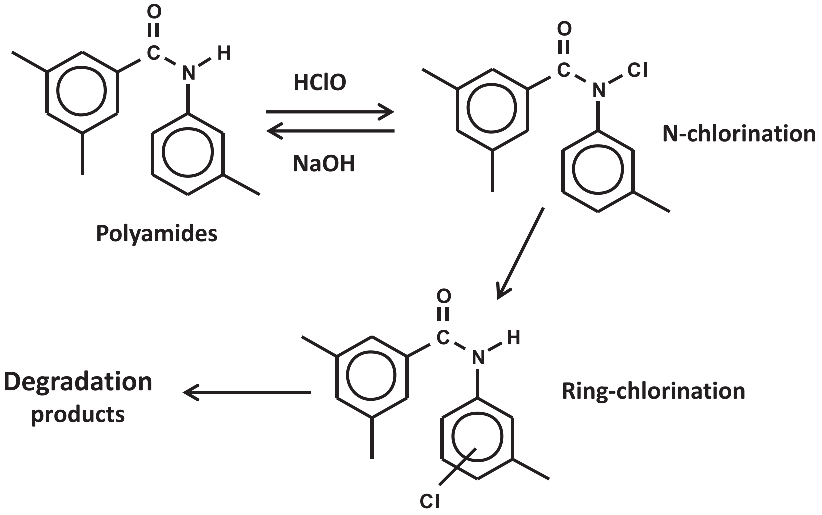

Fig. 2. Scheme proposed by Kang for hypochlorite degradation of polyamide membrane [13].

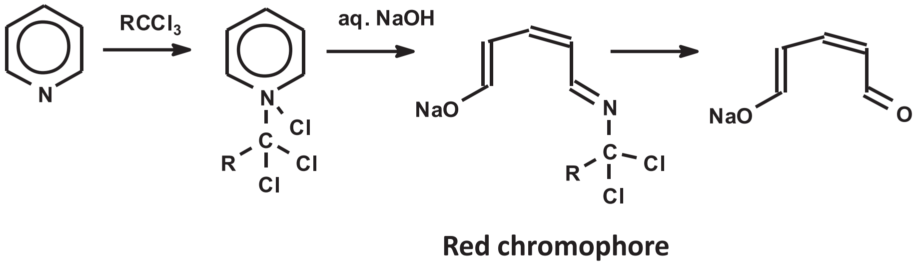

Fig. 3. Fujiwara reaction mechanism proposed by Moss [16].

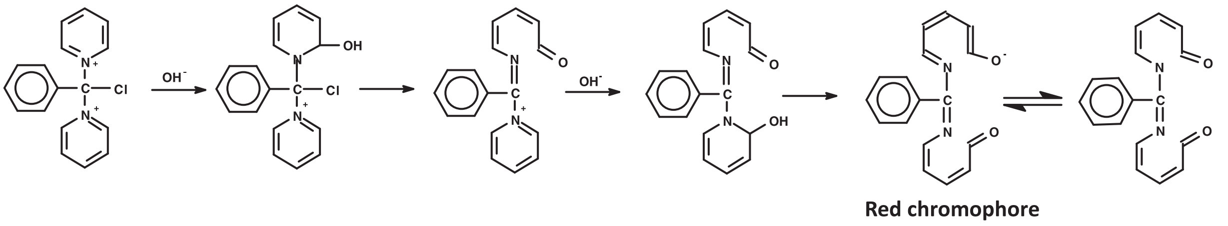

Fig. 4. Fujiwara reaction mechanism proposed by Uno [17].

polyamide membrane. This effect was previously studied by Kwon et al. [19].

In this work, sodium hypochlorite (NaClO) and ClO_2 were evaluated in different water matrices in order to shed light on the degradation effect caused by these two chlorinated oxidants on a conventional polyamide membrane.

2. Methods and materials

2.1. Membranes and chemicals

A commercially available polyamide RO membrane, SWHR-380, supplied by Dow Filmtec, was used in this study. Accelerated degradation experiments were performed with NaClO and ClO_2.

NaClO was supplied by Barcelonesa de Drogas and the desired concentrations were reached by means of its dilution with milli-Q water. The available chlorine concentration in this study was 50 mg/L and the duration of the exposure tests were conditioned to the achievement of a positive result on the Fujiwara test.

