Desalination 437 (2018) 121–132

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

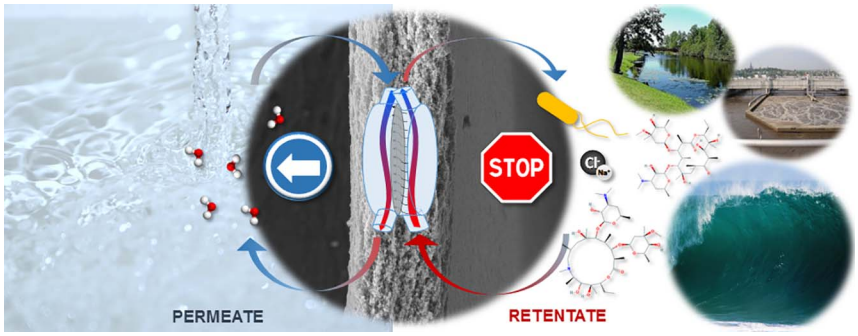
Desalination and removal of organic micropollutants and microorganisms by membrane distillation

Tânia L.S. Silva[a], Sergio Morales-Torres[a,*,1], Carla M.P. Esteves[a,b], Ana R. Ribeiro[a], Olga C. Nunes[b], José L. Figueiredo[a], Adrián M.T. Silva[a,*]

[a] Laboratory of Separation and Reaction Engineering, Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[b] LEPABE – Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Membrane distillation
Desalination
Membrane fouling
Organic micropollutants
E. coli and enterococci

ABSTRACT

The effect of different membranes, membrane modules, feed temperatures, flow rates and solute concentrations on the permeate flux and salt rejection in direct contact membrane distillation (DCMD) was first studied with synthetic seawater and compared to distilled water. After optimizing these operating conditions, DCMD was tested with real feed samples, namely river water (RW-R), seawater (SW-R), and a secondary effluent from a municipal wastewater treatment plant (MW-R). The permeate flux achieved with MW-R was significantly lower than those obtained with the other feed samples. Two membrane module configurations (H-cell and W-cell) were then studied using SW-S, spiking diphenhydramine (DP) as model organic pollutant in some experiments. The H-cell performed better in terms of permeate quality for the same volume of permeate collected. A long experiment (500 h) was conducted with SW-R employing a larger H-cell. Severe fouling was observed, but high rejections of ion species (> 99%) were recorded together with complete rejections of pharmaceuticals (diclofenac, azithromycin, clarithromycin and erythromycin) detected in SW-R at 9.53–73.53 ng L^{-1} (detection limits < 0.16 ng L^{-1}). Colonies of *Escherichia coli* or enterococci were not detected in 100 mL of permeate (distillate) solution, complying with the European Directive for drinking water.

* Corresponding authors.
E-mail addresses: semoto@ugr.es (S. Morales-Torres), adrian@fe.up.pt (A.M.T. Silva).
[1] Present address: Carbon Materials Research Group, Department of Inorganic Chemistry, Faculty of Sciences, University of Granada, Campus Fuentenueva s/n, Granada, Spain.

https://doi.org/10.1016/j.desal.2018.02.027
Received 30 June 2017; Received in revised form 20 February 2018; Accepted 26 February 2018
Available online 15 March 2018
0011-9164/

1. Introduction

Membrane science has attracted a great deal of attention during the last decades, since membrane processes are becoming more competitive in comparison to conventional separation technologies. These processes offer possible solutions for water desalination and/or treatment, and can mitigate concerns about water scarcity and pollution. Direct contact membrane distillation (DCMD), a particular configuration of membrane distillation (MD), is a non-isothermal process driven by the vapour pressure difference (ΔP) established between both sides of a porous hydrophobic membrane [1]. Some of the main advantages of this process include: (i) low temperature of operation in comparison to other distillation processes; (ii) theoretical 100% rejection of non-volatile solutes; (iii) low impact on the process efficiency when dealing with high solute concentrations; and (iv) less membrane fouling (since solutes are ideally not expected to be in direct contact with the membrane) [2,3].

MD has been widely studied for the removal of salts from sea and brackish waters, producing high quality water under competitive permeate fluxes compared to those achieved with the leading desalination technology (i.e. reverse osmosis, RO) [4]. However, less attention has been given to the application of MD to eliminate chemical and biological contaminants. During the last decades, the occurrence of contaminants of emerging concern (CECs) in effluents from urban/municipal wastewater treatment plants (WWTPs), groundwater, river water, seawater and even in drinking water, has been widely reported [5–9]. Hence, MD processes assuring elimination of these ubiquitous micropollutants as well as potential dangerous microorganisms are demanded.

There are few works dealing with the treatment of organic micropollutants by DCMD. Wijekoon et al. [10] reported high removals of 29 pollutants representing major trace organic compounds (TrOC) from municipal wastewaters using MD as post-treatment of a thermophilic membrane bioreactor. A few studies regarding a photocatalysis-DCMD hybrid system for the elimination of anti-inflammatory drugs have been also published [11–13], reporting complete removal (below the detection limit, DL) of diclofenac, ibuprofen and naproxen from different water matrices (ultrapure water, tap water, primary and secondary effluents). More recently, high removals of 37 micropollutants found in a wastewater effluent from a municipal WWTP located in Stockholm were achieved by using a pilot air-gap MD unit [14]. DCMD was also evaluated as a treatment option of the RO wastewater concentrate, with 85% water recovery, large fouling resistance and high rejection (96–99%) of 13 micropollutants, being obtained. However, low-moderate rejection (50–88%) was found for propylparaben (50%), salicylic acid (86%), benzophenone (62%), triclosan (83%), bisphenol A (84%) and atrazine (88%) [15]. Urine and hygiene wastewaters (from advanced life support systems used in space missions) were also treated by MD, and high rejections of the β-estradiol hormone, urea and ammonia were reported, together with a high water recovery [16]. Stable permeate fluxes and excellent rejections (> 97%) of dyes of different types and molecular weights were also obtained by DCMD [17]. Regarding biological contaminants, solar MD was demonstrated to produce a clean distillate when using a water feed containing *Escherichia coli*, *Fusarium solani* and *Clostridium* sp. spores [18]. In what concerns to drinking water production by DCMD, most of the literature deals with the removal of inorganic compounds [19], rather than organic micropollutants and biological contaminants.

In the present work, DCMD was studied as a technology to desalinate and remove organic micropollutants and microorganisms from real water matrices in a unique process, changes on the membrane surface (e.g., fouling) during long-term experiments were investigated, and an easy and effective cleaning procedure to regenerate the membrane was proposed. For that, operating conditions were first optimized with distilled (DI) water and synthetic seawater (SW-S). Different membrane modules, feed temperatures, flow rates and three commercial hydrophobic membranes, two of them made of polytetrafluoroethylene (PTFE) and one of polyvinylidene difluoride (PVDF), were studied. The optimized DCMD operating conditions were then employed with different real water matrices as feed solutions, namely river water (RW-R), seawater (SW-R), and secondary treated municipal WWTP (MW-R) effluents. Additional experiments were performed with SW-S spiked with diphenhydramine (DP), as model pollutant. DP is a first generation antihistamine drug, mainly used in the treatment of allergies, allergic rhinitis, common cold symptoms, insomnia, among others [20]. It was selected as model organic pollutant since it was the third most frequently detected CEC in the fillet and liver of fishes collected from five different locations across the United States [21], it has been found in surface water downstream WWTPs, as well as in their generated biosolids [22–24]. In addition, to the best of our knowledge, the DP removal by DCMD from different water matrices was not studied so far.

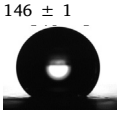
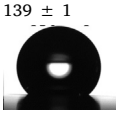
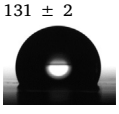
Desalination and removal of specific organic micropollutants found in SW-R (the anti-inflammatory diclofenac, and three macrolide antibiotics - azithromycin, clarithromycin and erythromycin) were investigated in 500 h experiments with SW-R. Enumeration of indicators of microbiological quality (enterococci and *Escherichia coli* [25]) was also performed on the resulting permeate stream from seawater desalination, in order to assess the feasibility of MD to treat water faecal pollution. Finally, membrane fouling was evaluated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS), and simple and effective approaches to mitigate it were studied.

