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End-of-life reverse osmosis membranes: Recycle procedure and its applications for the treatment of brackish and surface water

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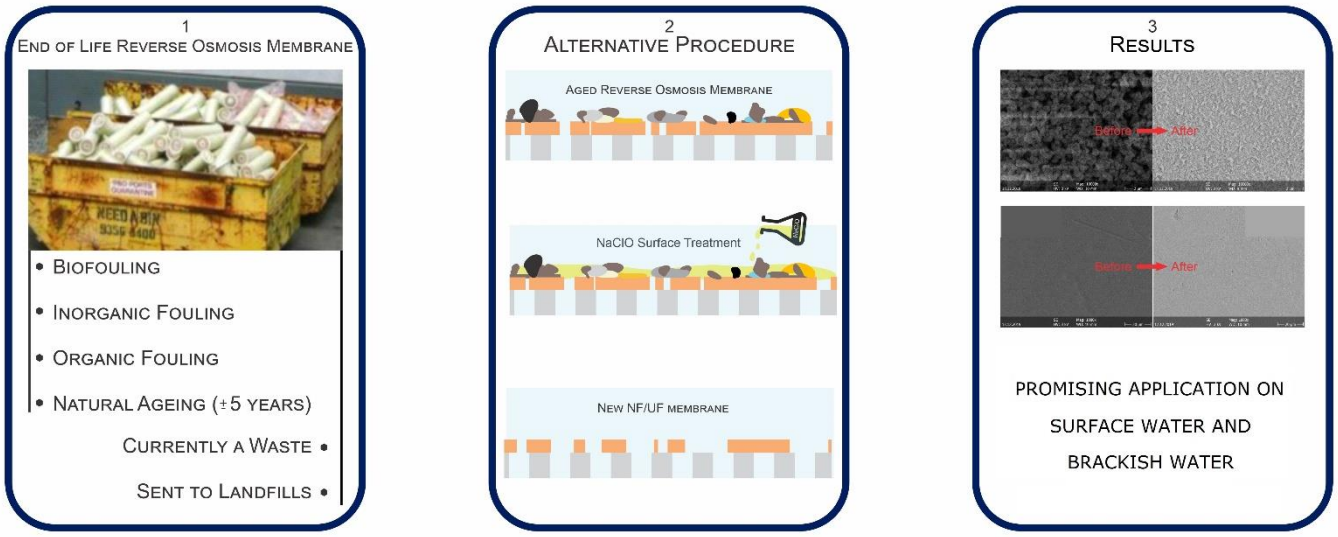
GRAPHICAL ABSTRACT



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ABSTRACT

As a result of population growth and potable water scarcity, an increasing number of reverse osmosis desalination plants are being installed and operated (more than 15,000 in the world). Reverse osmosis membranes tend to reach the end of the life cycle in around two to five years, becoming a solid waste. Recycling/repurposing these aged membranes could be a sustainable and profitable solution. This project aimed to transform end-of-life reverse osmosis membranes through the oxidation of their active layer using chlorine into nanoporous/microporous membranes, while searching possible applications for the resulting membranes. The results show that membranes oxidized at 10,000 ppm.h had a significant increase in permeability (3.1x), reaching NF-like capacity. On the other hand it was observed a decrease in the rejection of salt (4.35x) and acetaminophen (1.5x). Scanning Electron Microscopy (SEM) shows the positive effect of chlorine in the complete removal of particles deposited over the membrane. This oxidation condition also increased the average roughness (2.42x) of the membrane, as shown by Atomic Force Microscopy (AFM). Analysis by Fourier Transform Reflectance Spectroscopy (FTIR) suggests that chlorine oxidation replaced the hydrogen in the amide nitrogen. Both FTIR and SEM suggests the polyamide layer was not fully degraded. Application tests suggests that the recycled membrane can be used for the treatment of brackish and surface waters. The recycling of reverse osmosis membranes can be an alternative to simple landfill disposal, allowing owners to shift from disposal cost to revenue, as well as being a sustainable solution. The high permeability achieved on these oxidized membranes suggest many other NF/UF functions could potentially use recycled RO membranes.

1. Introduction

The sixth objective of Sustainable Development Goals from the United Nations is the supply of drinking water to the growing population (Sørup et al. 2020), which is an urgent demand from society (Hibbs et al. 2016). The need for water is estimated to yearly grow by 1 % (Al-Najar et al. 2020), pressured by population growth and water scarcity. In addition to strategies for preserving existing water sources, it is necessary to look for new sources and new techniques for potable water production, to meet this growing demand for this inevitable resource (Lilane et al. 2019). Reverse Osmosis (RO) has the capacity of producing potable water (Lilane et al. 2019; Aghababaei. 2017),

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either for the treatment of wastewater, or for the desalination of brackish and saline water. In fact, the annual growth rate of reverse osmosis desalination in the world is approximately 55 % (Okamoto and Lienhard. 2019). The intensive and worldwide use of RO membranes creates another issue: the aged membranes. Biofouling (Nejati et al. 2019), inorganic fouling (Ruiz et al. 2019) and organic fouling (Guo, Ngo and Li 2012; Sim et al. 2018; Oulad et al. 2018) can cause damages to RO membrane. In addition, these polymeric composite membranes (Liu et al. 2008; Zaidi et al. 2015; Zou et al. 2010) are likewise affected by the cycles of cleaning, as a result of the chemicals applied during the process (Benavente and Vázquez. 2004). Finally, the polymeric membranes are susceptible to chlorine attack, which also lead to lifespan remission (da Silva et al. 2021).

The aged RO membranes are becoming an environment liability (Lawler et al. 2012), given that they are currently being sent as solid waste to landfills, after all recycling is not the usual procedure to disposal (Goodship. 2007). Each year 14,000 tons of membranes are accommodated in landfills around the globe (Landaburu-Aguirre et al. 2016; Lee, Arnot and Mattia. 2011). Incinerating the membranes for thermal exploitation is possible, however, considering the side effects, a more sustainable alternative is required (Pontié et al. 2017). Thereby, giving these aged membranes a second life cycle could be a solution. Mohamedou et al. (2010) performed autopsies on aged RO membranes, the results demonstrate that aged RO membrane could be directly reused as Nanofiltration (NF) for seawater pretreatment. Rodríguez et al. (2002) proposed chemical treatments that could be applied to aged RO membranes to allow the recycling of these membranes. Veza e Rodriguez-Gonzalez (2003) modified aged RO membranes by surface oxidation using potassium permanganate, producing an efficient filtration membrane for tertiary treatment of municipal wastewater. Lawler et al. (2012) suggested that the treatment of the aged RO's surface prior to the recycling could increase the sustainability of this technology. Furthermore, Pontié (2014) pointed several strategies for the recycling of aged RO membranes and one proposal of the researcher was to transform aged RO membranes into ultrafiltration (UF) membranes after oxidation with sodium hypochlorite. Pype et al. (2016) showed that sodium hypochlorite modified the selective layer of aged membranes by introducing chlorine into the molecular structure of the membrane, resulting in the increase of the permeability and decrease of the rejection of interest compounds. Antony et al. (2016) reported that the RO's rejection to salt decreased from 99% to 40% on hypochlorite aged membranes, at the pace that the permeability increased by 261%. On the other hand, Donose et al. (2013) analyzed three types of commercially available RO membranes that were exposed to hypochlorite solutions and achieved high salt rejection even after oxidation, when the permeability only increased if the oxidation of the membrane occurred at basic pH. García-Pacheco et al. (2019) reported that these treatments ensued in the transformation of aged RO membranes into NF and UF membranes. Thus, the oxidation of aged RO membranes by hypochlorite is a promising alternative to convert aged RO membranes to recycled NF or UF membranes, extending the life cycle of membranes on other applications.