ClO_2 was generated using the standard method 4500-ClO_2-B [20]. ClO_2 aqueous solution was prepared by reaction of sodium chlorite with diluted sulfuric acid, immediately purified by bubbling air through 10% sodium chlorite aqueous solution to remove traces of chlorine, and finally absorbed in distilled water. Stock solutions of ClO_2 were stored in the dark at 5˚C. ClO_2 concentration was determined by DPD, Standard Method 4500-CLO_2-D [20]. To verify that the ClO_2 was free of chlorine, the selective amperometric sensors such as ChloroSense and ChlorodioXense, supplied by Palintest, were employed. The ClO_2 detector measured the ClO_2 concentration, while Cl_2 detector did not detect any amount of chlorine. The available ClO_2 concentration in this study was 50 mg/L and the duration of the exposure tests was conditioned to the obtainment of positive Fujiwara test results.

The study was carried out in three different water matrices, milli-Q water, milli-Q water with 40 g/L of sodium chloride, and seawater filtered with a 0.45 µm mesh, in order to establish the influence of conductivity and the amount of bromide on the degradation process.

2.2. Experimental methodology

The accelerated membrane degradation tests were performed by means of the immersion of membrane swatches in the particular solution of study placed in sealed amber vessels during the required time. Once the exposure test was finished, the membrane swatch was gently cleaned with milli-Q water to stop the degradation process and to ensure that all oxidant species were removed. Table 1 shows the chemical characterization of seawater sample employed in these experiments.

2.3. ATR-FTIR analysis

The ATR-FTIR characterization of the membrane surface was performed using a Perkin-Elmer Spectrum One FTIR spectrometer equipped with a

Table 1
Analysis of the seawater employed

Parameter	Value	Unit
pH	7.95	
Conductivity	62,300	µS/cm
Turbidity	0.3	NTU
Osmostic pressure	28	Bar
Total dissolved solid	39,205	mg/L
Total suspended solids	20	mg/L
Total organic carbon	0.5	mg/L
Alkalinity	236	mg/L as $CaCO_3$
Chloride	21,204	mg/L
Sulfate	2,890	mg/L
Bromide	72	mg/L
Sodium	12,244	mg/L
Magnesium	1,449	mg/L
Calcium	400	mg/L

diamond crystal ATR unit. All spectra were collected with four scan at 4 cm^{-1} of resolution.

2.4. X-ray spectroscopy (XPS) analysis

X-ray photoemission spectra were recorded with a SPECS PHOIBOS 100 spectrometer fitted with a hemispherical energy analyzer working at a constant pass energy of 50 eV. The base pressure of the analysis chamber was in the range of 10^{-10} Torr. Unmonochromatized MgKα was used as excitation source. As membrane samples are insulators, binding energy (BE) calibration of the spectra was done by referencing the recorded peaks to the C1s peak at 284.9 eV. Surface atomic concentrations have been calculated by estimating the area of the elastic photoemission peaks, by subtracting the Shirley type backgrounds [21], and then by correcting proper sensitivity factors [22]. The thickness of the analyzed top layer of the sample was estimated to be around 8 nm. Before their analysis, membrane samples subjected to oxidizing treatments with NaClO or ClO_2 solutions were thoroughly rinsed with pure water to remove the excess of oxidizing agent and then dried at room temperature for several days. In addition, virgin membrane samples were immersed in sodium chloride or sodium bromide diluted solutions and then dried at room temperature for several days. These last samples were used as references for chloride and bromide ions adsorbed on the polyamide network.

2.5. Fujiwara analysis

One square centimeter of membrane was cut and placed in a test tube. Sodium hydroxide and pyridine were added to the sample and allowed react at 90°C for one minute. The result was considered positive when a pink color was observed, while the results were considered negative when no color was observed.

In Fig. 5, a positive result (pink color) and a negative result (no color) are shown.

3. Results and discussion

3.1. ATR-FTIR analysis

A complete description of the characteristic bands of a fully aromatic polyamide can be found in the literature [23]. Peaks considered in the present study are described in Table 2.

ATR-FTIR spectra of a virgin and a degraded membrane are shown in Fig. 6 as an example of the graphical visualization that can be obtained for the characteristic bands of the two considered layers in the RO membrane. It is possible to appreciate the intensity decrease in the amide II band and its shift toward lower wave numbers; due to its sensitivity to degradation, this band was selected as the most appropriate indicator to control this particular degradation process.

