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Diffusion behavior of humic acid during desalination with air gap and water gap membrane distillation

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Abstract
Desalination and water reuse are important means to resolve local water scarcity and security issues worldwide where membrane distillation (MD) may be part of a solution. Natural organic matter and in particular, humic acids (HA), are widely present in water supplies to be treated but exhibit little understood behavior to diffuse through MD membranes into permeate. In this work, air gap (AGMD) and water gap (WGMD) were utilized to study HA behavior in MD using seawater and synthetic water over a range of typical MD temperatures, flow rates and membrane types. HA diffusion was first shown with seawater feed then on synthetic solutions at all process conditions. While electrical conductivity rejection was always above than 99%, HA rejection showed values of 33% and 90% for AGMD and 68% and 93% for WGMD with seawater and synthetic water, respectively. Analytical techniques were used to perform a preliminary organic matter characterization in permeate, obtaining clear differences between the feed and permeate HA property. Compared to hydrophobic membranes, uniquely oleophobic membranes inhibit HA diffusion suggesting hydrophobic surface diffusion of HA through the membrane. HA flux as well as potential undesirable effects of the organic matter in permeate should be considered for MD applications.
Keywords: humic acid, air gap membrane distillation, water gap membrane distillation, organic matter, diffusion, seawater.

1. Introduction

Water shortages and the loss in water quality are one of the main common global problems humanity faces (Anand et al., 2018; Voulvoulis, 2018). In addition, many anthropogenic compounds that cannot be treated with conventional wastewater treatments can be found in natural waters, posing a significant risk to the environment and to human health (Biel-Maeso et al., 2018; Han et al., 2017; Herce-Sesa et al., 2018; Wagner et al., 2016).

Of particular interest in water quality are natural organic matter (NOM) compounds which is present in natural water systems. NOM compounds are derived from the degradation of plants, animals, and microorganisms by chemical, biological and photochemical reactions. Among the compounds making up NOM, humic substances (HS) are important since they are the major carbon pool in the biosphere. Of the NOM presents in natural waters, up to 50% consist of HS and they are the main organic compounds in seawater (Lipczynska-Kochany, 2018; Naidu et al., 2015; Rodríguez et al., 2014).

HS are complex and heterogeneous mixtures of a wide range of molecular weight species. The two main categories of HS are fulvic acids (FA) and humic acids (HA), and can be distinguished in function of their solubility at pH 1 where the latter often form colloids because of their large size (Rodríguez et al., 2014; Wagner et al., 2016). Although HS do not cause any known adverse effects for human health, they are undesirable substances in water treatment and they can play a fundamental role as indicators of water quality. HS contributes to odor, color, taste and acidity problems in water supplies. Furthermore, HS, and especially HA, lead to a greater spending on disinfection when chlorination is used as they are precursors of toxic disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Liu et al., 2008; Roccaro et al., 2009). Finally, HS have been identified as one of the major compounds responsible for fouling in membrane processes as well as the complexes formation.
with a multitude of metal ions and organic pollutants promoting the formation of biofilm in water pipes (Bond et al., 2012; Chowdhury et al., 2016; Jermann et al., 2007; Liu et al., 2008; Roccaro et al., 2009). Therefore, HA and its behavior through a new proposed water treatment technology is important to be investigated.

Water desalination and reuse technologies have great potential to address the problems associated with water shortages and water quality by use of non-conventional water sources. These desalination technologies are mainly based on membrane and/or thermal processes, or a combination of both in a process train while reuse technologies are mainly based on membrane processes. Some of these technologies are reverse osmosis (RO), electrodialysis, nanofiltration (NF), multiple-effect distillation (MED) and multi-stage flash distillation (MSF). An alternative process combining membranes with thermal desalination is membrane distillation (MD) (Criscuoli and Carnevale, 2015; Ghaffour et al., 2013; Kim and Hong, 2018; Prisciandaro et al., 2016; Ziolkowska and Reyes, 2016). MD is a thermally driven separation using a membrane as a barrier for saline liquid water, while being permeable to fresh water vapor. In this way, the vapor pressure between both sides of this membrane, being microporous and hydrophobic in order to fulfill the liquid barrier and vapor permeable requirement, is the driving force in this separation process.

The advantages of MD proposed include the use of small and compact equipment and very low working pressures which could lead to lower material costs and greater process safety compared to other conventional technologies (Alkhudhiri et al., 2012a; Essalhi and Khayet, 2015; Khalifa, 2015). Additionally, MD can use low-grade and waste heat as well as alternative energy sources, increasing energy efficiency. In terms of membrane performance, the fouling of the membranes can be lower than in other membrane processes while a very high water quality is produced because of the 100% theoretical rejection of non-volatile components (Alkhudhiri and Hilal, 2017; Guillen-Burrieza et al., 2014). Among MD configurations, commonly investigated modes include direct contact MD (DCMD), air gap MD (AGMD) and water gap MD (WGMD). In DCMD, feed and cooling water are in contact with the membrane surfaces. In this way, the
transmembrane flow (membrane flux) is high but there are also high heat losses by conduction. As a result of this setup, obtaining an isolated distillate is not possible, since it is mixed with the cooling water. This is avoided with the AGMD setup as the distillate can be obtained separately from the cooling water, however the drawback is membrane flux is lower than in DCMD. Another configuration, WGMD, emerged as an improvement over these limitations of DCMD and AGMD. In WGMD, the gap is filled with distilled water. This configuration offers an improvement in the permeate flow in comparison with AGMD and it allows a separate distillate to be obtained, unlike DCMD (Francis et al., 2013; González et al., 2017).