2. Experimental

2.1. Membranes and their characterization

PVDF membranes were purchased from Millipore (GVHP Durapore®) and PTFE membranes from Sartorius AG and Millipore (FGLP Fluoropore®). Table 1 shows some physical properties of these commercial membranes. Hydrophobicity of the membrane surface was determined by water contact angle measurements, using an Attension Theta optical tensiometer (Biolin scientific, Finland). The water contact angle measurements were performed on dry membranes employing the sessile drop method. The overall porosity (ε) of the membranes was determined by the gravimetric method, following a procedure similar to that reported elsewhere [26]. The membrane morphology was examined by scanning electron microscopy (SEM) using a FEI Quanta 400 FEG ESEM/EDAX Genesis X4M equipment (accelerating voltage of 15 kV and a working distance of ca. 10–15 mm). For cross-section observations, the membranes were frozen and broken by using liquid nitrogen. Elemental microanalysis was performed by energy-dispersive X-ray spectroscopy (EDS).

Table 1
Properties of commercial membranes provided by the manufacturers. The overall porosity and the contact angle are also included for comparison.

Membrane label	FGLP	Sartorius	GVHP
Polymer	PTFE	PTFE	PVDF
Support	Polyethylene (PE)	None	None
Diameter (mm)	25	25	25
Pore size (μm)	0.22	0.2	0.22
Thickness (μm)	30[a]	65	125
Contact angle (°)	146 ± 1 	139 ± 1 	131 ± 2 
ε (%)	63 ± 2	54 ± 1	62 ± 1

[a] Thickness corresponding to the PTFE layer only. The total thickness of the membrane (i.e. including the PE support) is ca. 150 μm.

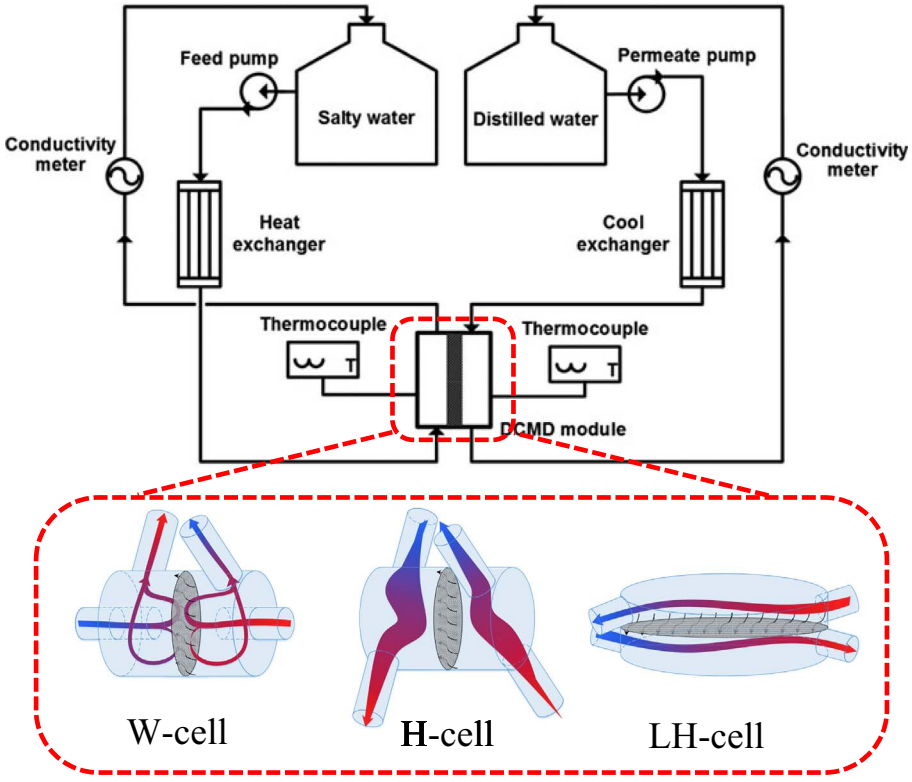


Fig. 1. Schematic representation of the experimental DCMD set-up; inset: membrane module configurations (left: W-cell; center: H-cell; right: LH-cell) (Figure adapted with permission from Ref. [27]; Copyright (2014), Elsevier).

2.2. Direct contact membrane distillation

The performance of the commercial membranes was evaluated in a home-made DCMD setup (Fig. 1), following a procedure reported elsewhere [27]. Two different module configurations were specifically designed, one labelled as "W-cell" and the other as "H-cell"; differing only on the direction of the inlet streams entering the cells: perpendicular or parallel to the membrane for the case of W-cell or H-cell, respectively (as shown in the inset of Fig. 1). The two membrane module configurations were tested and operating parameters were optimized, namely the vapour pressure difference, and permeate and feed flow rates. In a typical run, the membrane was placed into one of the glass modules operating in cross-flow (effective membrane area of 2 cm^2). SW-S (prepared with 35 g L^{-1} of NaCl 95%, purchased from Merck) and DI water were used as feed solutions during the DCMD system optimization in 1 h experiments. The flow rates tested were 24, 48, 94 and 125 mL min^{-1} ($Q_{feed} = Q_{permeate}$), while the temperature at both sides of the DCMD module was kept at ca. 20 °C in the permeate side and at ca. 43, 58, 67, 73 and 82 °C in the feed side (ΔP of ca. 8, 15, 24, 36 and 54 kPa, respectively). Experiments were also performed during longer periods of time (500 h) with SW-R in a larger H-cell, referred to as LH-cell in Fig. 1 (effective membrane area of 24 cm^2). Ionic conductivity was monitored over time in both retentate and permeate streams by online conductivity meter (VWR mod. 310) and by ion chromatography (Metrohm 881 Compact Pro) to determine respectively the percentage of salt rejection and the concentration of ions (sodium, potassium, calcium, magnesium, chloride, bromide and sulphate).

The cumulative permeate flux (J, kg m^{-2} h^{-1}) of the membranes was calculated by Eq. (1):

$$J = \frac{W}{A \times t} \quad (1)$$

where W is the mass of distillate (kg), A is the effective area of the membrane (m^2), and t is the sampling time (h). The solute rejection (R) coefficient was determined by Eq. (2):

$$R\,(\%) = 1 - \frac{C_p}{C_f}\, x\ 100 \quad (2)$$

where C_p and C_f are the concentrations of salt (or target organic pollutants or ions) in the permeate and feed solutions, respectively.

In the long-term experiment, three membranes (FGLP1, FGLP2 and FGLP3) were employed and some of them were cleaned with an alkaline reagent (NaOH) and then with an acid reagent (HNO_3), since they are among the most popular chemicals for cleaning in place (CIP) procedures [27]. Briefly, the membrane was washed by immersion in a 2 wt% sodium hydroxide (NaOH) solution placed in an ultrasound bath for 15 min. The membrane was then rinsed with DI water at room temperature and washed again using a 2 wt% nitric acid (HNO_3) solution in the ultrasound bath for 5 min. The washed membrane was rinsed again with DI water, dried in air at 40 °C overnight and stored until being used again. FGLP1 was washed twice (FGLP1-W and FGLP1-W2 membranes), while FGLP2 was only washed once (FGLP2-W). The cleaning efficiency (CE) was estimated using Eq. (3):

$$CE\,(\%) = \frac{J_f}{J_0}\, x\ 100 \quad (3)$$

where J_f represents the permeate flux of the used/cleaned membrane and J_0 the flux of the fresh membrane.