From the raw data, it is possible to calculate the transmittance bands ratio between peak at 1,540 cm^{-1} (due to amide II) and peak at 1,585 cm^{-1} (due to the polysulfone layer) in order to get the comparison between the degraded swatches and the virgin one of the studied membrane. Once the ratio is obtained, a new index is calculated named as degradation index (DI) (Eq. (1)) which considers the ratio obtained from the virgin membrane as the reference value. The higher the DI, the greater is the chemical attack to the polyamide layer.

$$\mathrm{DI} = \frac{\{T^N 1540\ \mathrm{cm}^{-1}/T^N 1585\ \mathrm{cm}^{-1}\}_{\mathrm{sample}} - \{T^N 1540\ \mathrm{cm}^{-1}/T^N 1585\ \mathrm{cm}^{-1}\}_{\mathrm{virgin}}}{\{T^N 1540\ \mathrm{cm}^{-1}/T^N 1585\ \mathrm{cm}^{-1}\}_{\mathrm{virgin}}} \qquad (1)$$

A previous kinetic study was carried out by collecting membrane samples at different exposure times to 50 mg/L of NaClO in milli-Q water, where the DI determination and the Fujiwara test were performed simultaneously (Fig. 7). Fig. 7 shows that Fujiwara test was positive after exposure for 220 h. However, the DI obtained by infrared spectroscopy indicates that the membrane is oxidized much earlier. According to these results, it can be stated that although the Fujiwara test is negative, the membrane is oxidized in terms of DI.

In order to confirm this observation, six independent tests were carried out, where RO membranes were exposed to oxidants in different experimental

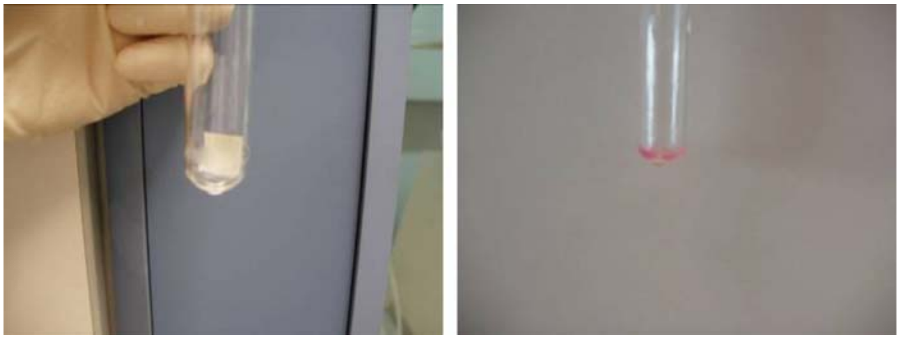

Fig. 5. Fujiwara negative (left) and positive (right) results.

Table 2
Assignment of the main characteristic peaks for polyamide and polysulfone polymer films

Peaks assignable to	FTIR peaks	Description
Polysulfone	1,587 cm^{-1}	Aromatic in-plane ring bend stretching vibration [30]
Polyamide	1,663 cm^{-1}	Amide I band (C=O stretching, C–N stretching and C–C–N deformation vibration in a secondary amide group [31])
	1,609 cm^{-1}	C=C ring stretching vibration [32]
	1,541 cm^{-1}	Amide II band (N–H in-plane bending and N–C stretching vibration of a –CO–NH-group [30])

conditions. The experiments were planned in order to assess the influence of the oxidant (NaClO and ClO_2), the salinity of the water matrix, and the presence of bromide. These experimental conditions are listed in Table 3.

3.2. Fujiwara analysis

Fujiwara tests were carried out on membrane swatches immersed in each particular solution (tests listed in Table 3) until the first sign of positive result or until the maximum set time, 1,000 h, is reached; whereas, water flux, salt rejection, DI, and XPS analyses were performed on membrane samples collected at a point of the experiment in which Fujiwara test still resulted negative. The obtained Fujiwara results for each experiment are shown in Table 4.

No positive results were obtained with 50 mg/L of ClO_2 after 1,000 h of contact in milli-Q water and in milli-Q water with 40 g/L of sodium chloride. How-

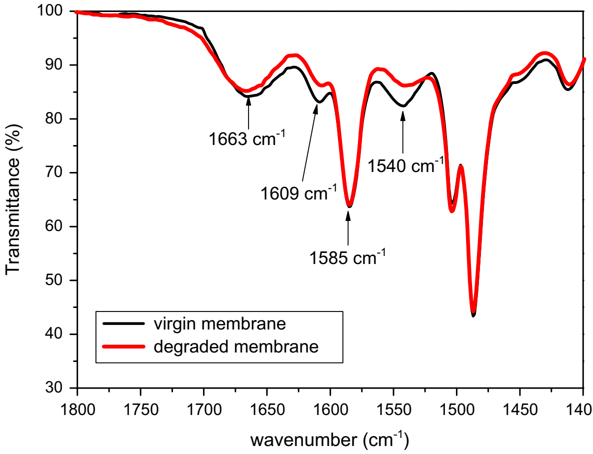

Fig. 6. ATR-FTIR spectra of virgin and degraded membrane swatches exposed to NaClO.