These MD advantages make it a promising alternative to conventional desalination and water reuse technologies for many environmental and industrial applications (Amaya-Vías et al., 2018; Cui et al., 2018; Silva et al., 2018). Nevertheless, MD is not fully commercialized and implemented by industry (Khayet, 2011; Qtaishat et al., 2009), since many aspects have still not been studied in detail; for example, the effect of organic matter (OM) and HA in the MD process. Many authors have focused their studies on the MD fouling and the HA influence in the rejection of different substances. However, the permeation of HA through the membrane into the permeate has so far only been observed as a side result in these DCMD fouling studies (Han et al., 2017; Khayet et al., 2004; Meng et al., 2014; Naidu et al., 2015, 2014; Wijekoon et al., 2014).

In view of their importance and consequences of HA presence in treated water supplies, the reason for the diffusion of this non-volatile molecule of large size into the treated MD permeate is clearly of interest to scientists and engineers. This work is therefore dedicated to explore the behavior of HA through the membrane in AGMD and WGMD configurations with the view to understand its diffusion mechanisms. Studies have been carried out in order to analyze the pure permeate and evaluate the behavior of the HA for different membranes, operating temperatures and flow rates. Different conditions have been studied with synthetic water as well as real seawater from a local seawater source.

2. Materials and methods
2.1. Reagents and membranes

Synthetic water composition used in this study was set at 1 g L\(^{-1}\) sodium chloride (NaCl), EMSURE® (Merck, Germany), 8 mM (~0.88 g L\(^{-1}\)) calcium chloride ≥96% anhydrous (CaCl\(_2\)), Sigma-Aldrich), 100 mg L\(^{-1}\) humic acid sodium salt (H16752 Sigma-Aldrich) and deionized water, in order to simulate surface water with a typical OM model, according to Han et al (Han et al., 2017). In addition, real seawater was obtained from Port Phillip (Melbourne, Australia) to study NOM behavior in MD.

A hydrophobic, microporous membrane from Ningbo Changqi Porous Membrane Technology Co, Ltd. (Ningbo, China) was used in the MD tests. The membrane consisted of a thin polytetrafluoroethylene (PTFE) active layer (40 µm) on top of a polypropylene (PP) support layer, with a nominal pore size and total thickness of 0.5 µm and 106 µm, respectively. Although this PTFE membrane was used as a reference throughout the study, another three membranes were used in order to study the HA behavior with different materials and membrane characteristics.

In this way, a hydrophobic polyethylene (PE) membrane and omniphobic PE membrane without support layer from Aquastill were used, featuring both a nominal pore size of 0.2 µm and thickness of 63 µm and 67 µm, respectively. In addition, a hydrophilic polyurethane (PU) coated hydrophobic PTFE membrane from Australian Textile Mills (ATM) was used. PU layer has a pore size less than 2 nm and the PTFE layer, 0.35 µm with a total membrane thickness of 164 µm. Some additional membrane characteristics used in this study are reported elsewhere (Mostafa et al., 2017; Qin et al., 2018; Villalobos García et al., 2018).

2.2. Experimental MD setup

MD testing was conducted in a laboratory system in AGMD and WGMD modes using a similar setup reported elsewhere (Amaya-Vías et al., 2018; Francis et al., 2013; Khalifa, 2015). Briefly, MD system consisted of a co-current flat sheet acrylic membrane module with an effective membrane area of 0.018 m\(^2\), a feed tank, a cooling tank and two peristaltic pumps (Masterflex®)
L/S 77800-62, Cole-Parmer. One spacer (thickness = 0.8 mm, porosity = 0.87) was placed on feed side to enhance the turbulence of the feed stream. In addition, for both MD configurations a 3 mm gap made with a perforated plate was used to support the membrane and prevent the membrane from possible deformation or damage (Alkhudhiri et al., 2012b; Attia et al., 2017b, 2017a; Duong et al., 2016; Khalifa, 2015; Khalifa and Alawad, 2018; Pal and Manna, 2010; Xu et al., 2016). Both tanks were covered to minimize losses by evaporation and a mass balance was calculated for all experiments. A heater (Thermo Scientific Neslab RTE7) and a chiller (PolyScience®) maintained the temperatures configured in the feed and cooling tanks, respectively. The permeate was collected in a measuring cylinder and the permeate flow was measured by the volumetric method, as described by Dow et al. (Dow et al., 2016). A simplified schematic flowsheet is shown in Fig.1.

Electrical conductivity (EC) and pH of the water samples were determined using a portable multi meter (Hach HQ40D, Loveland, CO, USA).

Several parameters were calculated based on experimental measurements. The first is the permeate flow rate (L h⁻¹) used to determine total flux, $J$ (L h⁻¹ m⁻²) by Eq. (1):

$$J = \frac{V_{perm}}{A \cdot \Delta t}$$  \hspace{1cm} (1)

Where $V_{perm}$ is the permeate volume produced in the time interval (L), $A$ is the membrane area (m²) and $\Delta t$ is the time interval (h).

HA flux, $J_{HA}$ (mg_{HA} h⁻¹ m⁻²), with respect to total flux in both MD configurations was also calculated as in Eq. (2), where $[HA]$ is the HA concentration (mg_{HA} L⁻¹) in permeate collected over time interval $\Delta t$, using the TOC calibration equation to specify the [HA]. Limits of detection (LOD) were calculated as $3\sigma/m$ where $\sigma_b$ is the standard deviation of ten blank samples and $m$ the slope of the calibration curve. Additionally, limit of quantification (LOQ) was calculated as $10\sigma/m$ (Miller et al., 2002).
Finally, rejection factor (RF) for a variable was calculated by Eq. (3):

\[ J \]

(2)

Where \( C_{\text{feed}} \) and \( C_{\text{perm}} \) are values in the feed and permeate, respectively. This equation was used to calculate the EC rejection factor \( (RF_{EC}) \) and Non Purgeable Organic Carbon (NPOC) rejection factor \( (RF_{NPOC}) \) using experimentally obtained EC and NPOC values respectively.