2.3. Feed solutions tested in DCMD

After DCMD optimization with SW-S, three real matrices were used to evaluate the DCMD performance, namely: SW-R, MW-R and RW-R. Regarding MW-R, effluent samples from a secondary clarifier of a WWTP located in the Northern region of Portugal were collected (March 2015) in pre-rinsed amber glass bottles (2 L) and transported at 4 °C to the laboratory. The same approach was used to collect SW-R from the beach of Leça da Palmeira, Matosinhos, Portugal

(supplementary data, Fig. S1, point 1), and RW-R from the Douro River estuary that can be considered as transitional water (supplementary data, Fig. S1, point 2). DCMD assays with the FGLP membrane were also performed using diphenhydramine (DP, 99% supplied by Sigma–Aldrich) as a model organic pollutant, which was spiked at different concentrations (2.3 mg L^{-1} and 2.3 g L^{-1}) in both SW-S and DI water.

2.4. Chemical analysis of organic pollutants

DP concentration was determined by HPLC with a Hitachi Elite LaChrom system (SpectraLab Scientific Inc., Canada) equipped with a Hydrosphere C18 column (250 × 4.6 mm i.d.; 5 µm particles), a diode array detector (L-2450) and a solvent delivery pump (L-2130). An isocratic method was used with the eluent consisting of a mixture of 20 mM NaH_2PO_4 acidified with H_3PO_4 at pH = 2.80 and acetonitrile (70/30, v/v), at a flow rate of 1 mL min^{-1}. Regarding the micropollutants in SW-R, 1 L of seawater was pre-concentrated and cleaned up by solid phase extraction (SPE) using Oasis® HLB cartridges (150 mg, 6 mL) purchased from Waters (Milford, Massachusetts, USA). Analyses were carried out by ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC–MS/MS), using a Kinetex™ XB-C18 100 Å column (100 × 2.1 mm i.d.; 1.7 µm particles) supplied by Phenomenex, Inc. (California, USA) and ethanol/water (50/50, v/v) as mobile phase. Quantification was performed by selected reaction monitoring (SRM), evaluating the two SRM transitions between the precursor ion and the two most abundant fragment ions. The TOC content was determined using a Shimadzu TOC-5000A analyser (Japan).

2.5. Enumeration of microorganisms

The membrane filtration technique was used to evaluate the efficiency of the DCMD continuous recirculation process on the removal of microorganisms from SW-R. Enumeration of heterotrophic bacteria (including halotolerant), marine bacteria (halophiles), fungi, *Escherichia coli* and enterococci, in both retentate and permeate, was performed before (0 h) and at the end (500 h) of DCMD continuous recirculation operation. Non-treated SW-R was used as control. Variable volumes of sample, ranging between 100 mL and 1 mL of decimal serial dilutions thereof, were filtered through cellulose nitrate membranes (0.22 µm pore size, 47 mm diameter, Sartorius Stedim – Biotech), which were placed onto different culture media (supplementary data, Table S1). After the incubation period, colony forming units (CFU) were enumerated in the membranes containing up to 80 CFU. Each sample was analysed in duplicate. To assess possible regrowth, the same samples were analysed after storage at room conditions for 72 h.

3. Results and discussion

3.1. Optimization of DCMD operating parameters with SW-S in 1 h experiments

Several operating parameters are useful to determine the overall membrane performance in DCMD Fig. 2a shows the permeate flux obtained with the three commercial membranes (GVHP, FGLP and Sartorius) and two of the module configurations (H-cell and W-cell) in 1 h experiments (stationary conditions). The vapour pressure difference (ΔP) was fixed at near 54 kPa in these experiments, small deviations to this value being observed due to slight variations in the cell temperature (± 2 °C in each side corresponding to ± 6 kPa). Total salt rejection was always obtained in these short-term experiments. The permeate flux was nearly halved when the H-cell was used instead of the W-cell, regardless of the membrane tested and the solution used as feed (DI or SW-S). The much better performance obtained with the W-cell may be due to a decrease in the thickness of both temperature and concentration boundary layers (lower temperature and concentration polarization effects) adjacent to the membrane surfaces, as a consequence of the arrangement of the inlet streams (Fig. 1) [28,29]. Despite the improvements achieved, the risk of membrane wetting is higher when using the W-cell due to the application of continuous stressing conditions, although under our experimental conditions (1 h) the salt concentration in the permeate side was below the DL (herein designated total salt rejection).

Among the three membranes tested, FGLP (i.e. PTFE Millipore Fluoropore®) presented the highest permeate flux, followed by GVHP (i.e. PVDF Millipore Durapore®) and then by Sartorius (PTFE), in both module configurations. Since the mean pore size is comparable in all cases (Table 1), the superior performance of the FGLP membrane may be mainly related to its higher: (i) porosity, i.e. FGLP (63%) ≈ GVHP (62%) > Sartorius (54%); and (ii) hydrophobicity (determined by contact angles), i.e. FGLP (146°) > Sartorius (139°) > GVHP (131°). In addition, the lowest thickness of FGLP (only 30 µm in comparison to 65 and 125 µm for Sartorius and GVHP membranes, respectively) leads to a reduced structural parameter of the membrane and consequently, an enhancement of water flux [30], while the FGLP support layer (polyethylene) gives stability to the membrane under the W-cell intensified stress conditions. It is also important to note that only a slight flux decrease was observed when a salty solution (SW-S) was used as feed in DCMD instead of DI water, suggesting a low impact of the solute content on the FGLP membrane performance. Therefore, FGLP was selected to perform additional experiments.

Fig. 2b shows the effect of increasing ΔP from 8 to 54 kPa (i.e., increasing the feed temperature from 43 to 82 °C, and keeping the permeate side at 20 °C). Since DCMD is thermally driven, increasing temperature differences between the two sides of the membrane is expected to enhance mass transfer [31,32], the vapour pressure being an exponential function of the temperature. As expected, the permeate flux increased with ΔP, regardless of the type of cell tested and feed used. In addition, total salt rejection was always achieved regardless of the type of membrane module and ΔP selected. Permeate fluxes obtained with W-cell and FGLP membrane were high considering those reported in literature [33–35].

Fig. 2c shows the influence of feed and permeate flow rates (kept similar, $Q_{feed} = Q_{permeate}$) on permeate flux achieved with the FGLP membrane. In general, the flux increased with the flow rate, regardless of the cell configuration tested, although this behaviour was more evident when operating with the W-cell, suggesting a more significant decrease of the boundary layer in this case (i.e. lower thermal and concentration resistances) [36–38]. The slightly lower permeate flux when using the 35 g L^{-1} NaCl solution (SW-S), instead of DI water, may be related to the lower efficiency caused by the reduction of vapour pressure at these concentrations and the effect of both concentration and temperature polarizations at the membrane surface [39]. Higher non-volatile solute concentrations in the retentate side originate lower water activity, i.e. the effective water vapour pressure decreases and as consequence, so does the respective driving force in MD [1]. In general, the DCMD system should operate under high flow rates since a higher permeate flux can be achieved as consequence of the minimization of the boundary layer resistance. However, the difference on permeate flux when increasing the flow rates from 94 to 125 mL min^{-1} was not as evident as that obtained from 48 to 94 mL min^{-1}. In addition, a compromise between flow velocities and membrane wetting risk should be considered in order to achieve high rejection of salts, micropollutants and microorganisms in long-term DCMD experiments. In this context, the subsequent experiments were performed using the FGLP membrane at a flow rate of 94 mL min^{-1} and ΔP ≈ 54 kPa.