The use of recycled RO membranes must be studied to identify potential applications, such as for the treatment of surface water, tertiary treatment of wastewater, or for the removal of emerging pollutants from water sources. The presence of emerging pollutants is being frequently reported worldwide, not only in superficial water (Geissen et al. 2015; Mutiyar, Gupta and Mittal. 2018; Heidarzadeh et al. 2020), but also in groundwater (Sacher et al. 2001), lakes (Daneshvar et al. 2010) and rivers (Wiegel et al. 2004). The long-term effects of these emerging contaminants in humans are still uncertain (Taheran et al. 2018). Paracetamol, also known as acetaminophen, is a clinical use substance of 151, 2 g/mol. Acetominophen is an emerging contaminant, traces were found in a river source of potable water in northern Brazil (Veras et al. 2019). Most water and wastewater treatment plants are unable to remove such compounds (Veras et al. 2019). Post-treatments may still be required to remove these emerging contaminants from treated water, and the recycled RO membranes could be introduced in such treatment plants. Thereat acetaminophen was chosen as an interesting compound, representing medium size molecules. Fig. 1 shows the size range of several molecules, and some characteristics of the membrane separation processes. As the oxidation widens the pores on the selective layer, the selectiveness of the membrane is lowered, while the permeability increases. This procedure may allow the usage of recycled membranes for applications that natively utilize NF or UF.

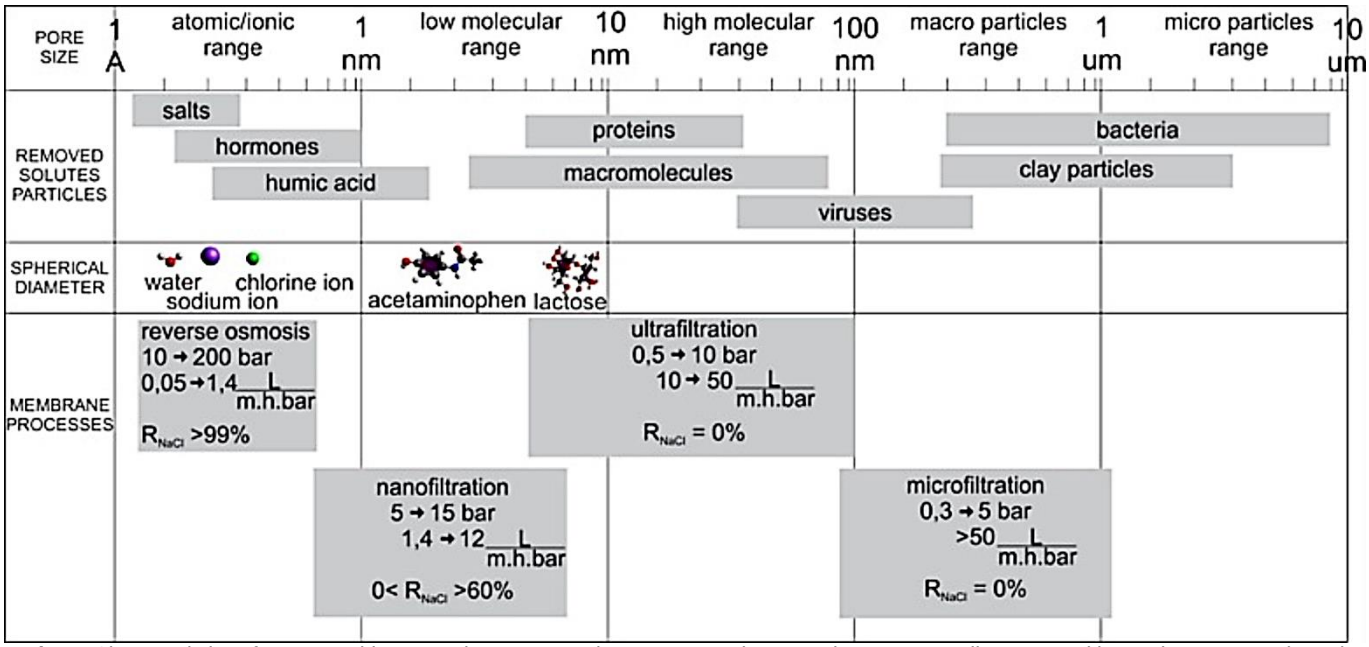


Fig. 1. Characteristics of pressure driven membrane separation process and some substances usually separated by each process. Adapted from Warsinger et al. (2018).

In order to enter the circular economy, these recycled membranes must prove to be able to perform in specific applications. There are several application niches for these recycled membranes (Raval et al. 2012), such as the water demineralization, pre-treatment of brackish water, pre-treatment for desalination, surface water treatment, post-treatment of drinking water, clarification of effluents, grey water reuse systems, rainwater reuse system or even specific compound removal. In fact, Lawler et al. (2013) reported that each recycled membrane requires its own characterization and individual attribution for proper application. While several works describe and break down the processes involved in membrane oxidation and its effects, few articles actually applied the recycled membranes for individual applications.

The aim of this work was to transform end-of-life RO membrane into a technically viable lower selectiveness membrane as NF or UF by oxidizing the selective layer of the aged RO membrane and test possible applications for the recycled membrane. The membrane oxidized at 10.000 ppm.h presented an increase in permeability, approaching NF-like membranes. A decrease in the rejection of salt and acetaminophen was observed as a result of oxidation. Scanning Electron Microscopy (SEM) evidences the complete removal of particles over the membrane after oxidation. Average roughness

increased after oxidation, Fourier Transform Reflectance Spectroscopy (FTIR) suggest polyamide layer still remains over the membrane. Application tests suggests the membrane 10.000 ppm.h could be applied to treat brackish water and surface water. By recycling these aged membranes, there could be a shift from disposal cost to source of revenue, benefiting both society and environment.

2. Materials and methods

2.1. Materials

The aged RO membrane was a 4" Ultra Low Pressure 2012 – 100 from Vontron. The membrane is of spire-wound configuration, made of polyamide and with an area of 1.4 m². The aged membrane was gently donated by Purificatta Company (Brazil). The first life cycle of the membrane was to treat well-water in self-service machines (please see https://purificatta.com.br/).

For the cleaning procedure, Analytic Standard Nitric Acid (Synth), Sodium Hypochlorite 12 % (Synth) and WClean-Enz (WGM) were used. The clean membranes were stored in Analytic Standard Glycerin (Dinamica Química Contemporanea). Acetaminophen (Sigma Aldrich) and Lactose Monohydrate (Synth) were used for the rejection tests.

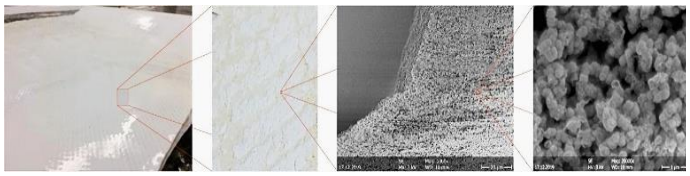
2.2. Methodology

Methodology was divided in related subsections further detailed below.

2.3. Membrane autopsy and cleaning

The membrane was stored in wet conditions into permeate of RO. An autopsy of the membrane was performed prior to the cleaning procedures and oxidation tests (Fig. 2). The membrane was disassembled, and the flat sheets were rinsed using an appropriate protocol. In order to simulate the mechanical effect of the high flux during standard cleaning procedures of membrane systems, the membranes were gently brushed for exact 5 minutes while submerged in a series of different pH solutions, as follows: 7,0 (H_2O), 11 (NaOH), 7, 4 (HNO_3) and 7,0 (H_2O). The cleaning procedure inspired upon the protocol of García-Pacheco et al. (2019) with the addition of the extra mechanical procedure.

Coupons of 200 cm^2 (20 cm x 10 cm) were cut from different areas of the membrane and stored in Milli-Q water. Note that even after standard cleaning procedures, the coupons were not scaling free (Fig. 2b).



(a) (b) (c) (d)

Fig. 2. (a) and (b) pictures of the membrane during the autopsy procedure of the aged membrane, (c) and (d) scanning electronic microscopy (SEM) of the aged membrane at 20 µm and 1 µm, respectively.

The characteristics of the aged membrane can be found along with the results. In summary, the hydraulic permeability is 5.59 L/h.m^2.bar (Table 3) and the salt rejection is 64.2 % (Fig. 6a).

2.4. Oxidation of the membrane

The oxidation solution was prepared by diluting NaOCl with Milli-Q water without pH correction. Table 1 summarizes the conditions of each treatment as well as the oxidation solution pH.