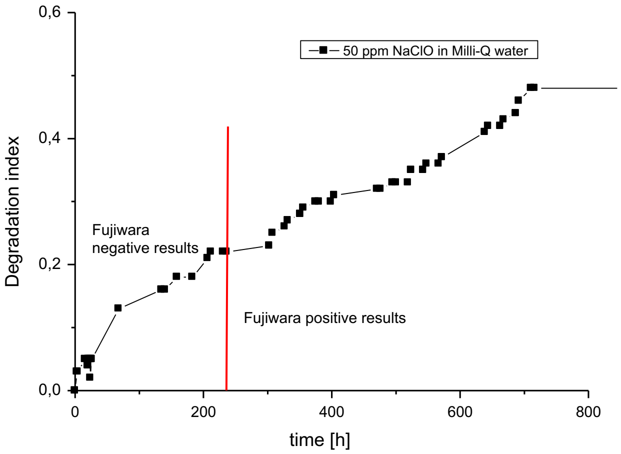

Fig. 7. DI during different exposure times.

ever, when this oxidant was present in seawater, the Fujiwara test was positive in only 16 h. The suggested reason for the different behavior is related to the bromide content of seawater, which can be oxidized to hypobromite in the presence of ClO_2. It is known that ClO_2 has a low halogenation capacity, while hypobromite has a strong halogenation effect, which is even higher than that of hypochlorite [24,25]; thus, this observation agrees with the accepted mechanism of polyamide degradation which involves its halogenation [10–13].

When the studied oxidant was NaClO, Fujiwara positive results were obtained in all cases. Longer times were needed when the exposure test was in milli-Q water, while the presence of sodium chloride caused a significant acceleration in the degradation process and the seawater matrix made this process even faster. Once again, the suggested reason for the faster oxidation in seawater is the generation of hypobromite, which is the predominant hypohalite present in a solution with hypochlorite [24,25].

Table 3
Experimental conditions of the membrane exposure tests performed in this work. The oxidant concentration was 50 ppm in all tests

Test	Experimental conditions
1	NaClO in Milli-Q water
2	ClO_2 in Milli-Q water
3	NaClO in water with 40 g/L of sodium chloride
4	ClO_2 in water with 40 g/L of sodium chloride
5	NaClO in seawater
6	ClO_2 in seawater

Table 4
Results of the Fujiwara tests performed on membrane samples in contact with 50 mg/L of NaClO and ClO_2

Test	Negative Fujiwara (analyzed sample) (h)	Positive Fujiwara test (h)
1	300	320
2	1,000	ND
3	10	12
4	1,000	ND
5	6	7
6	15	16

Note: ND: Not detected.

3.3. *Water flux and salt rejection*

Permeability and salt rejection of the virgin exposed to NaClO or ClO_2 membranes were determined. The standard test was carried out following the manufacturer specifications: 32 g/L NaCl, 55 bar (25˚C), and pH 8. As can be seen in Fig. 8, the salt rejection decreased and the normalized permeate flow increased in all the samples exposed to oxidant agents. The observed losses of hydraulic properties are characteristic of degraded membranes attacked by oxidants that are not working properly and must be replaced.

The increase in permeate flux due to the oxidative process was evaluated by means of the ratio of the flux obtained for the virgin membrane sample (J_{virgin}) and the flux determined in samples exposed to oxidants (J_{oxidized}). The increase in flux is expressed as a percentage and it is defined in Eq. (2).