3.2. DCMD of different feed samples in < 200 h experiments

After optimizing the operating conditions of the DCMD system, four feed solutions were tested (three real and one simulated samples) for

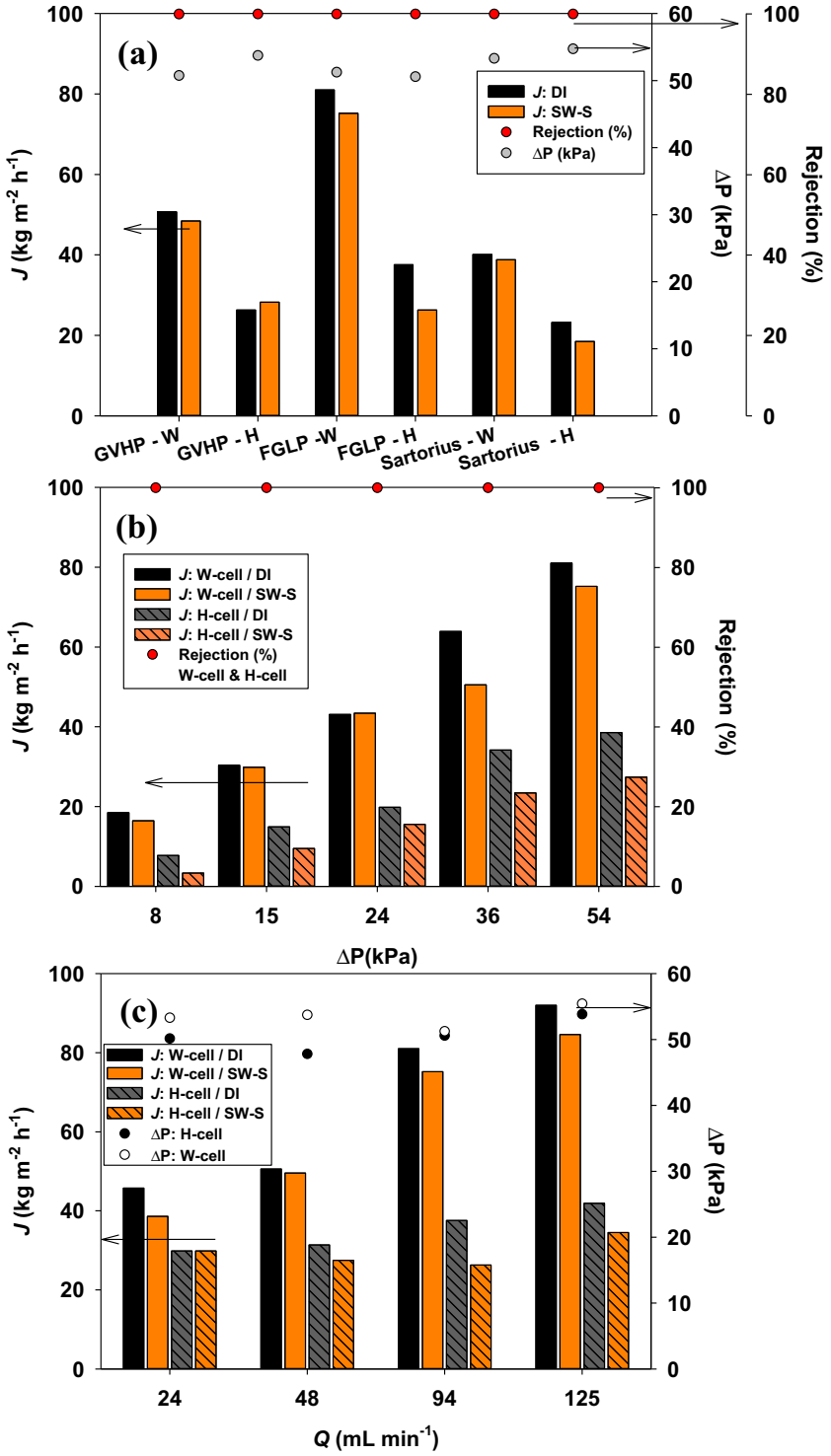


Fig. 2. SW-S and DI water with both W-cell and H-cell configurations: permeate flux and salt rejection for different (a) membranes (ΔP ≈ 54 kPa; $Q_{feed} = Q_{permeate} = 94\ mL\ min^{-1}$) and (b) vapour pressure differences (FGLP membrane; $Q_{feed} = Q_{permeate} = 94\ mL\ min^{-1}$); (c) permeate flux and vapour pressure difference for different flow rates (FGLP membrane; $Q_{feed} = Q_{permeate} = 94\ mL\ min^{-1}$).

48 h. The chemical composition of these solutions is shown in Table 2. As expected, due to the salt content, higher TDS and conductivity values were registered for SW-R and RW-R than for MW-R. In contrast, MW-R exhibited higher TOC and lower concentrations of ions than SW-R and RW-R.

DCMD experiments (48 h) with SW-R, MW-R and RW-R were then performed under the operating conditions optimized with SW-S in 1 h experiments (W-cell; FGLP membrane; ΔP ≈ 54 kPa; $Q_{feed} = Q_{permeate} = 94\ mL\ min^{-1}$). Fig. 3 shows that the permeate flux decreased faster for MW-R than for the other feeds tested, probably due to the more complex matrix composition of this water sample. According to other authors [40], who studied the performance of DCMD (membrane flux and fouling) for the treatment of the effluent from an anaerobic bioreactor, a significant decrease in the membrane flux was also observed over time. In the experiments performed with SW-S, SW-R and RW-R, ion rejection was higher than 95% for all ion species

Table 2
Chemical characterization of each sample tested.

	SW-S	SW-R	MW-R	RW-R
TDS ($g\,L^{-1}$)	34.9	33.2	0.6	10.0
TOC ($mg\,L^{-1}$)	0.40	20.8	24.4	18.5
Conductivity ($mS\,cm^{-1}$)	53	51	0.7	17
pH	6.9	8.0	7.1	7.2
Na^+ ($g\,L^{-1}$)	13.55	10.20	0.29	3.27
K^+ ($g\,L^{-1}$)	n.d.	0.43	0.06	0.16
Ca^{2+} ($g\,L^{-1}$)	n.d.	0.47	0.09	0.05
Mg^{2+} ($g\,L^{-1}$)	n.d.	1.22	n.d.	0.53
Cl^- ($g\,L^{-1}$)	21.21	17.50	0.11	4.93
SO_4^{2-} ($g\,L^{-1}$)	n.d.	2.34	0.04	0.47
Br^- ($g\,L^{-1}$)	n.d.	0.03	n.d.	n.d.

n.d. – not detected.

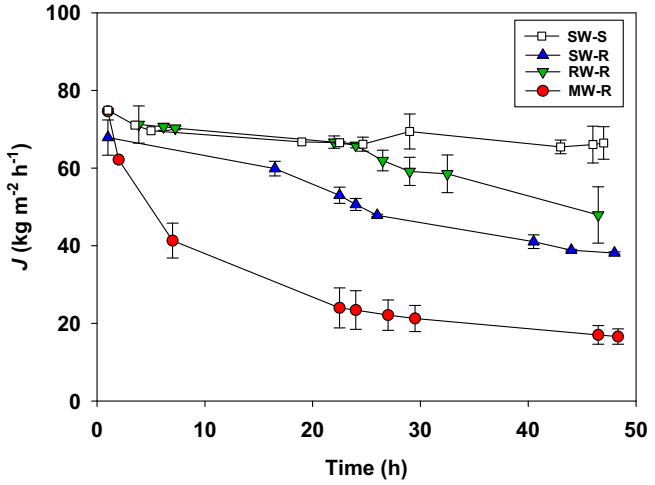


Fig. 3. Permeate flux as function of operating time obtained with each water sample tested (W-cell; FGLP membrane; $\Delta P \approx 54$ kPa; $Q_{feed} = Q_{permeate} = 94\,mL\,min^{-1}$).

measured. In the tests using MW-R as feed, ions were totally rejected (i.e. the ion concentrations were below their DL, corresponding to a rejection > 99.5%). More information concerning the concentrations of ions in the different permeates can be found in supplementary data, Table S2.

3.3. SW-S spiked with diphenhydramine (DP) in < 200 h experiments

The DCMD performance to remove organic pollutants was validated for possible application of this technology as a single treatment process for water desalination and purification. Considering the more stable permeate flux achieved with SW-S after ca. 50 h operation (Fig. 3), most probably due to the absence of organic substances (which presence significantly enhances membrane fouling and subsequently declines the flux), the experiments with the organic model pollutant DP were performed with DI water first, and then with SW-S in order to assess the effect of the matrix complexity on the capacity of DCMD for the removal of organic pollutants from salty water. These DCMD assays were performed under the same conditions selected before (FGLP membrane; $\Delta P \approx 54$ kPa; $Q_{feed} = Q_{permeate} = 94\,mL\,min^{-1}$) and two different DP concentrations, at $mg\,L^{-1}$ and $g\,L^{-1}$ levels, were tested.