Table 1. Experiments conditions of oxidation of the aged RO membranes.

Test name	Exposure dose (ppm.h of Cl_2)	Oxidation Solution pH
0	0	-
8,000	8,000	11.32
9,000	9,000	11.56
10,000	10,000	12.08

The oxidizer solution was poured into 1 L beakers, and each coupon was submerged in the solution for 1 h. The oxidation process protocol was inspired from García-Pacheco et al. (2019). Following the exposure time, coupons were soaked in Milli-Q water five times for the complete removal of any residual chemical. The residual chlorine and pH of the rinse water were measured by quick tests (Genco - Brazil) to ensure that the membrane was chlorine free and in neutral pH. Note that "Test 0", which is also referenced as 0 ppm.h refers to the aged RO membrane (not oxidized).

2.5. Investigation of membrane performance

The methodologies of membrane performance evaluation were further divided in related subsections and detailed below.

2.5.1. Permeate flux and hydraulic permeability

The experiments were conducted using a commercially available bench-scale membrane test cell (Sepa CF, GE Osmonics) for flat sheets membranes. Fig. 3 shows the schematic of the equipment. The feed solution (6) had the temperature recorded (7) during the process. The pump (5) forced the solution through the test cell (2), the internal pressure was measured using a gauge (3). A valve (4) was used to manage the flow and the pressure. The concentrated was poured back to the feed solution (6) while the permeate was stored (1) for further analysis. To evaluate the flux of the membrane, the operation time was recorded using a regular stopwatch and volume of permeate was measured by a graduated cylinder. During the procedures, the coupons (200 cm^2) were placed inside the test cell (2). The hydraulic permeability test utilized Milli-Q water, being the first test of each membrane. Followed by membrane rejection of salt, acetaminophen and lactose (2.3.2) and finally the application test. During the batch of experiments, the membranes were not removed from the test cell, since it would dislocate the membrane, which can cause procedural errors.

The flux and permeability procedure were inspired by methodologies published elsewhere (García-Pacheco et al. 2015; García-Pacheco et al. 2019; Lawler et al. 2012; Lawler et al. 2013; Rodríguez et al. 2002).

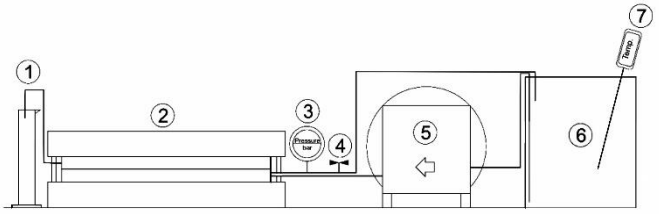


Fig. 3. Schematic of the bench-scale membrane test cell, (1) graduated cylinder, (2) test cell, (3) pressure gauge, (4) recirculation valve, (5) pump, (6) feed solution storage beaker, (7) thermometer.

We studied the mechanism of transport through reverse osmosis membranes by the hydration-diffusion mass transfer well-known model (Eq. 1).

$$J = A\,\Delta P - \Delta\pi \quad (1)$$

$$R = A\,\frac{(\Delta P - \Delta\pi)}{A(\Delta P - \Delta\pi) + B} \quad (2)$$

where, A = the hydraulic permeability, B the ions permeability, ΔP-Δπ the effective transmembrane pressure, ΔP is the difference in pressure across the membrane, Δπ is the osmotic pressure of the feed solution.

For the attacked end-of-life RO membranes, another simple model of liquid flow through these membranes is to describe the membranes as a series of cylindrical capillary pores of diameter d. The liquid flows through a pore (q) is given by Poiseuille's law (Eq. 3).

$$q = \frac{\pi \times d^4}{128 \times \mu \times l} \times \Delta P \quad (3)$$

where, ΔP is the pressure difference across the pore, µ is the liquid viscosity and l is the pore length. The permeate flux (Jp) is the sum of all the flows (q) through the individual pores and can be obtained by the Eq. 4.

$$J_p = L_p\,\Delta P \quad (4)$$

where, Lp is the hydraulic permeability expressed in L/h.m^2.bar, ΔP is the difference in pressure across the membrane.

The permeate flux (J) was determined by volumetrically measuring the permeated at different feed pressures. The permeate was always recirculated back to the feed tank, maintaining the feed solution at a constant concentration. The hydraulic permeability can also be

obtained from the slope of the linear regression of the permeate flux versus the feed pressure.

The effect of the temperature was adjusted to 20 ºC using correlation with the viscosity of water at different temperatures (3 % per degree). In addition, we compared the transport through the membrane by advection and hydration/diffusion mass transfer. Plotting Cp vs 1/Jp each part of solute mass transfer (diffusion and convection) may be obtained separately. Furthermore, to better quantify hydration/diffusion and advection, both contributions of mass transfer in NF, a new adimensional number was defined by Ould Mohamedou E. et al. (2010), denoted in Eq. 5.

$$Pe' = J_p \frac{C_{advective}}{J_{diffusive}} \quad (5)$$

This means that an advective mass transfer is dominant if Pe' > 1, and a diffusional mass transfer is dominant if Pe'< 1 and both masses transfers are equivalent for Pe'=1.

2.5.2. Membrane rejection

We evaluate the membrane rejection regarded to three parameters: salt, acetaminophen and lactose. The rejection to salt is a fundamental parameter since most RO membranes are used for desalination. The salt rejection can be easily predicted by measuring the electrical conductivity of the permeate. A solution of NaCl 0.1 mol L^{-1} was used as a model. The electrical conductivity was measured using portable conductivity meter Cond 3151 from WTW (Xylen Analytics - Germany). A solution with 5 % (w/v) of lactose and NaCl (0.1 mol L^{-1}) was used to evaluate lactose rejection. Lactose was measured by spectroscopy in the near infrared by a Soma Scope MK2 coupled with a Lactoscope FTIR (Delta Instruments, Canada). A solution of 100 mg/L of acetaminophen and 0.1 mol L^{-1} of NaCl was utilized as a standard solution for the permeate tests. Acetaminophen was measured according to the procedure of Mbokou et al. (2016). The method is based upon the redox potential of acetaminophen measured by glassy carbon probe, in our study the probe was attached to the equipment PG581 from Uniscan Instruments Further details can be on Mbokou et al. (2016).

The membrane rejection (R) for each parameter was calculated using Eq. 6.

$$R = \left(1 - \frac{Cp}{Cf}\right) x100 \quad (6)$$

where, R is the membrane rejection in %, C_p is the concentration in the permeate, and C_f is the concentration in the feed solution.

2.5.3. Morphology of the aged and oxidized membranes

The membranes were analyzed by Scanning Electron Microscopy (SEM) with an acceleration of 3 kV using the equipment JSM JEOL 6301F manufactured by JEOL (USA) and Atomic Force Microscopy (AFM) using the equipment CPII manufactured by Veeco (USA).

2.5.4. Membranes' FTIR spectra

The function groups of the membranes were analyzed by Fourier-transform infrared (FTIR) spectroscopy. Coupons of 1 cm² of membranes were inserted in a Cary 630 spectrophotometer reader in the spectral region of 0 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

2.5.5. Simulation of permeation flux and salt rejection

The software from Dow Chemical® ROSA 9.1 was primarily created to simulate and predict the behavior of membranes only at standard conditions. Since the software can accurately reproduce the performance of pristine membranes (Boulahfa et al. 2019; Sahinkaya et al. 2019), it was utilized to generate references in order to compare with the aged and oxidized conditions. All the simulations of rejection on ROSA utilized 5840 mg/L of total dissolved solids (TDS), the equivalent of 0.1 mol/L of NaCl.