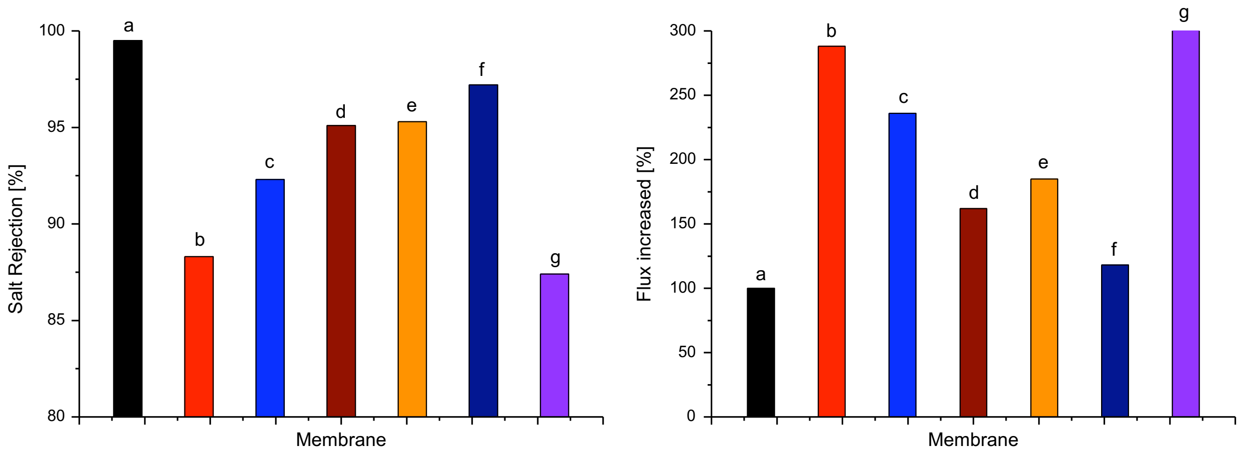

Fig. 8. Salt rejection and flux increase of the damaged membranes in comparison with the virgin one. (a) Virgin, (b) Milli-Q NaClO, (c) Milli-Q ClO_2, (d) NaCl NaClO, (e) NaCl ClO_2, (f) seawater NaClO, and (g) seawater ClO_2.

$$\% J = J_{\text{oxidized}} / J_{\text{virgin}} \times 100 \tag{2}$$

As the sampling was conditioned to Fujiwara negative results, it has no sense to compare the oxidative processes that the damaged samples have suffered during this study, from the hydraulic properties point of view. One can only state that all degraded membrane samples have experienced an oxidative process which leads to a significant decline in membrane performance (higher water flux and lower salt rejection).

Although all membrane samples resulted in negative Fujiwara test, the oxidation can be confirmed by the hydraulic parameters.

3.4. Degradation index

The DI values obtained by infrared spectroscopy of all the membrane samples exposed to oxidants are shown in Table 5. DI values higher than 0.05 units are indicative of membrane degradation; thus, it can be stated that the damage on the polyamide layer was initiated in all the studied cases, in terms of DI.

Infrared spectroscopy can also detect the oxidation on the membrane active layer at an earlier stage than the Fujiwara test.

Table 5
DI of the membrane samples exposed to oxidants

Sample	DI
Milli-Q NaClO	0.098
Milli-Q ClO_2	0.060
40 g/L NaCl NaClO	0.056
40 g/L NaCl ClO_2	0.188
Seawater NaClO	0.099
Seawater ClO_2	0.215

3.5. XPS analysis

The application of XPS analysis to membrane science is very useful to clarify the membrane oxidation, because this technique can detect and quantify the presence of halogens in the membrane surface and, which is more relevant, it can show the chemical state of the incorporated species. In short, the BE and other spectral characteristics of X-ray excited photoemission peaks from atoms located at the surface of solids allow to determine the chemical state of these elements, while the intensities of their signals can be used for quantifying their relative atomic concentration.

Thus, photoemission Cl2p and Br3d spectra obtained for membrane samples subjected to oxidative treatments with NaClO are shown in Fig. 9, where they are compared with those ones from membranes immersed in chloride and bromide solutions. (Similar results were obtained for samples treated with ClO_2, but the spectra are not shown for sake of simplicity).

As expected, differences in BE values were significant enough to determine if the chloride or bromide are linked to C atoms in the membrane or are just adsorbed as chloride or bromide.