Regarding the experiments with DP at $mg\,L^{-1}$ level (2.3 $mg\,L^{-1}$) in DI water, both cell configurations (W-cell and H-cell) were able to remove this micropollutant, which was below the DL in the permeate. Once again, the W-cell performed better than the H-cell, concentrating DP faster in the retentate side (Fig. 4a, showing nearly 7-fold concentration in 52 h), as well as showing a higher permeate flux (Fig. 4b) than the H-cell. In fact, permeate flux was twice as that obtained when

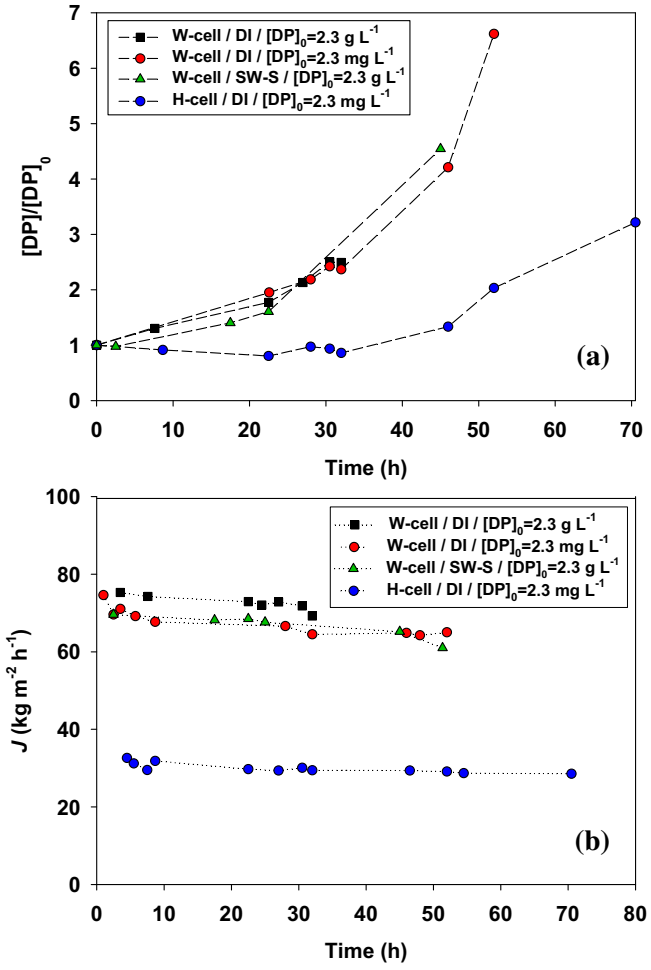


Fig. 4. (a) DP normalized concentration in the retentate and (b) permeate flux as function of operating time ($\Delta P \approx 54$ kPa; $Q_{feed} = Q_{permeate} = 94\,mL\,min^{-1}$).

using the H-cell, in agreement with results obtained without DP (Fig. 2b). The permeate flux observed in these experiments (Fig. 4b) was quite stable over time for both membrane module configurations, highlighting the good properties of the membrane employed in these experiments, including its fouling resistance. Theoretical DP concentrations as a function of operating time were calculated considering total DP rejection and the permeate flux obtained experimentally, these concentrations being plotted together with the experimental ones (supplementary data, Fig. S2). As predicted theoretically, it is possible to increase the DP concentration in the retentate by a factor of 1000 in < 65 h when the volume decreases by a factor of 1000 (i.e. 1 mL); in other words, the DP concentration increasing from 2.3 $mg\,L^{-1}$ to 2.3 $g\,L^{-1}$ in DI water. This was not performed experimentally due to some limitations of our DCMD unit, namely the minimum feed solution volume possible to operate the set-up (ca. 150 mL).

In order to assess the effect of a higher DP concentration (×1000), a shorter experiment was conducted with the DP feed concentration of 2.3 $g\,L^{-1}$ using the W-cell and DI water also. The flux values were quite similar to those obtained with DP at $mg\,L^{-1}$ level (Fig. 4b), and a 2.5-fold concentration increment was observed after 32 h (corresponding exactly to the increment observed with 2.3 $mg\,L^{-1}$ of DP at similar operating conditions) (Fig. 4a). However, when using 2.3 $g\,L^{-1}$ of initial DP concentration, ca. 30 mg of DP were detected in the permeate from the original 2300 mg in the feed, corresponding to 1.3 wt% of DP in the permeate at the end of the experiment. The rejection mechanism of organic compounds in DCMD depends on their volatility, surface charge and hydrophobicity [15]. In our study, DP was almost

completely rejected (above 98.7%), which is in agreement with non-volatile trace organic contaminants with pK_H above 8, where K_H is the Henry's law constant [41]. In addition, DP is positively charged and may be strongly attracted onto the negative PTFE membrane used in the assays, the DP leakage to the permeate side being facilitated.

The performance of DCMD to simultaneously reject DP and desalt an aqueous solution was then studied using a feed solution containing both 2.3 g L^{-1} of DP and 35 g L^{-1} of NaCl (SW-S) under the same operating conditions (i.e. $\Delta P \approx 54$ kPa, $Q = 94$ mL min^{-1}) with the W-cell. Again, a highly concentrated DP solution in the retentate was achieved by the end of the experiment (Fig. 4a) and a quite stable permeate flux of ca. 69 kg m^{-2} h^{-1} was registered during the experiment (Fig. 4b). Moreover, it is important to highlight that not only DP was concentrated, but also the NaCl salt, its concentration increasing by a factor of 4.5 (i.e. 160 g L^{-1}). However, NaCl passed through the membrane after 23 h operation (0.05 wt%), reaching a maximum of 0.4 wt% in the permeate after 45 h operation (99.6% of salt rejection). DP (0.3 wt%) was also present in the permeate (corresponding to 7 mg from the initial 2300 mg in the feed). This fact could be due to possible electrostatic interactions established between the chloride anions contained in NaCl and the positively charged DP molecules, decreasing its adsorption on the negative membrane surface, as well as its leakage to the permeate in comparison to the DI water assay.

At this stage, it was decided to compare the H-cell and the W-cell, in terms of salt retention for the same volume of permeate obtained when performing these experiments. Fig. 5 shows the NaCl concentration, in both retentate and permeate solutions, obtained with SW-S only (without DP). The better performance of the W-cell to concentrate the retentate in a shorter period of time is clearly demonstrated by these results (besides a significantly higher permeate flux of ca. 72 kg m^{-2} h^{-1} for the W-cell in comparison to ca. 25 kg m^{-2} h^{-1} for the H-cell). However, when comparing the H-cell and the W-cell for a fixed permeate volume of 230 mL (achieved after ca. 19.5 h with the W-cell and ca. 50 h with the H-cell, as pointed out in Fig. 5), 62.1 mg of salt were found in the permeate with the W-cell, representing almost 12 times more salt crossing the membrane than in the H-cell (4.76 mg) for the same permeate volume.

These results demonstrated that the W-cell performed faster to concentrate the retentate under a superior permeate flux. However, the permeate achieved with the H-cell was of higher quality, for the same volume of permeate obtained with the W-cell. In addition, despite the higher permeate fluxes obtained with the W-cell configuration, this design shows more potential to damage the membrane, due to the flow arrangement selected (as it tends to curve in the flow direction).