For the experimental design, real seawater was tested with the purpose of checking the presence of NOM in MD permeate. It was decided to use seawater for two main reasons. Firstly, seawater desalination is one of the main applications in which MD can be potentially used. Secondly, taking into account that HS are the main component of the NOM in seawater (Naidu et al., 2015; Rodríguez et al., 2014), HA flux can be evaluated easily, assuming that all NOM in seawater samples was HA. Therefore, HA flux is estimated by the TOC-HA calibration curves used for synthetic water. Then to ensure tests with a consistent feed, the seawater was replaced with a synthetic saline water in order to study the influence of the both sides (feed and cooling) temperatures, operation flow rates and the different membranes described previously. The initial feed volume was 2.5 L and the operation time for each test was 4 h being sufficient time to show steady state performance. Permeate samples were taken every hour, while feed side was monitored taking a sample at the start and at the end of the test. New membranes were used for each operating condition.

Firstly, AGMD and WGMD tests were performed at different temperatures, flow rates and cross flow velocity (CFV) using four different MD membranes as indicated in Table 1.
Table 1. Operating conditions (temperatures, flow rates, CFV and MD membranes) studied in AGMD and WGMD tests.

| Temperature tests at 90 L h\(^{-1}\) (0.034 m s\(^{-1}\)) cross flow using PTFE membrane |
| Feed temperature (°C) / Cooling temperature (°C) |
| 50 / 18 | 60 / 18 | 70 / 18 | 70 / 35 |

| Flow rate tests at 70°C (feed) and 18°C (permeate) using PTFE membrane |
| Flow rate (L h\(^{-1}\)) / CFV (m s\(^{-1}\)) |
| 60 / 0.023 | 75 / 0.029 | 90 / 0.034 | 105 / 0.04 | 120 / 0.046 |

| Membrane tests at 70°C (feed), 18°C (permeate) and 90 L h\(^{-1}\) (0.034 m s\(^{-1}\)) cross flow |
| PTFE | PTFE-PU | PE-hydrophobic | PE-omniphobic |

Further experiments were conducted to better understand the behavior of HA in AGMD, by implementing a double gap width (total thickness of 6 mm) into the module. In this case, feed water was slightly changed using deionized water and 50 mg L\(^{-1}\) of HA to avoid saline interferences and a high HA concentration. This mode was compared to AGMD and WGMD keeping the same feed water and the experimental conditions.

Finally, Naidu et al. (Naidu et al., 2015) reported thermal degradation of HA where lower molecular sized HS and other organics were observed. Hence, tests using a rotary evaporator (Tokyo Rikakikai SB-650 N-N, Japan) were carried out, recreating MD tests with seawater and synthetic water in order to determine if HA presence in the permeate was because of the MD process or to a greater volatility of HA thermal degradation byproducts.
2.3. Analytical techniques

The concentration of HA in the feed and permeate was measured mainly by total organic carbon analyser (TOC-V CSH, Shimadzu, Kyoto, Japan), as suggest Meng et al (Meng et al., 2014). NPOC method was used for all organic carbon measurements. Complementary measurements
using a UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan) at the wavelength of 254 nm were used, according to Han and Myat et al (Han et al., 2017; Myat et al., 2012). Both instruments were calibrated, resulting in a linear relationship in the HA concentration range of 0-100 mg L\(^{-1}\), with a regression coefficient of 0.999 and 0.998, respectively. Furthermore, fluorescence excitation-emission spectra (EEM) were recorded on a fluorescence spectrophotometer (Horiba Scientific Aqualog, Kyoto, Japan). These spectra were compared with previous studies related to HA and OM (Rodríguez et al., 2014; Wang et al., 2009).

Contact angle with deionized water and with HA solution was examined for each membrane, using a Contact Angle Analyser (Kruss DSA25). An average of four measurements at different locations of the membrane were taken by the static sessile drop method and the average value is reported.

Finally, the various MD tests and sample measurements were carried out at least in triplicate, in order to demonstrate the confidence of the results obtained. In addition, all results were verified with calibration curves, as well as TOC and HA flow data were found above with LOD (0.30 mg L\(^{-1}\)) and LOQ (0.44 mg L\(^{-1}\)) in all cases.

3. Results and discussion

3.1. MD performance with real seawater and synthetic saline water with HA

Results for all experiments performed with both MD configurations and feed solutions are shown in Table 2. In all cases, the saline rejection factor, \(RF_{EC}\), (based on EC measurement) was above 99%. This shows that membrane wetting has likely not taken place and membranes were intact during the experiments. Meanwhile \(RF_{NPOC}\) showed lower values, reaching a minimum value of 33 ± 11 % and no higher than 93% in all cases. Seawater tended to show lower \(RF_{NPOC}\) values suggesting a different property of the organics. The carbon and representative HA flux are shown in Table 3. However the lower rejection of organics compared to EC shows that even for synthetic saline water, organic material is diffusing through the membrane. In the case of
synthetic water where the only organic material added was HA, it confirms that this diffusion is by HA molecules.