In particular, the BE of Cl2p peak in the virgin sample immersed in sodium chloride is 198 eV, while its value is around 200.4 eV for the sample exposed to halogens (NaClO or ClO_2). These BE values are in good agreement with those ascribed in the literature to chloride anions or Cl covalently bonded to carbon, respectively [26,27]. Note that for the samples treated in milli-Q water or in seawater, regardless of the oxidizing agent used (NaClO or ClO_2), the intensity of the Cl2p peak is quite different. More precisely, as seen in spectra in Fig. 9 left, or in Table 6, the surface atomic concentration on Cl–C species is much higher for the samples oxidized in pure water than for those

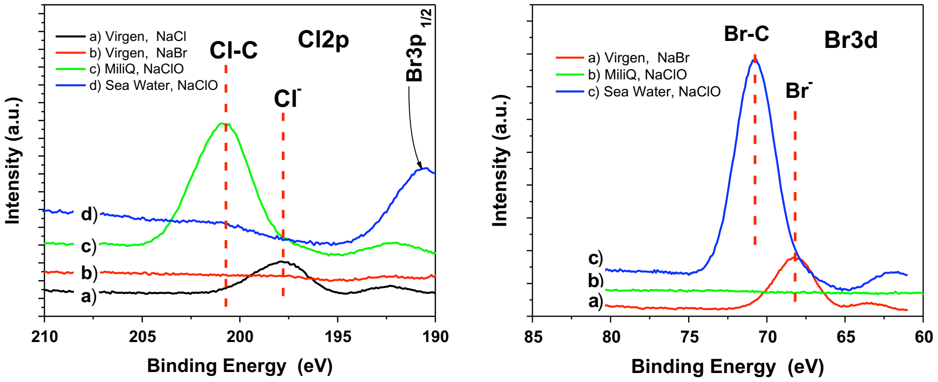

Fig. 9. Cl2p spectra (left) and Br3d spectra (right) of samples subjected to oxidizing treatment with NaClO in milli-Q water (left) or in seawater (right). Spectra for adsorbed Cl^- and Br^- anions are also shown.

Table 6
Quantitative analyses of the surface top layers (8 nm depth) of membranes determined by XPS

Sample	% C	% O	% N	% Cl	% Na	% Ti	% Br	% Ca	Total
Milli-Q NaClO	67.80	20.00	9.10	2.10	0.59	0.15	0.00	0.26	100.00
Milli-Q ClO_2	67.60	24.20	6.80	0.73	0.22	0.25	0.00	0.20	100.00
40 g/L NaCl NaClO	68.20	21.90	8.40	0.70	0.17	0.00	0.50	0.13	100.00
40 g/L NaCl ClO_2	66.40	21.70	8.20	1.06	0.16	0.13	2.21	0.14	100.00
Seawater NaClO	66.90	21.71	8.30	0.00	0.00	0.00	3.09	0.00	100.00
Seawater ClO_2	65.00	27.54	4.80	0.00	0.00	0.00	2.55	0.11	100.00

oxidized in seawater. Table 6 shows the quantitative analyses of all treated samples.

Moreover, as shown in Fig. 9 right, where the Br3d peak is recorded for samples treated with NaClO, a very strong signal for Br covalently linked to C is found (at 70.6 eV BE) [28,29] in the sample treated in seawater. As no signal from Br species can be detected in the virgin sample (not shown in Fig. 9) or in that one treated in milli-Q water, it must be conclude that Br species comes from seawater. In other words, when the degradation process was carried out in milli-Q water, chlorination was produced in the polyamide membrane. However, in seawater, bromination was produced instead. This fact is produced because the hypobromite has a stronger halogenation effect than hypochlorite [24,25]. Finally, the degradation of water with 40 g/L NaCl agrees with an attack caused by the combination of hypochlorite and hypobromite; this effect was indeed expected because of the bromide impurities that the NaCl, used for preparing the solution, can contain.

Once again, although Fujiwara test was negative in all cases, chlorination and/or bromination of the polyamide layer was detected by XPS analysis.

4. Conclusions

The decline in the hydraulic properties of six membrane samples studied at different experimental conditions confirmed a significant degradation on their active layer to the extent that they would have to be replaced if they were in a real plant. However, Fujiwara test did not warn about this dramatic situation.

The degradation of the polyamide membrane was followed by using ATR-FTIR spectroscopy and a new index was defined to evaluate the degradation process. All the membrane samples analyzed by ATR-FTIR were degraded in terms of DI.

The XPS analysis allowed clarifying the chemical state of Cl^- and Br^- due to the different BEs observed. In all cases, chlorination and/or bromination of the polyamide layer was detected.

Both spectroscopic techniques were able to detect a significant degradation on the active layer of the membrane samples when the Fujiwara was still negative and could explain that an oxidation of the polyamide was produced.

To conclude, both spectroscopic techniques allow justifying degradation in polyamide membranes when Fujiwara could not explain it.

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