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# Desalination and removal of organic micropollutants and microorganisms by membrane distillation

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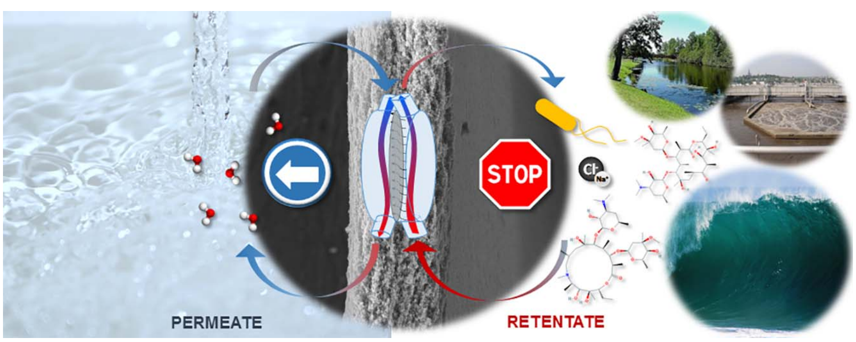
## GRAPHICAL ABSTRACT

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## 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.

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## 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 ($\Delta P$) 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 $\beta$-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.

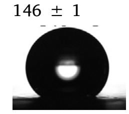
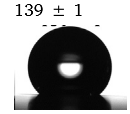
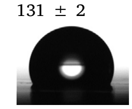
Desalination and removal of specific organic micropollutants found in SW-R (the anti-inflammatory diclofenac, and three macrolide antibiotics - azithromycin, clarithromycin and erythromycin) were investigated in 500 h experiments with SW-R. Enumeration of indicators of microbiological quality (enterococci 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 ($\varepsilon$) 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 |
| |  |  |  |
| $\varepsilon$ (%) | 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.