**Table 2.** Average permeate EC, NPOC, $RF_{EC}$ and $RF_{NPOC}$ for different MD configuration and feed water. Initial conditions for feed seawater: EC: 44057 ± 1858 µS cm$^{-1}$, NPOC: 2.6 ± 0.2 mg L$^{-1}$. Initial conditions for feed synthetic water: EC: 3340 ± 180 µS cm$^{-1}$, NPOC: 16.3 ± 1.8 mg L$^{-1}$. TOC LOD: 0.30 mg L$^{-1}$; TOC LOQ: 0.44 mg L$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>EC µS cm$^{-1}$</th>
<th>NPOC mg L$^{-1}$</th>
<th>$RF_{EC}$ %</th>
<th>$RF_{NPOC}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGMD Seawater</td>
<td>40 ± 21</td>
<td>1.7 ± 0.3</td>
<td>99.9 ± 0.1</td>
<td>33 ± 11</td>
</tr>
<tr>
<td>AGMD Synthetic water</td>
<td>14 ± 1</td>
<td>1.7 ± 0.7</td>
<td>99.6 ± 0.0</td>
<td>90 ± 4</td>
</tr>
<tr>
<td>WGMD Seawater</td>
<td>51 ± 20</td>
<td>0.8 ± 0.2</td>
<td>99.9 ± 0.0</td>
<td>68 ± 7</td>
</tr>
<tr>
<td>WGMD Synthetic water</td>
<td>3 ± 0</td>
<td>1.2 ± 0.3</td>
<td>99.9 ± 0.0</td>
<td>93 ± 2</td>
</tr>
</tbody>
</table>

**Table 3.** Carbon and representative HA flux for MD test using real seawater and average results (all operating conditions) for MD test using synthetic saline water with HA. Feed and cooling temperatures for seawater: 70°C and 18°C, respectively. Steady state fluxes for seawater tests: 3.3 ± 0.2 L h$^{-1}$ m$^{-2}$ for AGMD and 8.1 ± 1.0 L h$^{-1}$ m$^{-2}$ for WGMD.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Seawater Carbon Flux mgC h$^{-1}$ m$^{-2}$</th>
<th>Seawater HA Flux mgHA h$^{-1}$ m$^{-2}$</th>
<th>Synthetic water Carbon Flux mgC h$^{-1}$ m$^{-2}$</th>
<th>Synthetic water HA Flux mgHA h$^{-1}$ m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGMD</td>
<td>5.9 ± 1.4</td>
<td>21.5 ± 5.4</td>
<td>6.0 ± 2.5</td>
<td>21.6 ± 9.7</td>
</tr>
<tr>
<td>WGMD</td>
<td>6.4 ± 1.0</td>
<td>19.7 ± 4.4</td>
<td>8.2 ± 2.7</td>
<td>27.9 ± 10.3</td>
</tr>
</tbody>
</table>

3.2. Rotary evaporator tests with real seawater and synthetic saline water with HA

Results obtained in the rotary evaporator tests are shown in Table 4. The experiments were carried out under the same conditions as in MD for convenient comparison. EC was measured in some permeate samples, where EC values below 3 µS cm$^{-1}$ were obtained in all cases. The $RF_{EC}$ therefore reached where >99% and compared well with the MD tests shown in Table 2. However a major difference was to NPOC rejection, where the distillate concentrations were very similar to the blank (deionized water) in all cases showing that HA compounds and OM contained in both synthetic water and seawater are not volatile. In addition, it is verified that HS
thermal degradation byproducts do not pass into the vapor phase. In this sense, HA diffusion process through the membrane is inherent to the MD process. Therefore the next part of this work will be to explore the effect of typical MD operating conditions on the diffusion of HA.

Table 4. NPOC values for seawater and synthetic water using rotary evaporator.

<table>
<thead>
<tr>
<th>NPOC (mg L$^{-1}$)</th>
<th>Seawater</th>
<th>Synthetic water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Condensate Blank</td>
<td>Feed Condensate Blank</td>
<td></td>
</tr>
<tr>
<td>2.6 ± 0.2</td>
<td>0.4 ± 0.2</td>
<td>0.4 ± 0.2</td>
</tr>
</tbody>
</table>

3.3. Effect of MD operating conditions on HA diffusion

3.3.1. Effect of operating temperatures

Fig.2 shows the influence of different operating temperatures on the HA flux through the membrane. As it can be seen, HA flux was increased (from 15.6 to 37.1 mg h$^{-1}$ m$^{-2}$ for AGMD and 13.1 to 38.1 mg h$^{-1}$ m$^{-2}$ for WGMD) with higher feed temperatures in the same manner as the total flux (from 1.7 to 3.9 L h$^{-1}$ m$^{-2}$ for AGMD and 3.8 to 7.6 L h$^{-1}$ m$^{-2}$ for WGMD). Nevertheless, when the cooling temperature set to 35°C keeping feed temperature at 70°C, total flux decreased (3.1 L h$^{-1}$ m$^{-2}$ and 4.7 L h$^{-1}$ m$^{-2}$ for AGMD and WGMD, respectively) since there was a lower vapor pressure across the membrane. Likewise, HA flux decreased to 18.0 mg h$^{-1}$ m$^{-2}$ for AGMD and 16.0 mg h$^{-1}$ m$^{-2}$ for WGMD. Based on this result, it appears that HA flux generally follows total flux, supporting the concept that HA is entrained through the membrane with water following the model proposed by Meng et al (Meng et al., 2014). However it is not a direct correlation since there was little or no increase in HA flux from 50°C to 60°C, but a large increase occurred from 60°C to 70°C. Meanwhile water flux increase was proportionately similar at each temperature step (cases of 18°C permeate cycle temperatures). This is evidence that water and HA diffusion are not entirely connected which will be further explored later in this paper. Comparing the HA flux obtained for AGMD and WGMD, both MD configurations showed a similar behavior where it should be expected no non-volatile HA would be present at all in AGMD permeate. In this way, several types of condensation may occur in AGMD
systems as is suggested by Warsinger et al (Warsinger et al., 2018) and therefore, the presence of HA flux in AGMD suggests liquid contact between the membrane and condensing plate. Additionally, in Figure 2 a discrepancy of HA fluxes for AGMD and WGMD in the test at a temperature of 60°C is reported. This performance could be also attributed to liquid contact between membrane and condensing plate (water bridging) in AGMD. Thus, water bridging could be different as the flux is lower, but when more water flux occurs, the risk of bridging increases rapidly, potentially due to rapid coalescence of condensed water clusters. This is potentially a reason why it rose suddenly for AGMD when water flux is higher.