2.5.6. Prediction of pore diameter and Molecular Weight Cut-Off of the membranes

The pore diameter of an unknown membrane can be estimated using Equation 7. The equation derived from Poisseuile's law, when a well-known membrane can be used as a reference to determine the pore diameter (dp) in nm of similar membranes for specific operation temperatures.

$$d_p = \sqrt{\frac{Ap}{A_0}} \, X \, d_{p0} \quad (7)$$

where, A_0 is the permeability of the reference membrane, dp0 is the pore diameter of the reference membrane, and Ap is the permeability of the similar membrane. In this case, the reference membrane at the temperature of 20 °C had a permeability of 4.23 L/h.m^2.bar, and the pore diameter of 0.69 nm. The Molecular Weight Cut-Off (MWCO) is defined as the molecular weight at which 90% of the macromolecular solute is rejected by the membrane (Singh. 2005). The MWCO of a membrane can be also calculated using the empirical Eq. 8 (Bacchin and Maurel. 2017).

$$MWCO = \sqrt[0,4]{\frac{d_p}{0,076}} \quad (8)$$

2.6. Application of the recycled membrane to the treatment of brackish water and surface water

We choose the best oxidation condition to evaluate the capacity for the treatment of brackish water and surface water. This procedure allows to point some direction for possible applications of these recycled membranes. Brackish water was sampled from surface water in hydraulic annexed of the Loire River between Nantes and St Nazaire (estuarine) in France. We collected 5 L of the water in plastic vessels and immediately took the water for the experiments on the recycled membrane. The same procedure of sampling brackish water was performed to collect surface water from St Nicolas Dam water in the vicinity of Angers (France). The characterization of the samples is shown in Table 2.

Table 2. Characteristics of the brackish water from Loire River and surface water from Saint Nicolas Dam river in France.

Physico-chemical parameters	pH	TDS, mg/L	Turbidity, NTU	Electrical Conductivity, µS/cm, at 20 °C
Brackish water	7.4	1800	15	2808
Surface Water	8.4	540	16	842

2.7. Data Analysis

The statistical analysis of the results was performed using Statistica 7.0 at 5 % of significance.

3. Results and discussion

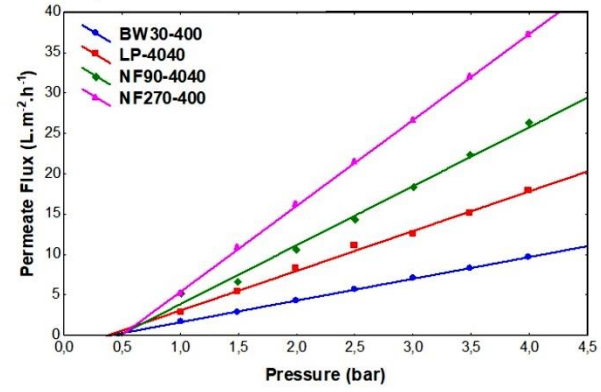
3.1. Permeate flux and hydraulic permeability

The average permeate flux of the oxidized membranes showed a broad increase when comparing to the reference aged RO membrane (0 ppm.h), as shown in Fig. 4a. The surface of polyamide membranes is modified during the chlorinated oxidation, since it breaks and weakens hydrogen bonding, and this breakage/weakening can lead to alteration in the permeability and membrane rejection (Kwon and Leckie. 2006). Terrero et al. (2015) showed that chlorinated oxidation impairs the polyamide active layer of the membranes. The authors suggested, the intensity of amide I and amide II peaks from the polyamide layer were reduced after the exposure, and nearly vanished after long exposure time (420 hours of exposure time at 124 ppm). We simulated the permeated flux of different loose RO (BW30 – Dow Chemical and LP-4040 – Vontron) and tight NF membranes (NF270 and NF90 from Osmonics) in Fig. 4b to compare with the permeate flux of the oxidized membranes. The aged membrane (0 ppm.h) showed a higher flux than the references LP-4040 and BW30-4040. The intrinsic deterioration of the membranes during operation was reported to increase the size and the number of pores on the membrane (García-Pacheco et al. 2019); this fact contributes for the permeability increase (Lawler et al. 2013). Permeate flux of oxidized aged RO membranes can be compared with the NF membranes. However, the doubt is if the selectivity of the aged RO membrane could be also compared with NF. The average hydraulic permeability of the oxidized and the reference membranes was normalized by the aged RO membrane. The comparison between the effects of the oxidation on the permeability with the references membranes is summarized in Table 3.

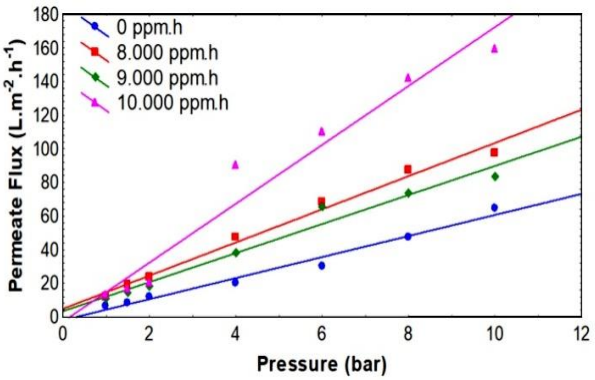
Table 3. Summarized hydraulic permeability of aged, oxidized and reference membranes.

Membrane	Simulated on ROSA				Aged (0) and oxidized membranes (ppm.h)			
	BW30-400	LP-4040	NF90-4040	NF270-4040	0,000	8,000	9,000	10,000
Hydraulic Permeability (L/h.m^2.bar)	2.69	4.93	7.31	10.65	5.59	9.87	8.65	17.36
Normalized hydraulic permeability	0.48	0.88	1.31	1.90	1.00	1.76	1.55	3.10

The aged membrane (0 ppm.h) presented 13 % higher permeability than the reference LP-4040 - Vontron (generated by ROSA software), as a consequence of the cycles of use/cleaning (Lawler et al. 2013) during the two years of use. Note that the BW-30 membrane is meant for the desalination of brackish water, with a lower permeability than LP-4040. On the other hand, the aged membrane has a lower permeability than the tight NF-90, it means that in terms of permeability, the aged membrane is in a range between NF and RO membranes. Furthermore, the oxidation process drives to permeabilities higher than NF-90 and NF-270 membranes.



(a)



(b)

Fig. 4. Permeate flux at different pressures (a) of the aged RO and oxidized membranes and (b) Simulation of permeate flux of membranes references on ROSA software.

Additionally, the end-of-life membrane used in this work had the presence of inorganic scaling (Figure 2), which could contribute to the increase of permeability due to mechanical or chemical degradation of the polyamide layer (García-Pacheco et al. 2019). Fig. 5 shows the statistic comparison of hydraulic permeability of the aged and oxidized membranes. The permeabilities of the membranes were also statistically analyzed. The results confirmed that the 0 ppm.h, 8,000 ppm.h and 9,000 ppm.h are in the same statistical group (b). On the other hand, the oxidized membrane in 10,000 ppm.h showed the higher permeability among all membranes, and it is the only member of the second statistical group (a).

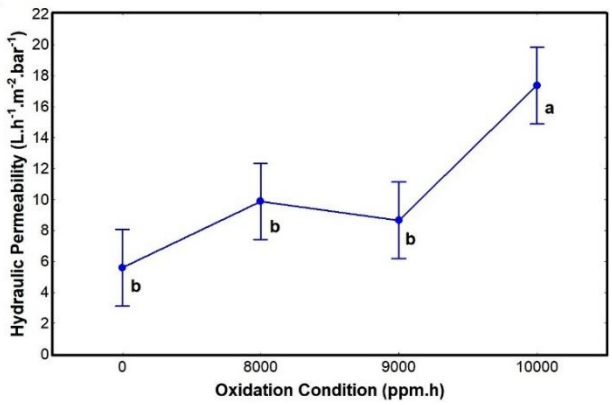
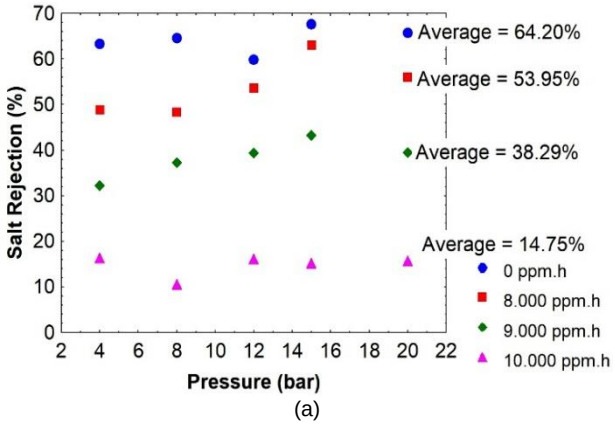
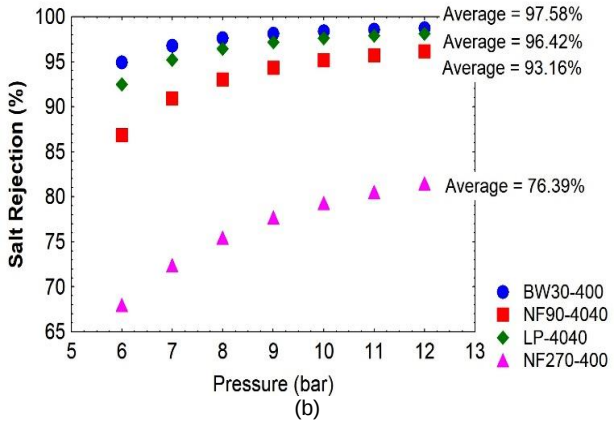


Fig. 5. Average hydraulic permeability of the aged RO membrane and oxidized membranes.