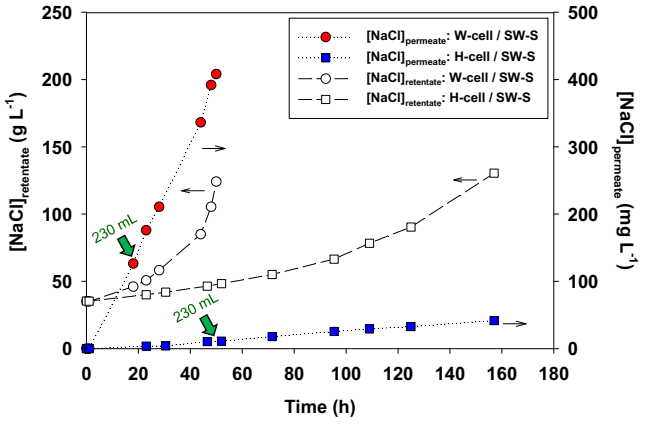


Fig. 5. NaCl concentration in the retentate (dashed lines) and permeate (dotted lines) as function of operating time ($\Delta P \approx 54$ kPa; $Q_{feed} = Q_{permeate} = 94$ mL min^{-1}), obtained for SW-S as feed solution.

3.4. Long-term (500 h) desalination of seawater (SW-R)

Considering the higher permeate quality obtained with the H-cell (compared to the W-cell) when the same volume of permeate is achieved, and aiming at reaching high volumes of permeate in short periods of time, a larger H-cell was fabricated and tested, so-called LH-cell (Fig. 1), with an effective membrane area of 24 cm^2. This experiment was performed with SW-R under the same conditions ($\Delta P \approx 54$ kPa; $Q_{feed} = Q_{permeate} = 94$ mL min^{-1}). Since long-term stable flux and high salt rejection are two major aspects for the successful full-scale implementation of DCMD, the extended experiment was conducted with the aim of treating 20 L of fresh SW-R and to evaluate the DCMD system effectiveness in the removal of salts, organic micropollutants and microorganisms.

In this long-term DCMD operation (500 h) experiment, the first fresh membrane (FGLP1) was replaced by a second one (FGLP2) after 98 h. Meanwhile, the first membrane (FGLP1) was washed and reused (FGLP1-W) in the experiment after 190 h, in replacement of the FGLP2 membrane. The same washing procedure was applied to the second membrane (FGLP2), which was reused (FGLP2-W) in the experiment after 288 h, in replacement of the FGLP1-W membrane. After that, FGLP1-W was washed (FGLP1-W2) and reused in the experiment after 357 h, in replacement of the FGLP2-W. Finally, a third fresh membrane (FGLP3) was used after 406 h to discard the possibility of membrane damaging or ageing, eventually promoted by cleaning. The cleaning procedure was apparently effective in the removal of foulants, restoring the brownish surface of the spent FGLP membranes back to white.

The permeate flux obtained up to 24 h with the LH-cell (i.e., 25 kg m^{-2} h^{-1}) is in agreement with the fluxes obtained with the smaller H-cell, even if the later has a membrane contact area 10 times smaller. The washed membranes significantly recovered the permeate flux of the fresh membranes, resulting in CE values of ca. 95% and 86% for FGLP1-W and FGLP2-W, respectively. However, a marked decrease of the permeate flux was noticed with FGLP2-W after 357 h, and the membrane was replaced by FGLP1-W2. In this case the washing procedure was not so effective, allowing to recover only 33% of the permeate flux of the fresh membrane (FGLP1). After 406 h, a new fresh PTFE membrane (FGLP3) was used. However, FGLP3 reached the lowest permeate flux (< 1.0 kg m^{-2} h^{-1}) in the assay, probably due to the high contents of salts and other substances in the retentate at the last stages of the experiment.

3.4.1. Concentration of ions

The normalized concentration of ions found in the retentate is shown in Fig. 6a, while their net concentration values in the permeate side are presented in Fig. 6b over the 500 h long-term experiment. After that time, a 4-fold concentration factor was observed in the retentate (Fig. 6a), as the volume was reduced to ca. 5 L from the initial 20 L of SW-R used as feed. High salt rejection was registered ($> 99\%$) in the permeate for all the ion species measured (99.1% for sodium, 98.8% for potassium, 99.3% for calcium, 99.4% for magnesium, and 99.1% for chloride). The same 4-fold concentration increase in the retentate was observed for bromide (data not shown), but this species was not detected in the permeate, probably due to its low concentration in the retentate.

However, Fig. 6b shows that most of the ions passed through the membrane after 357 h operation, corresponding to the significant and permanent permeate flux decrease. Indeed, the ion concentrations determined in the permeate stream up to 400 h of operation were still below the threshold values established for drinking water according to the Portuguese Decree-Law nr. 306/2007, August 27th, transposed from the European Directive 98/83/CE. Sodium and chloride appeared at higher concentrations by the end of the experiment (i.e. ca. 330 mg L^{-1} for both ions), but still close the threshold values (200 and 250 mg L^{-1} for sodium and chloride, respectively).

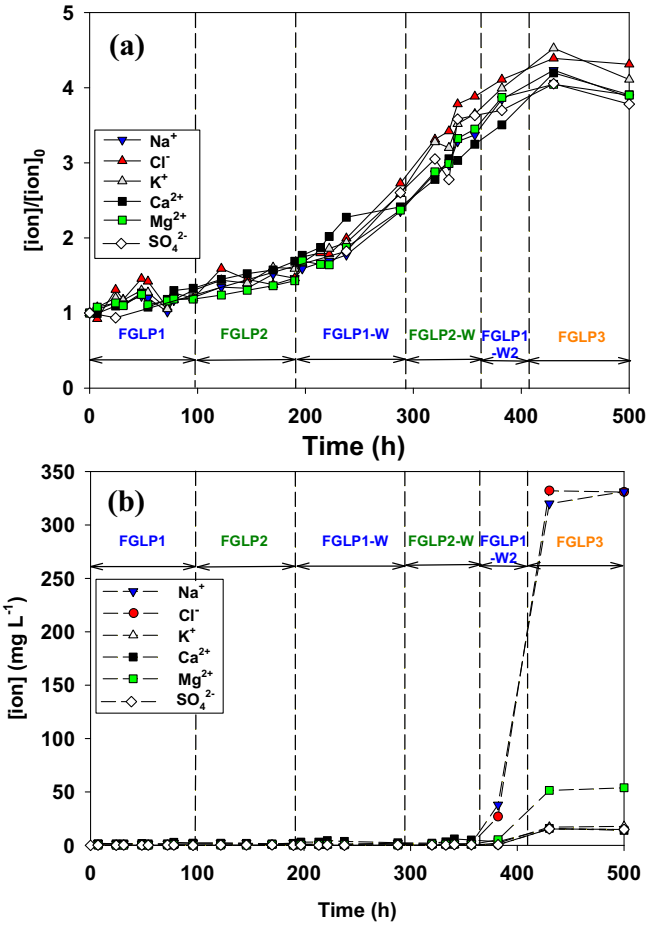


Fig. 6. Ion concentrations in the (a) retentate (normalized) and in the (b) permeate (absolute value) versus operating time for fresh and washed PTFE membranes (LH-cell, $\Delta P \approx 54$ kPa; $Q_{feed} = Q_{permeate} = 94$ mL min^{-1}).

3.4.2. Characterization of the membranes

The consistency and thickness of the fouling layer formed at the membrane surface depend on the nature and concentration of the fouling agents found in the feed water [42], as well as on the operating conditions (e.g. feed temperature and flow velocity) [43]. SEM micrographs of the fresh and used FGLP membranes (Fig. 7) confirmed the occurrence of scaling and fouling, showing the presence of a thick compact layer on the top surface of the membrane (Fig. 7c and d), which was not found in the fresh membrane (Fig. 7a and b), resulting in a serious level of obstruction to vapour permeation through the membrane pores.