Looking more closely at the chemistry, pH is known to play an important role in the behavior and solubility of HA (Khayet et al., 2004). However no large differences in pH were observed in the experiments carried out using synthetic water. The pH on average for AGMD was 6.39 ± 0.26 while for WGMD was 6.66 ± 0.21. Feed pH was 6.81 ± 0.31. According to the results obtained, it can be assumed that HA behavior is not attributed to pH changes between feed and permeate. In terms of EC rejection, AGMD was slightly less effective than WGMD but both were >99%. The salinity may also play a role in the HA diffusion, where future work could consider the effect of total dissolved solids concentration, including effects of other trace minerals including calcium and iron.
Fig. 2. HA flux obtained for PTFE membrane and both MD configurations at different operating temperatures. Total flux is represented by lines graphed on the secondary axis. Feed and cooling cycle flow rate: 90 L h\(^{-1}\). Feed water: 1 g L\(^{-1}\) NaCl, 0.88 g L\(^{-1}\) CaCl\(_2\) and 100 mg L\(^{-1}\) HA. PTFE membrane with effective area of 0.018 m\(^2\). Due to low errors on some points, error bars cannot be seen.

3.3.2. Effect of cross flow rate

Figure 3 shows the total flux and HA flux from MD testing on synthetic saline water with HA at varied cross flows with fixed feed and permeate temperature conditions. AGMD total flux was mostly constant (3.9 L m\(^{-2}\) h\(^{-1}\)) for flow rates of 90, 105 and 120 L h\(^{-1}\) but slightly increase by 7.75\% over the entire range. WGMD showed large variations in total flux for flow rates of 60 and 75 L h\(^{-1}\) but was generally higher than AGMD with flux values between (7 L m\(^{-2}\) h\(^{-1}\) and 9 L m\(^{-2}\) h\(^{-1}\)). These total flux and HA flux variations in WGMD could be caused by the specific operational features. For example, in WGMD, permeate is collected by overflow of the water gap while AGMD is collected by gravity. Therefore, as a possible effect, WGMD permeate is affected by the feed flow pushing on the membrane surface and in turn, membrane movement generates a pulse effect in the gap. In this sense, flow rates greater than 75 L h\(^{-1}\) generated a constant total flux in all experiments. Nevertheless, for the studied flow rates of 60 L h\(^{-1}\) and 75 L h\(^{-1}\), the membrane pulse was lower, and consequently, total flux was more variable over time.

In any case, errors in WGMD did not show a discernible trend, and the total flux overall trend for both MD configurations indicated a low sensitivity of the total flux to CFV within the range studied. However, considering this more carefully, temperature must also be considered with varying cross flow as it is a key factor for MD process. In all cases, high EC rejections were obtained (99.9\% for WGMD and 99.6\% for AGMD) and pH values (6.5 and 6.4 for WGMD and AGMD, respectively) were similar and comparable to temperature tests. In the studied range, a change in flow rates keeping temperatures constant does not significantly affect the vapor pressure difference across the membrane and consequently, total fluxes are almost constant. This does not mean that in other flow rate conditions, the reduced polarization effects and a higher temperature profile uniformity, added to a thermal energy increase by higher CFV, would in turn substantially increase the total flux.
Looking at HA fluxes the behavior was independent to that of total flux and showed a unique effect. Therefore, it has been further shown that HA can diffuse independently of water, where effects of cross flow will impact its diffusion. The functional effect cross flow has on HA diffusion may be its effect on the fluid-membrane interface (i.e. boundary layer).

![Graph](image)

**Fig. 3.** HA flux obtained for PTFE membrane and both MD configurations at different flow rates and CFV. Total flux is represented by lines graph on a secondary axis. Feed and cooling temperatures: 70°C and 18°C, respectively. Feed water: 1 g L⁻¹ NaCl, 0.88 g L⁻¹ CaCl₂ and 100 mg L⁻¹ HA. PTFE membrane with effective area of 0.018 m². Due to low errors on some points, error bars cannot be seen.

In these tests, HA flux showed a clear trend. At lower CFVs, 2.28 and 2.86 cm s⁻¹, HA flux for AGMD showed low values. The explanation could be related to a higher mass transfer resistance of the AGMD, as will be discussed in section 3.4. However, it peaks considerably at the middle range CFV at 3.43 cm s⁻¹. Meanwhile, HA flux for WGMD showed a similar peak at this CFV but gave higher initial values at the lower CFVs tested. For higher CFVs to 3.43 cm s⁻¹, a clearly descending trend can be observed for HA flux in both MD configurations, reaching a minimum HA flux by WGMD at CFV of 4.57 cm s⁻¹. A mechanisms of HA diffusion related to the flow across the membrane surface has become evident, which will be discussed later. The next section will consider the membrane surface chemistry to further explore the effect of the liquid-membrane surface interactions on HA flux.
3.3.3. Effect of membrane chemistry