The permeability of the membrane oxidized in 10,000 ppm.h reached 17.36 L/h.m^2.bar (3.10 times the permeability of the aged membrane). Antony et al. (2016) reached a similar increase on the permeability when oxidized a RO membrane at 10,000 ppm.h of chlorine, and the oxidized membrane has shown a hydraulic permeability of 7.3 L/h.m^2.bar while the reference had 2.8 L/h.m^2 bar (2.6 times the permeability of the aged membrane). The permeability of the membrane 0 ppm.h, 8,000 ppm.h and 9,000 ppm.h presented commercial NF-like range, since most NF membranes have MWCO between 100 Da and 1000 Da. On the other hand, the most oxidized membrane (10,000 ppm.h) reached commercial UF-like range, since UF membranes MWCO usually ranges between 1,000 Da and 100,000 Da. A similar fact was described by García-Pacheco et al. (2019), but instead, the authors used the concentration of 300,000 ppm.h to oxidize the aged tight RO membrane SW30 from Osmonics. The permeability achieved in this work by the membrane 10,000 ppm.h was higher than the SW30 RO membrane, since only a fraction of oxidizer was needed to reach UF-like permeability, different from García-Pacheco et al. (2019). Each membrane is designed for specific purposes, the 300,000 ppm.h oxidized by García-Pacheco et al. (2019) could have had a denser polyamide layer, thus requiring more oxidation. Also, as mentioned by Lawler et al. (2013), each membrane must be studied separately and individually, since the ageing of each membrane depend on many factors. Many researchers have been evaluating the benefits of increasing membrane permeability. Okamoto and Lienhard (2019) described that higher permeability benefits the operation of these membranes for desalination. Reyes-Contreras, Leiva and Vidal (2019) demonstrated that increasing permeability leads to reduction in the water production cost and Cohen-Tanugi et al. (2014) found that the increasing of three times the permeability would result in 63% fewer pressure vessels or 46% less energy for desalinate brackish water by RO. The permeability is indeed a key factor in this subject, during the last few decades, the permeability improvements of membranes is one of the main reasons of water production cost decrease (Reyes-Contreras, Leiva and Vidal 2019). On the other hand, Table 4 shows that as the permeability increase as the MWCO also increases. Thus, harm to the selectivity of the membrane could be expected in these extreme oxidization conditions, impairing the selectiveness and rejection to solutes, subject that will be approached in the sequence.



(a)



(b)

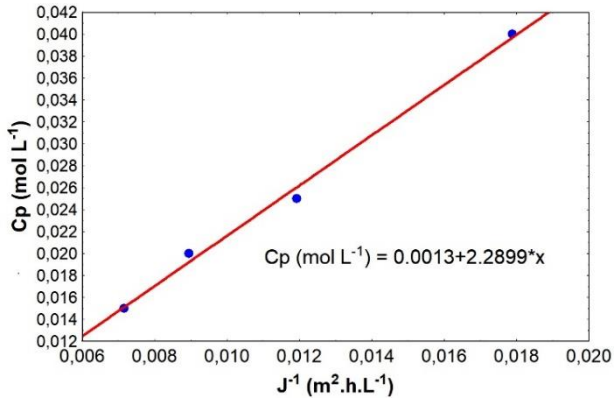
Fig. 6. (a) Salt rejection of the aged and oxidized membranes; (b) Salt rejection of references membranes simulated on ROSA software.

3.2. Membrane rejection

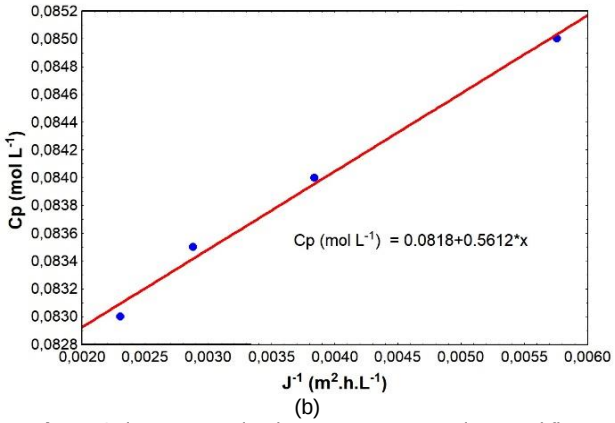
Fig. 6 shows the salt rejection of the aged and oxidized membranes (a) in different pressures as well as the reference membranes simulated on ROSA software (b) and the averaged rejection obtained by different pressures of the tested membranes (c). The simulated rejection of references membranes NF 90-4040 and LP-4040 reproduced the theoretical rejection pattern at increasing feed pressure. On contrary, the aged and oxidized membranes did not follow the same behavior and there was no correlation between the pressure and the rejection. We highlighted the average rejection for each oxidation condition in Figure 6a. ROSA software considers a diffusional flux when predicting the salt rejection on references membranes and maybe the oxidation of the membranes takes to higher salt transmission through the membranes due the convective flow because the pores of the membranes become wider (as predicted in Table 3). The aged RO membrane (0 ppm.h) achieved the highest salt rejection (64.20%) among the tested conditions. However, this rejection is lower than all the simulated rejections of pristine-reference membranes. Indeed, as reported by other references (Do et al. 2012; Ettori et al. 2011; Kwon, Tang and Leckie 2006; Simon et al., 2009), aged membranes have lower salt rejection than pristine membranes due to the damages during their lifetime. Figure 6a shows that as the higher oxidation conditions as the lower the salt rejection. Antony et al. (2016) reported a similar behavior on pristine membranes that were oxidized at 10,000 ppm.h; the rejection to NaCl decreased from 99 % to 40 % after the oxidation. As shown in Figure 7a, the oxidation at 10,000 ppm.h decreased the average rejection of the aged membrane by 77 %, similar to the 60 % reported by Antony et al. (2016). Fig. 7 shows the linearization of the diffusive and convective fluxes, that is used to find the modified Pe' number (Table 4). The Pe' number (Eq. 5) expresses the relationship between the advective and hydration-diffusive mass transfer through the membrane (Diawara et al. 2003; Ould Mohamedou et al. 2010). When Pe' > 1 convective mass transfer is dominant; when Pe < 1 diffusional mechanism masters the mass transfer.

Table 4. Predicted pore diameter and molecular weight cut-off of reference, aged and oxidized membranes.

Membrane	Simulated on ROSA		Oxidized membranes, ppm.h			
	NF90-4040	NF270-400	0,000	8,000	9,000	10,000
dp (nm)	0.91	1.09	0.79	1.05	0.99	1.40
MWCO (Da)	492.28	787.59	352.17	716.41	607.04	1451.05



(a)



(b)

Fig. 7. Salt concentration in permeate versus inversed flux (J^{-1}), for prediction of diffusive and convective mass transfer across the aged (a) and oxidized in 10,000 ppm.h (b) membranes.