EDS analyses confirmed the presence of gypsum ($CaSO_4{\cdot}2H_2O$) crystals (Fig. 7e) and NaCl crystals (Fig. 7f), as well as other salts of magnesium and calcium (e.g., calcium carbonate - $CaCO_3$) in the fouling layer of the spent membranes. Inorganic salts are referred to in the literature as dominant for membrane scaling in DCMD [44,45]. The presence of divalent ions, such as Ca^{2+}, may result in the formation of metal-natural organic matter complexes, which may form a highly compacted fouling deposit, decreasing the membrane performance [46]. In fact, $CaCO_3$ and $CaSO_4$ are fouling agents commonly found in thermally driven desalination processes, which solubility decreases as the temperature increases, thus enhancing scaling propensity during DCMD [44]. In the long-term DCMD experiment, the large flux decline at the end could be explained by the formation and deposition of these salts, in particular $CaSO_4$, which is known to produce a higher flux decline than $CaCO_3$ [15].

3.4.3. Organic micropollutants

The anti-inflammatory diclofenac and three antibiotics (azithromycin, clarithromycin and erythromycin), listed in the watch list recently launched for European Union wide monitoring [47,48], were found in SW-R, whereas DP was not detected in this sample (Table 3). Therefore, a specific screening of these watch list compounds in the DCMD retentate and permeate was performed, in order to assess the ability of MD to remove these micropollutants.

In fact, antibiotics were not found above the DL of the analytical method (0.02–0.04 ng L^{-1}) either in the permeate or in the retentate streams at the end of the experiment (500 h). Thermal degradation appears as a possible explanation for this phenomenon, which is favoured by the long duration of the assay. Other authors [49] studied the stability of different pharmaceuticals commonly found in the environment and reported low stability for azithromycin, clarithromycin and erythromycin, when kept in water one week after sampling. These authors also reported that the concentration of most of the analysed antibiotics was significantly lower (< 80%) after 12 weeks, even when preserved at −20 °C or in an ETDA solution. Regarding diclofenac, this compound was found in the feed stream and revealed a signal almost 4 times more intense in the retentate after DCMD treatment. The diclofenac rejection can be explained by its low volatility ($pk_H = 8.28$), negative surface charge and hydrophilic character (Log D = 1.06) [15]. These physical and chemical properties favoured its concentration in retentate and avoided its leakage to the permeate side, as well as its adsorption on the negatively charged and hydrophobic PTFE membrane. In addition, the enrichment factor of diclofenac matches those achieved for the ion species previously described (Fig. 6a), indicating that DCMD can retain such pollutant in retentate, producing a clean permeate (Table 3).

3.4.4. Microbiological analyses

In order to assess the efficacy of DCMD for the removal of potential dangerous microorganisms from SW-R, several cultivable microbial groups were enumerated in SW-R and DI water before (0 h) and after the DCMD treatment (retentate and permeate, 500 h), and after 3 days storage at room conditions (Stored). As control, non-treated SW-R was run and analysed simultaneously.

As expected, marine bacteria was the most abundant group of microorganisms in SW-R (~2 × 10^2 CFU mL^{-1}) whereas the abundance of fungi, *E. coli* and enterococci was low (0.3, 0.03 and 0.03 CFU mL^{-1}, respectively). After 500 h, all the analysed bacterial groups were below the DL of the method (0.01 CFU mL^{-1}) in the retentate stream, while the initial concentration of fungi was reduced almost by a factor of 100. Such results are explained by the harsh conditions faced by the microorganisms in the retentate water, which was kept at 80 °C during the treatment and reached a salt concentration of about 250 g L^{-1} at the end of the DCMD treatment. The salinity, and mainly the thermal stress, most probably prevented the bacterial development, the spore producers (fungi) being the only ones standing the prevailing conditions. In fact, after cooling down during storage at room conditions for 3 days, the density of the marine bacteria in the retentate reached their initial values in SW-R (Fig. 8a). Most probably due to the high salinity, the number of the halotolerant heterotrophic bacteria was almost 1 log lower in the stored retentate water than in SW-R (Fig. 8a).

One of the main objectives of this study was to assess whether the DCMD treatment ensures the microbiological quality of the permeate stream. The microbial load and composition of the permeate water remained stable not only after the treatment, but also after the storage period at room conditions. The number of heterotrophic bacteria after 500 h of operation or after 3 days storage was slightly higher than in the DI water at the beginning of the treatment (Fig. 8b). This increment was probably due to the contact with air and the plastic material of the open container used to collect the permeate. In the permeate, the density of *E. coli* and enterococci was below the DL in all the samples, while that of fungi and of bacteria able to grow on Zobell Marine agar after 500 h

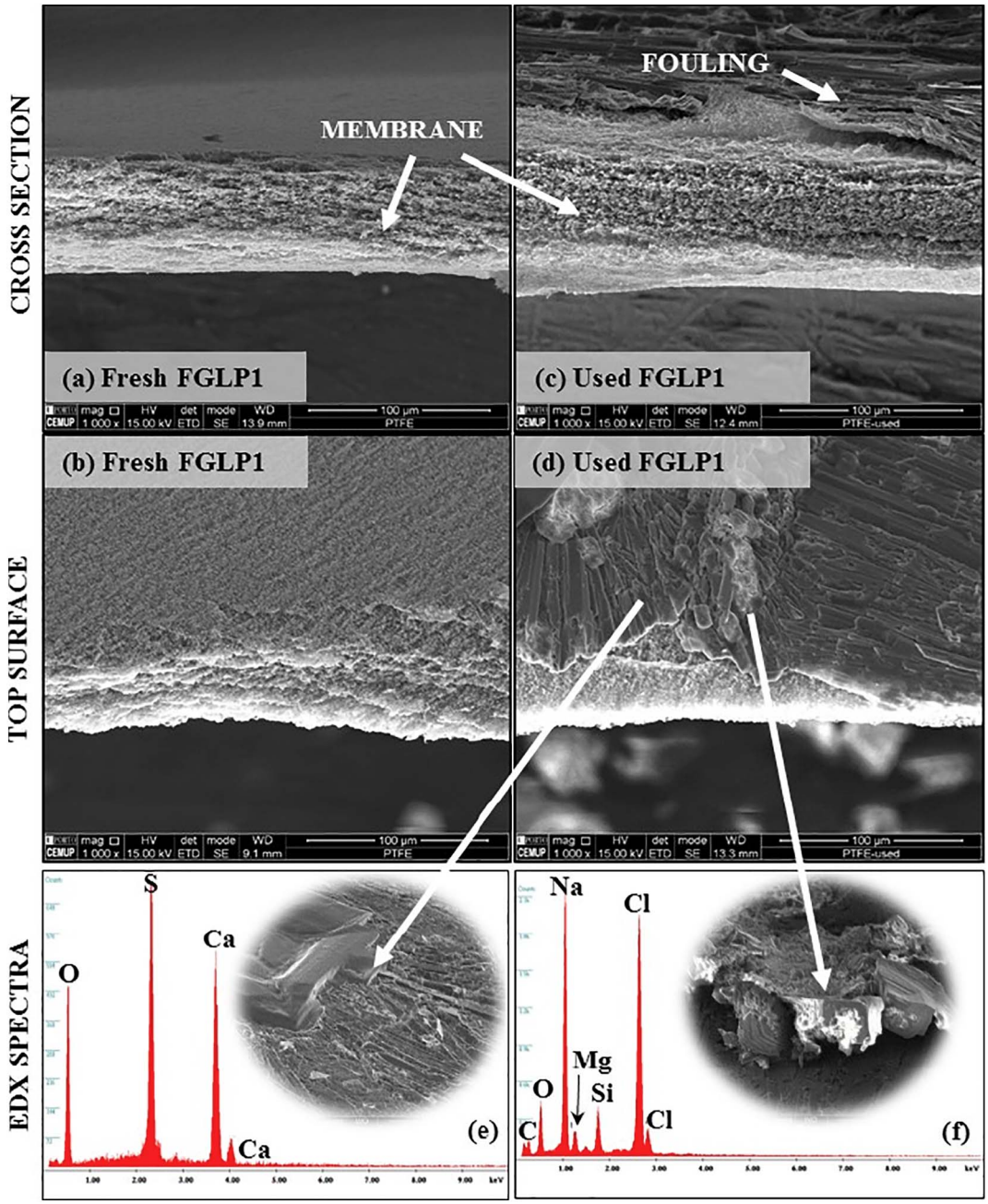


Fig. 7. SEM micrographs of the (a, c) cross-section and (b, d) top surface of (a, b) fresh and (c, d) spent FGLP1 membrane (after SW-R desalination for 406 h); (e, f) EDS spectra for two different zones of spent FGLP1.