Fig. 4 shows the results for tests on the standard hydrophobic PTFE membrane compared to other membrane types to explore the influence of different materials on the HA flux in permeate. PU-PTFE (hydrophilic PU coated hydrophobic PTFE), hydrophobic PE and omniphobic PE showed similar results to the standard PTFE membranes in terms of total flux. EC rejection (99.6% AGMD and 99.9% for WGMD) and pH of AGMD and WGMD permeates (6.4 and 6.5, respectively) were similar in all cases and behavior similar to both temperature and flow rate cases. However, differences were observed between the membrane chemistries for HA flux. HA flux through the PTFE membrane is highest in both AGMD and WGMD, and similar to PU-PTFE within error. Meanwhile, PE hydrophobic was only similar in HA flux for WGMD mode, while AGMD mode showed HA flux was about 50% of any of these higher values. This small value was similar for PE omniphobic, uniquely in both AGMD and WGMD.

![Figure 4](image-url)  
**Fig. 4.** HA flux obtained for different membranes and both MD configurations. Total flux is represented by lines graph on a secondary axis. Feed and cooling temperatures: 70°C and 18°C, respectively. Feed and cooling cycle flow rate: 90 L h⁻¹. Feed water: 1 g L⁻¹ NaCl, 0.88 g L⁻¹ CaCl₂ and 100 mg L⁻¹ HA. Each membrane has an effective area of 0.018 m². Due to low errors on some points, error bars cannot be seen.

In relation with other membranes tested, omniphobic PE membrane with about 50% of the HA flux through PTFE in both AGMD and WGMD while at the same time as maintaining a similar
level of total flux. Clearly membrane chemistry is influencing the HA flux, where a hydrophobic chemistry favours HA diffusion in the liquid-liquid feed-permeate contact WGMD mode. This is also true for PU-PTFE where despite the hydrophilic PU coating facing the feed solution, HA still diffused into the permeate through the underlying hydrophobic PTFE layer. The omniphobic membrane possessed also the ability to repel hydrophobic interactions indicating the HA diffusion through MD membranes is due to hydrophobic interactions between the membrane and the HA molecule. The outstanding result was for the hydrophobic PE membrane which gave HA fluxes for WGMD similar to the PTFE membranes, but gave lower HA flux in AGMD similar to the omniphobic PE membrane. This result cannot be fully explained based on the present data, and may be due to differences in the hydrophobicity of the PE material compared to PTFE that yielded differences between the MD modes where AGMD may have had less water bridging and in turn reduced HA flux.

Contact angle (CA) was measured on virgin membranes using synthetic water (1 g L\(^{-1}\) NaCl, 0.88 g L\(^{-1}\) CaCl\(_2\) and 100 mg L\(^{-1}\) HA) and deionized water measurement in order to confirm the hydrophobicity of the membrane surfaces. A MD membrane with a water contact angle above 90º is considered hydrophobic (García-Fernández et al., 2015). In this way, according to water CA measured, PTFE (97º) and both PE membranes (106º for hydrophobic and 122º for omniphobic) exhibited hydrophobic surfaces, while hydrophilic PU-PTFE membrane showed a water CA around 69º showing a hydrophilic surface, due to the PU coating on the underlying hydrophobic PTFE that blocks liquid water. Furthermore, CA measurements using synthetic water supported the same theory explained previously using deionized water. In this way, synthetic water CA measured for each membrane was 88º for PTFE, 72º for PTFE-PU, 114º for PE hydrophobic and 127º for PE omniphobic. Although HA interaction with the membrane surface cannot be completely explained only by the CA analysis, a trend is observed among the CA and the HA flux using synthetic water, even for the PTFE-PU membrane, which is a composite membrane where only its surface facing the liquid is hydrophilic.
In this sense, it is important to highlight the CA analysis to omniphobic PE membrane, which presents the lowest values of HA flux and, in turn, the highest CA values (122° and 127° for deionized water and synthetic water, respectively). These results suggest that modified membranes could play an important role in OM rejection and other elements with the same features. Meanwhile, the unusual result for the hydrophobic PE membrane in Figure 4 observed earlier may be explained by the relatively higher CA. When the gap is filled with water in the case of WGMD, HA may freely diffuse from the membrane surface into the permeate liquid. On the other hand, for AGMD the more hydrophobic surface could have assisted in repelling the bridging of liquid water from the permeate membrane surface across the gap to the condensing plate sufficiently more than both PTFE membranes. The more intact air gap therefore acted as a barrier to HA flux being more like the rotary evaporator test where HA could not be entrained into the distillate through the vapour phase. Furthermore, the study of other membrane properties such as thickness, porosity and tortuosity would play a role, so a detailed analysis of such properties on these membranes is needed to extend our current study to explore means to understand and control HA diffusion through MD membranes.

In conclusion, even though there are no large changes in the total flux, a clear decrease in the HA flux was obtained for omniphobic PE membrane and for the high CA hydrophobic membrane in AGMD mode. Therefore, according with works from other authors (Damtie et al., 2018; Duong et al., 2018; Wang et al., 2018; Woo et al., 2016; Zheng et al., 2018) and the results obtained in this study, we conclude that MD membranes play an important role in the quality of the permeated water.