For the aged membrane (0 ppm.h), the flux is mastered by diffusion. On the other hand, as more open the pore size (as predicted on Table 3) as more diffusive mass transfer occurs through the membrane. This implies that the mechanism of mass transfer of salts through the membrane changes as more severe is the oxidation. Still, as more drastic the oxidization, as higher is the predicted MWCO of the recycled membrane (Table 5), reaching the range of NF or even UF. Thus, new applications for these recycled membranes must be tested. The rejection to acetaminophen by the aged and oxidized membranes is shown in Fig. 9.

Table 5. Peclet`s (Pe') number for aged RO membrane (0 ppm.h) and oxidized membrane in 10,000 ppm.h of Cl_2.

0 ppm.h	10,000 ppm.h
0.03	25.30
0.04	37.96
0.06	50.61
0.07	63.26
Diffusional membrane	Advective membrane

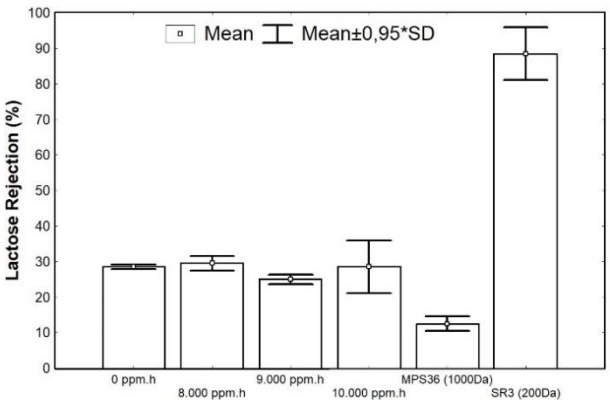


Fig. 8. Lactose rejection of the aged, oxidized and references NF membranes.

The aged membrane has a rejection to acetaminophen of approximately 42 %. On the other hand, the statistical analysis has shown that all the oxidized membranes achieve a lower rejection than the aged membrane, separated in another statistical group (thus, present the same rejection to acetaminophen, between 24 % and 30 %. The low rejection to acetaminophen molecule (molecular diameter of 0.285 nm) by NF membranes was reported by Azaïs et al. (2016). The authors suggested that the molecule is smaller than the pores of the membrane NF270 (0.40 nm). The rejection to acetaminophen in pure water on the NF-270 ranged between 5 % and 35%. The authors also reported that the high polarity caused by the substitution of benzene ring by hydroxide and amide groups can contributes to the low rejection of acetaminophen. GE et al. (2017) utilized the same NF-270 membrane model in order to test acetaminophen rejection from ultra-pure water solution. The rejection only reached 16.4 %. Higher rejection was achieved by changing the solution's pH into alkaline condition and results show that electrostatic repulsion has a stronger impact on the rejection rate than steric exclusion. On the other hand, the aged RO membrane (0 ppm.h) had also shown a low acetaminophen rejection, possibly as a consequence of its lifetime.

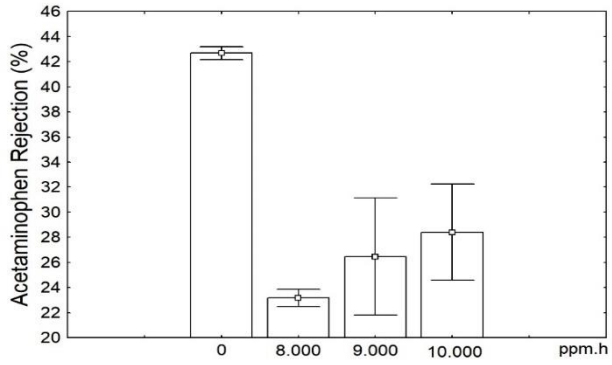


Fig. 9. Acetaminophen rejection of the aged and oxidized membranes.

As reported by Kwon (2006), the oxidation of RO membrane increases hydrophilicity and made zeta potential slightly more negative. In this context, the Fig. 9 suggests that the rejection of acetaminophen seems to increase at higher concentration of oxidizers. Increasing zeta potential of the membrane during oxidation may have created a coated surface dispelling acetaminophen and increasing the rejection.
The rejection of several pharmaceuticals on NF (NF90) and RO (BW30) membranes were tested by Licona et al. (2018). The study found that acetaminophen as well as caffeine rejection were the lower among all the tested pharmaceuticals, including ibuprofen, dipyrone, and diclofenac. Since acetaminophen was in the non-ionic form at the tested pH, there was no electrostatic interaction with the membrane, which is negatively charged, enforcing the idea of the coated oxidized membrane. For this reason, the author suggests that rejection by size (sieving) was the main removal mechanism for the NF90. For the BW30, acetaminophen accumulated on the surface of the membrane due to size exclusion. Radjenović et al. (2008) utilized a full-scale drinking water treatment plant treating groundwater with pharmaceuticals. The acetaminophen rejection (44.8 %-78.3 %) was lower when compared to other pharmaceuticals, possibly due to its small molecular size and low polarity. The rejection of acetaminophen using UF (4.5 % - 16.1 %) and NF (13.4 % - 39.6 %) was also evaluated by Acero et al. (2010) on water and municipal secondary effluent. According to the author, adsorption is the main retention mechanism for UF membranes, while for NF membranes size exclusion and electrostatic repulsion of negative species at high pH are responsible for micropollutant rejection. The removal of acetaminophen (5 mg/L) was also tested on a nanofiltration NF90 membrane for the sake of comparison and the results are shown in Fig. 10. Note that the acetaminophen rejection by both membranes has a similar behavior, but the pristine NF90 rejected this pharmaceutic specie in a high rate. At a feed pressure of 20 bar in NF90, the permeate reached 0.2 mg/L. In comparison to regulations, the phenol index for influent is 0.3 mg/L. Thus, this NF 90 membrane allowed to nearly eliminate acetaminophen from water.

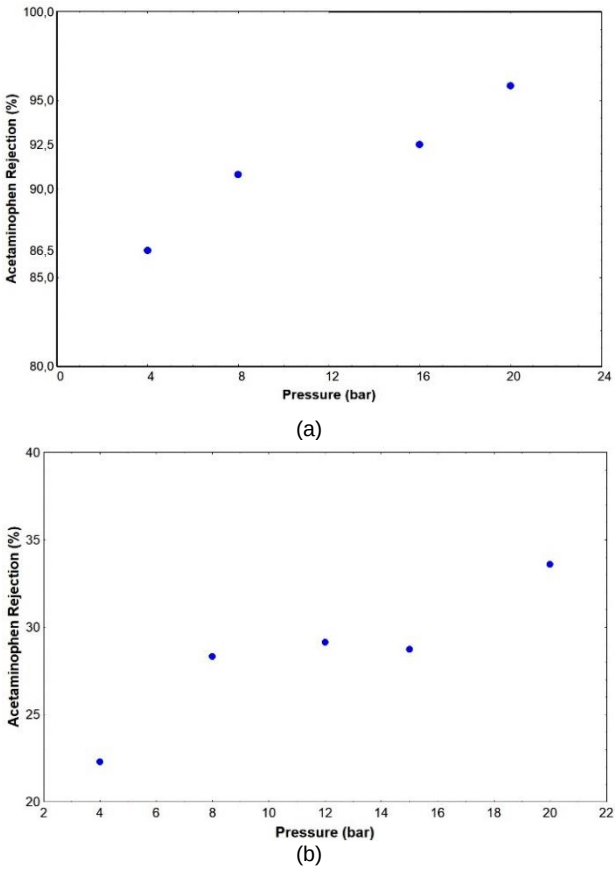


Fig. 10. Acetaminophen removal in different pressures (a): using pristine NF90 nanofiltration membrane and (b) recycled aged RO membrane by oxidation in 10,000 ppm.h of Cl_2.