Table 3
Concentrations and DL of organic micropollutants in SW-R.

	SW-R	Retentate	Permeate	DL (rejection %)
Diclofenac (ng L^{-1})	73.53 ± 2.35	290.6 ± 9.29	< DL	0.16 (> 99.8)
Azithromycin (ng L^{-1})	20.31 ± 2.38	< DL	< DL	0.03 (> 99.9)
Clarithromycin (ng L^{-1})	9.53 ± 0.28	< DL	< DL	0.02 (> 99.6)
Erythromycin (ng L^{-1})	9.97 ± 0.81	< DL	< DL	0.04 (> 99.8)
DP (ng L^{-1})	< DL	< DL	< DL	0.03 (−)

DL, detection limit.

or storage (1.7, < DL and 0.03 CFU mL^{-1}, and 0.6, 0.01 and 0.05 CFU mL^{-1}, respectively, Fig. 8b) was lower than in DI water. On the contrary, in the non-treated SW-R used as control, the marine bacteria and heterotrophic bacteria loads increased by a factor higher than 100 and 1000, respectively, over the 572 h of incubation at room conditions (Fig. 8c).

The results herein obtained indicate that the FGLP membrane prevented the contamination of the permeate stream with marine bacteria or faecal indicators present in SW-R at the beginning of the assay. In addition, the DCMD treatment seems to prevent the contamination of the permeate stream with organic micropollutants which could, eventually, be used by the microbial cells during a storage period to re-grow. Hence, DCMD was effective in reducing significantly the load of microorganisms present in seawater, achieving a distillate in conformity with the legal recommendations of drinking water microbiological

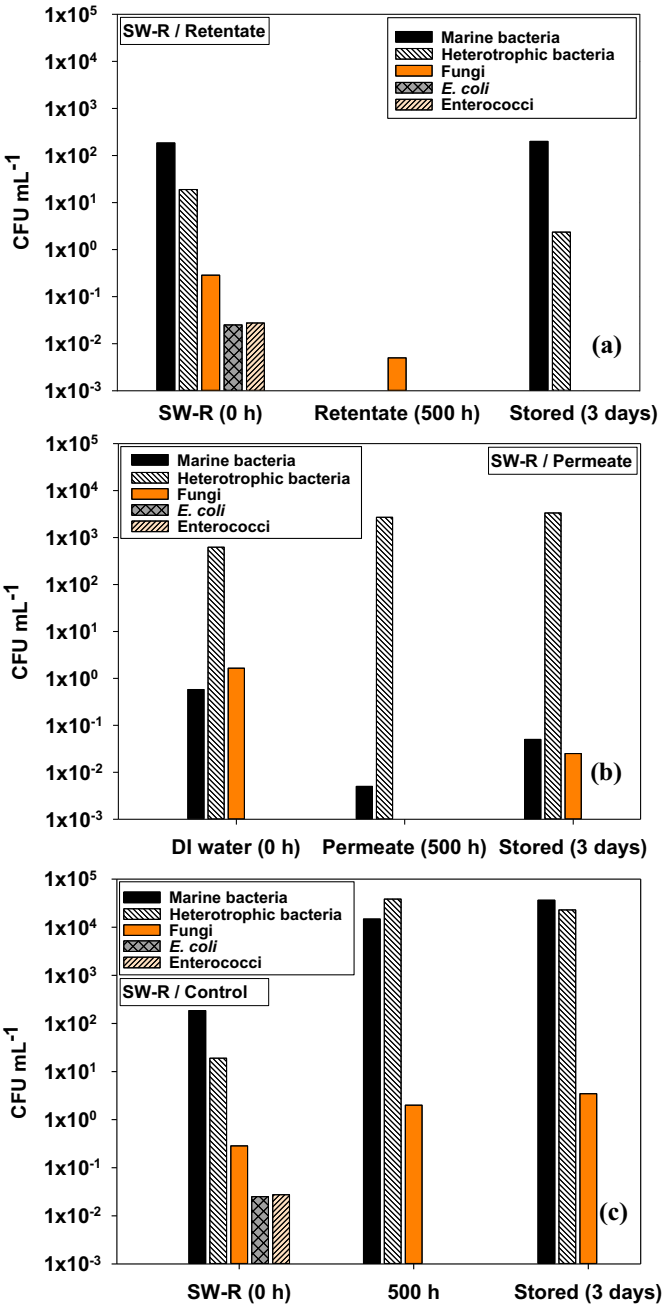


Fig. 8. Microbial densities (a) in the retentate (after 500 h), (b) in the permeate (after 500 h), and (c) in the non-treated SW-R incubated at room conditions (control), measured before DCMD ("SW-R" and "Distilled water"), after 500 h DCMD ("Retentate" and "Permeate") and after storage for 3 days at room conditions ("Stored"). Except in SW-R before DCMD, the density of *E. coli* and enterococci was < DL.

parameters (Directive 98/83/CE), even after storage at room conditions for 3 days.

4. Conclusions

Among the three commercial membranes suggested in literature for DCMD (FGLP, GVHP and Sartorius PTFE), better performances for SW-S desalination were achieved with the FGLP membrane, most probably due to its high porosity and hydrophobicity and low thickness. Similar ion rejections were obtained with real feeds (SW-R, RW-R) in short run experiments (< 200h). Nevertheless, permeate flux depended on the matrix and decreased significantly when operated with MW-R, probably due to the high complexity of this matrix.

The performance of two membrane module designs (W-cell and H-cell) on the removal of the model pollutant DP were compared; the W-cell concentrated DP faster in the retentate side (with twice the permeate flux as in the H-cell), but the H-cell performed better in terms of solute rejection for the same volume of permeate achieved.

A larger H-cell (LH-cell) was selected for longer experiments (500 h) with SW-R. Cleaning procedures (using NaOH and then HNO_3) were effective to recover the permeate flux of the fresh membranes, but only up to ca. 350 h. This seems to be related with the high content of ion species in the retentate after this stage (such as sodium, chloride and magnesium), as confirmed by ion chromatography. In fact, EDS analysis confirmed the presence of these species in the fouling layer of the spent membranes. Among the micropollutants found in SW-R (diclofenac, azithromycin, clarithromycin and erythromycin at 73.53, 20.31, 9.53 and 9.97 ng L^{-1}, respectively), none of the antibiotics were detected in

the permeate or retentate, suggesting their thermal degradation, whereas diclofenac was found in the retentate only and concentrated ca. 4 times (up to 290.6 ng L^{-1}). Thus, other technologies must be employed to treat the resulting concentrate containing some organic micropollutants such as diclofenac. Rejection rates as high as 99% were registered for all ion species measured, along with a significant reduction in the microbial loads of SW-R. Contamination of the permeate stream with marine bacteria or faecal indicators initially present in SW-R was prevented, complying with the legal recommendations of drinking water microbiological parameters.

Acknowledgments

This work a result of project "AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020", with the reference NORTE-01-0145-FEDER-000006, supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the Portugal 2020 Partnership Agreement, through the European Regional Development Fund (ERDF) and of Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM funded by ERDF through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) – and by national funds through FCT - Fundação para a Ciência e a Tecnologia. TLSS and ARR acknowledge financial support from SFRH/BDE/99835/2014 and SFRH/BPD/101703/2014, respectively. AMTS and SMT acknowledge the FCT Investigator 2013 (IF/01501/2013) and 2015 (IF/00573/2015) Programmes, respectively, with financing from the European Social Fund and the Human Potential Operational Programme. SMT also acknowledges the financial support from University of Granada (Reincorporación Plan Propio). Dr. Carlos Sá and CEMUP team (Portugal) are gratefully acknowledged for the technical assistance with SEM analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.desal.2018.02.027.

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