3.4. HA diffusion models

According to results obtained for MD tests using synthetic water, HA diffusion models can now be proposed based on the key operating conditions of temperature and flow rate. Experimental data suggest that the HA diffusion as a function of temperature can be explained by Fick's Law. Thus, the diffusivity of HA within the membrane and the HA driving force
across the membrane surfaces are the main phenomena that could affect the flux. Hence, it is observed that the increase in feed temperature increased the HA flux and therefore, the temperature influences the HA diffusivity. However, the increase in permeate temperature showed a considerable decrease in HA flux, so it seems to be strongly related to the HA driving force based on the surface concentrations of HA. Taking the latter into account as well as the results obtained for flux and membranes tests, it is suggested that the increase in feed temperature raised the concentration of HA on the membrane surface by increasing its access from the bulk to the surface, potentially from increased diffusion through the boundary layer. So, when permeate temperature increased, total flux decreased and the concentration polarization of HA from water flux on the feed declined. Figure 5 shows the proposed model for the HA diffusion because of temperature.

In addition, another phenomenon could affect in a complementary way to overall HA flux, by which, the adsorption of HA on the surface of the membrane decreases with the increase in temperature, while the diffusivity of HA increases.

In this sense, the discrepancy obtained for the HA flux in AGMD at 60°C (Figure 2) could be explained both to the effect of the water bridges, to the diffusion models, discussed above, and to small structural changes of the HA with temperature. In the latter case, some authors (Giovanela et al., 2010, 2004; Kolokassidou et al., 2007) reported that there are small changes in the structure of HA resulting in a loss of mass in the temperature range of 40°C to 80°C. These changes are related to the reversible and irreversible losses of different types of water molecules contained in the HA. Thus, reversible structural changes occur at around 60°C, while irreversible changes become important at 70°C (formation of more condensed and hydrophobic polyaromatic structures) (Giovanela et al., 2010, 2004; Kolokassidou et al., 2007). Based on these studies, in MD tests at temperatures of 60°C, it is suggested that HA molecules loaded with water coexist with HA molecules with more condensed reversible structures. Therefore, while for WGMD both types of molecules could be diffused without high resistance to permeate, the heavier HA molecules would have lower diffusion because of the higher mass
transfer resistance of AGMD due to the air gap (Alkhudhiri et al., 2012a). In addition, the effect of less water bridges in AGMD at lower fluxes (section 3.3.1) could be considerable. For these reasons, the HA flux in the AGMD is lower than the WGMD under these experimental conditions. However, there is not enough evidence to conclude if the sudden rise in HA flux at 70°C is due to altered HA chemistry or an accelerated water bridging effect.

Fig. 5. HA diffusion in AGMD and WGMD because of temperature. Low temperatures imply a low particle speed and therefore, less diffusivity through the boundary layer (a). Higher temperatures assisted HA flux by improving diffusion of accumulated HA at the membrane surface (b). Permeate side temperature increase implies a HA concentration polarization decrease (c).

HA flux trend for flow rates tests can be explained by three different process as is illustrated in Fig.6. Firstly, at lower flow rate and cross flow velocity (2.28 cm s\(^{-1}\)), concentration polarization and boundary layer phenomena are significant leading to high HA concentration at the surface under relatively quiescent conditions. In this way, most of molecules and colloids of HA were deposited on the membrane surface, inhibiting HA diffusion through the membrane. For AGMD, at lower CFV (2.28 and 2.86 cm s\(^{-1}\)), lower HA flux compared to WGMD was obtained, as it was shown in Figure 3. These results suggested a CFV influence by concentration polarization and boundary layer phenomena. Thus, at low CFV, the residence time of HA on the membrane surface is longer. Therefore, with low velocity, higher concentration polarization, as well as a higher AGMD resistance to mass transfer, this resulted in a lower HA diffusion in this
MD configuration. Nevertheless, in WGMD, as a result of lower mass resistance, the HA diffuses more easily to permeate under the same experimental conditions.

As the flow and CFV increased, the feed water mixture was increasingly homogeneous. For this reason, the concentration polarization and associated boundary layer and HA fouling layer phenomena were weakened, and HA diffusion to permeate reached a maximum at 90 L h$^{-1}$. From this point, although the mixture is homogeneous at higher flow rates, HA flux dropped noticeably at CFV of 4.00 and 4.57 cm s$^{-1}$. The latter process suggests the influence of shear forces, which complicate HA transport to the membrane surface. It appears some accumulation within the boundary layer is needed for HA flux to occur. With too much mixing and the surface condition approaching the bulk solution, HA flux becomes reduced.

![Fig. 6. Influence of the flow rates in HA diffusion for AGMD and WGMD. Predominance of boundary layer phenomena and concentration by polarization (a). Complete mixture of feed cycle, reaching the maximum diffusion (b). Shear forces play an important role at higher flow rates (c).](image)

To date, only a few studies have detected HA in permeate and their migration through the membrane in DCMD. According to Meng et al (Meng et al., 2014), the process involves HA adsorption-desorption onto the membrane surface, because of amphiphilic nature of HA. Thus, HA migrates through the membrane pores by hydrogen bonding between water vapor and humic molecules. This process suggests a dependence between migration mechanism and vapor pressure and therefore, with the total flux for DCMD.
According to the results obtained for all tests carried out in this work and diffusion models suggested, HA behavior based on diffusion is proposed for AGMD and WGMD. The diffusion mechanism is independent of total flux and consequently, vapor pressure as well. AGMD and WGMD have been used with the purpose of analyzing an isolated permeate, avoiding the dilution effect in DCMD and therefore, not underestimating the amount of HA or NOM present in permeate.

3.5. Complementary studies

3.5.1. Double gap width for AGMD

Following our finding earlier where HA flux occurred in AGMD as well as WGMD, water bridges have been proposed by which HA could diffuse into permeate. These water bridges can play an important role in this phenomenon, because of an additional sweeping effect of the membrane cold side (Warsinger et al., 2018).