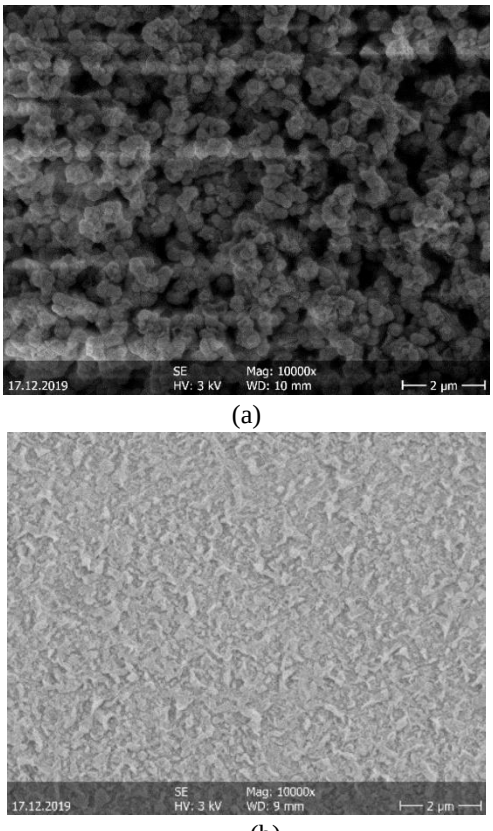


Fig. 11. (a) SEM image of the 0 ppm.h membrane and (b) 10,000 ppm.h.

3.3. Membrane Morphology

Fig. 11 a and b shows the micrographs from SEM analysis of the 0 ppm.h and 10,000 ppm.h membranes, respectively. The cleaning procedure associated with the oxidation likely removed the inorganic scaling from the membrane surface, since the oxidized membrane 10,000 ppm.h did not show any presence of scaling (Fig. 11b). Differences on the morphology of aged RO membrane (0 ppm.h) and oxidized membrane in 10,000 ppm.h of HClO can be observed in Fig. 12. Fig. 12a present some impacts on the surface of the membrane, as could be expected for an aged membrane. On the other hand, the Fig.12b shows a more damaged membrane, which could also be expected for the oxidized membrane. It can be understood that even though the oxidation (10,000 ppm.h) partially damaged the membrane (Fig. 12b), the characteristics of the polyamide layer is still present on the surface of the membrane (Fig. 11b). These differences in oxidized membranes were also identified by García-Pacheco et al. (2019). The authors also confirmed that shorter exposure periods, such as those carried out during this work, are linked to less damage to the polyamide layer.

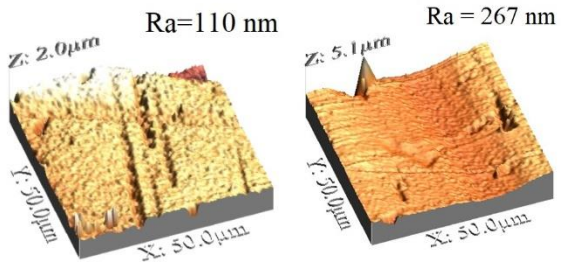


Fig. 12. SEM image and AFM analysis of the (A) aged RO membrane and the (B) membrane oxidized in 10,000 ppm.h of Cl_2.

The SEM and AFM analysis in Fig. 12 confirms a higher average roughness (Ra) for the oxidized membrane in 10,000 ppm.h when compared to the 0 ppm.h. The usual application of RO membranes can modify the roughness of the membrane, as shown by Mohamedou et al. (2010) when compared new and aged membranes. However, our work suggest that the severity of oxidation can increase the roughness of the membrane. This is of concern for the reuse of the oxidized membranes because higher roughness is linked to fouling. As a reference, the roughness of the pristine NF-270 membrane was reported by Tang (2007) as low as 9.0 nm, and the NF90 presented 129.5 nm. In contrast, our recycled membrane showed a roughness of 276 nm.

3.4. FTIR analysis

The FTIR spectra of the aged (0 ppm.h) and oxidized (10,000 ppm.h) membranes were overlapped and analyzed, as shown on Fig. 13. FTIR analysis detects bonds between atoms in a molecule and provides information about functional groups as well as the chemical structure of the analyzed material. As reported by Kwon (2006), the chlorinated oxidation modified the peaks at 1541 and 1609 cm^{-1}, which are mainly contributed by the N-H bending motion of amide (Socrates. 1994). The author further explained that the amide nitrogen is the dominant reaction site with chlorine, where the hydrogen attached to the amide nitrogen are replaced by chlorine. The author also demonstrated that the content of chlorine on the surface of the oxidized membrane is linked to the concentration of nitrogen in the membrane. Analyzing the FTIR of the 10,000 ppm.h membrane, a subtle difference can also be observed on these bands, meaning that the same phenomenon may have occurred on the oxidized membranes. Kwon (2006) used exposure time of the membranes into HCLO in different times. The researcher reported changes in N-H bending of amide, which is the dominant reaction site with chlorine.

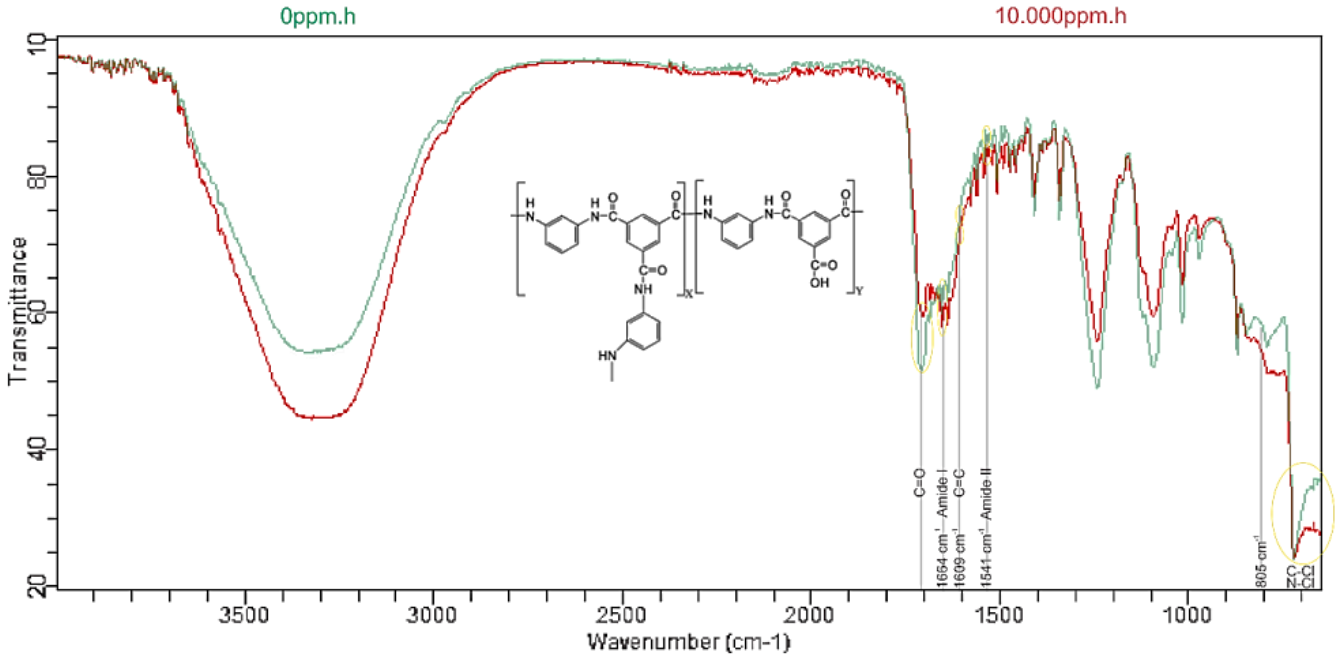


Fig. 13. FTIR of the aged RO membrane (green line) and oxidized membrane (red line).

On the other hand, Pacheco et al. (2019), submerged the membranes into chlorine solutions for as high as 242 h of exposure time, finding that Amide I, II and band C=C nearly vanished at 124 ppm for 242 hours. The same behavior did not occur when the exposure time was proportionally reduced and free chlorine concentration increased. It can be deduced that the oxidation begins breaking N-H and continues with the degradation of the remaining polyamide molecule if the exposure maintained. The bands in the range of 805 cm^{-1} and 690 cm^{-1} are assigned to the vibration of N-Cl (Petterson. 1960) performed a peak lowering on the oxidized membrane when compared to the aged membrane. This confirms the idea that hydrogen from amide nitrogen were replaced by chlorine molecule. As reported by Kwon (2006), the insertion of chlorine in the membrane surface increases hydrophilicity of the membrane, which can then lead to permeability increase.

3.5. Applications of the recycled membranes

Previous results of our work have shown that the oxidized RO membrane has the characteristics of a loose NF membrane. Thus, we investigated applications for this recycled membrane for desalination of brackish water and treatment of surface water.

3.5.1 Brackish water demineralization

The hydraulic permeability of the membrane 10,000 ppm.h when treating brackish water is shown in Fig. 14. The permeability of the membrane with pure water (17.4 $L/h.m^2$.bar) was approximately 5 times higher than the experiment performed with brackish water (3. $L/h.m^2$.bar) at 20 °C. In fact, the concentration of salt in the solution reduces the driving force (pressure) due to the osmotic pressure,

lowering the permeability of the system. The salt rejection from brackish water by the recycled membrane (oxidized in 10,000 ppm.h of Cl_2) is shown in Fig. 15. There was a typical behavior of the membrane rejection and, as the pressure is increased, the rejection also heightens. The rejection by NF membranes is a consequence of the sieving effect, electrostatic and steric interactions (associated with charge shielding), Donnan exclusion, and ion hydration (Paugam et al. 2004). Thus, rejection in NF depends on several factors, such as MWCO, pH, ionic strength, water composition, and sieving effects. In 18 bar of pressure, the salt rejection of membrane 10,000 ppm.h reached 81 %; this value is near the 82 % of TDS rejection found by Brião et al. (2019) in the desalination of groundwater using SR3 NF membrane from Koch (MWCO 200 Da).

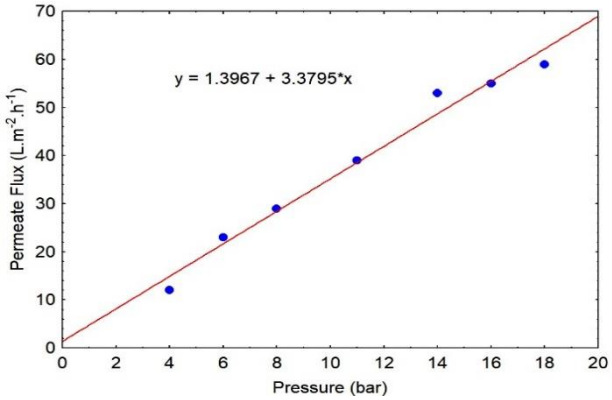


Fig. 14. Permeate flux of the oxidized RO membrane in 10,000 ppm.h when treating brackish water.

The well-known NF-270 membrane from Dow (MWCO 200-400 Da) has the rejection higher than 97 %, whilst the rejection of NF ESNA1 from Nito-Denko (MWCO 100-300 Da) is 89 % (Mohammad et al. 2015). Thus, the behavior of our recycled membrane is similar of a NF membrane in terms of permeability and salt rejection. The recycled RO membrane has good prospect of use for desalination of brackish water for the production of drinking water in such relation of TDS concentration, which is below 500 mg/L, as suggested by the World Health Organization guidelines for drinking water (WHO. 2011). In addition, to achieve the goal of 500 mg/L, a rejection of 75 % is required to adjust the TDS of the brackish water, and only 8 bar of pressure is required (Fig. 15) for the operation of the desalination system using this recycled RO membrane.

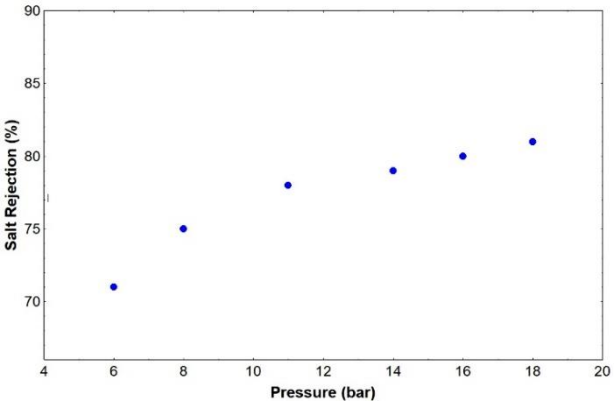


Fig. 15. Salt rejection of the oxidized RO membrane in 10,000 ppm.h when treating brackish water.

3.5.2. Surface water treatment

The permeability of the oxidized membrane in 10,000 ppm.h was only 26 % (4.54 L/m^2 h) of the permeability of the membrane with pure water (17.40 L/m^2 h). Fig. 16 shows the permeate flux of the recycled membrane in different pressures. Contrary to the application on brackish water, the reduction of permeate flux is attributed to fouling of organic material, such as humid acids and colloidal material. In fact, the presence of humid acids has been preventing the use of these membranes on the treatment of surface water. On the other hand, the membrane has shown typical permeability of NF applications (Mohammad et al. 2015). This fact, associated with the rejection of turbidity higher than 99.2 % and 20 % of salts, shows that the recycled membrane could be an option for removal of turbidity as post-treatment of wastewater with low turbidity. Environmental application has been the main focus of NF studies (Mohammad et al. 2015), and there is a great potential for polishing water from water treatment stations.

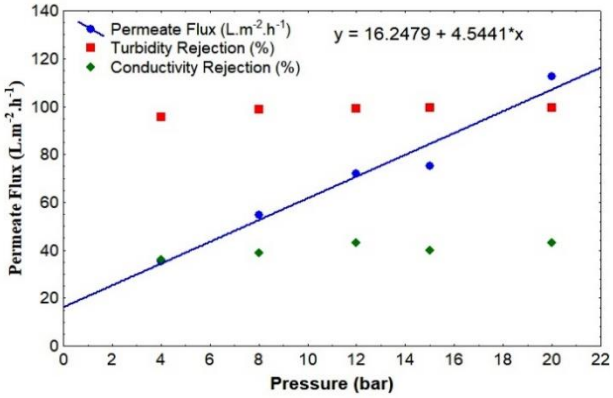


Fig. 16. Permeate flux, salt and turbidity rejection of the oxidized membrane in 10,000 ppm.h treating surface water from St Nicolas Dam river (France).

The Fig. 17 shows the membrane after the permeation of surface water. We can see the deposition of material on the membrane surface. As discussed in item 3.3, the high roughness of the oxidized membrane can be a crucial factor for the operation of these recycled membranes.

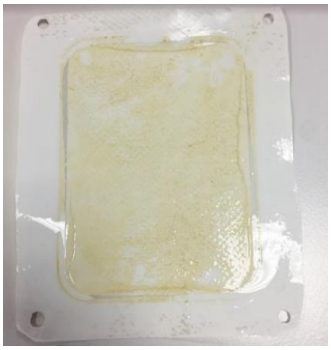


Fig. 17. Picture of the oxidized membrane in 10,000 ppm.h of chlorine after treating surface water.

4. Conclusions

This paper evaluated the recycling of aged RO membranes by oxidation of active layer in sodium hypochlorite. The obtained evidences suggest that chlorine reacts on the polyamide layer of the membrane, widening pores thus decreasing rejection to salt. However, this oxidation condition does not fully harm the active layer and the recycled membrane could be useful for a second life. The normalized permeability of the recycled membranes suggests membrane 10,000 ppm.h a NF like permeability. On the other hand, conditions of 8,000 ppm.h and 9,000 ppm.h of oxidation did not change the permeability. The lack of relation between operation pressure and salt rejection suggests these recycled membranes could be operated in low pressure without negative consequence to the membrane rejection. The salt rejection decreased 77 % after the 10.000 ppm.h oxidation, and the oxidation promotes a more convective flux as the pores are more open. As the recycled membranes have similar characteristics of NF membranes, the rejection to acetaminophen of the oxidized membranes are also similar to NF membranes and near in a range between 23 % and 28 %. The membrane 10,000 ppm.h was tested to the treatment of brackish water, the results of permeability and salt rejection suggest that is similar to other NF membranes while treating brackish water. The same membrane was also tested for the treatment of surface water, and a high rejection of turbidity was achieved, but the membrane fouled during the procedure and this fact needs further studies. The high permeability achieved on these oxidized membranes suggest many other NF/UF functions could potentially use recycled RO membranes.

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