In relation to this suggestion, an additional frame was installed in order to double the gap size to 6 mm. Thus, a significant decrease in both total and HA fluxes could be expected. In this regard, as it can be seen in Fig. 7, while the total flux dropped noticeably, the HA flux detected was greater (around 36%) than that obtained for 3 mm gap. Although a wider gap implied less water bridging as well as total flux drop, slightly increased HA flux was obtained. These results suggest that HA flux is not relying on total flux, and HA diffuses through the membrane in any case. In addition, HA flux increase may be due to new conditions for wider gap as for example, a favorable change in the temperature profile for HA diffusion. For example, at lower fluxes, temperature polarization will be lower leading to larger temperature differences over the membrane. As concluded earlier, the higher temperature on the feed side assisted HA flux by improving its ability to diffuse through boundary layers containing accumulated HA at the membrane surface which could also be eliminated by increasing cross flow (but only up to a certain point).
Fig. 7. HA flux obtained for different gap tests. Total flux is represented by the lines with the values indicated on the secondary axis. Feed and cooling temperatures: 70°C and 18°C, respectively. Feed and cooling cycle flow rate: 90 L h⁻¹. Feed water: Deionized water and 50 mg L⁻¹ HA to avoid influence of salts and high HA concentrations. PTFE membrane with an effective area of 0.018 m². Due to low errors on some points, error bars cannot be seen.

3.5.2. HA preliminary characterization

Using appropriate calibration curves for UV spectrometer and TOC analyzer, a good correlation was achieved for the synthetic water. This means that the absorbance could be known from the NPOC value and, therefore, the concentration of HA in the sample, indistinctly. Errors using the correlation between both techniques were less than 10%, with an average value of 7%. It is important to underline that different high and low range HA calibration curves were applied in order to cover the entire range of concentrations.

On the contrary, when these correlation equations were applied for UV spectrophotometer and TOC analyzer in permeate samples, errors obtained were above 87%. In addition, the absorbance values obtained in the permeate samples did not correspond to the absorbance that would have a feed water with the same concentration of HA measured with TOC analyzer. For
these reasons, a profile change in the HA molecule is suggested, since it seems that the HS found in permeate absorb UV differently and therefore, they have different properties to the original HS contained in the feed water.

The composition differences of HA in feed and permeate was also analyzed using fluorescence spectrophotometry. Nevertheless, Excitation – Emission Matrix (EEM) fluorescence spectra can be altered by pH and salt concentrations in the sample. In order to study the possible saline interferences and differences between feed and permeate EEM spectra (Fig. 8), fluorescence measurements were made using different concentrations of HA in deionized water without salts, as well as synthetic water (MD feed water) at different concentrations of HA. In all these measurements, EEM spectra similar to each other were obtained. In Fig. 8a an EEM spectrum of HA in deionized water (without added salts) is shown.

In Fig. 8b, an EEM fluorescence spectrum obtained from a synthetic water feed sample is shown. This spectrum presents typical values for a standard HA, showing two Ex/Em peaks around 250-350/450 nm (Rodríguez et al., 2014). High similarities between the EEM spectra of synthetic water feed and HA with deionized water are observed. Both EEM spectra showed the same profile as well as the peaks related to HA. Additionally, EEM spectra for AGMD and WGMD permeate samples are shown in Fig. 8c and 8d, respectively. The spectra obtained for the permeate samples in both MD configurations are very similar to each other, showing a maximum Ex/Em peak around 250/350-400 nm. Although these permeate EEM spectra showed fluorescence characteristics corresponding to humic acid-like substances (Wang et al., 2009), clear differences in relation to the feed EEM spectrum and also, with HA in deionized water EEM spectrum were observed. These results suggest and confirm a change in the HA profile diffused through the membrane, as was previously proposed with the UV spectrometer measurements.
Fig. 8. a. EEM spectrum for HA in deionized water; b. EEM spectrum for synthetic feed water sample; c. EEM spectrum for AGMD permeate sample; d. EEM spectrum for WGMD permeate sample.

4. Conclusions

Tests with different operating temperatures, flow rates and MD membranes were performed in order to study HA behavior, using AGMD and WGMD configurations. Non-volatile compounds have been detected in permeate, and humic flux through the membrane was affected by feed and cooling temperatures, boundary layers phenomenon, polarization concentration and shear forces. In addition, omniphobic PE membrane showed better HA rejection than the other membranes tested. In this way, MD membrane could play an important role in MD, which suggests that MD membrane is not only a passive element in the process. The same HA or
NOM behavior was obtained using both seawater and synthetic water. Therefore, a HA and NOM diffusion mechanism is proposed for AGMD and WGMD configurations.

On the other hand, a sweeping effect on the membrane cold side was detected in AGMD because of the frame, which separates the membrane and the cooling plate, acts as an intermediate condenser. Humic flux in AGMD could be similar as in WGMD because of this sweeping effect of the membrane.

Finally, a preliminary characterization of HA in MD permeate was carried out. HA differences in permeate and feed were detected. In this way, it is necessary to go in depth with HA characterization of MD permeate in order to analyze the OM complexation capacity and the transport of undesired compounds through the membrane.

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Membrane Distillation Trial on Textile Wastewater Containing Surfactants Using
Hydrophobic and Hydrophilic-Coated Polytetrafluoroethylene (PTFE) Membranes.


Diffusion behavior of humic acid during desalination with air gap and water gap membrane distillation

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Abstract

Desalination and water reuse are important means to resolve local water scarcity and security issues worldwide where membrane distillation (MD) may be part of a solution. Natural organic matter and in particular, humic acids (HA), are widely present in water supplies to be treated but exhibit little understood behavior to diffuse through MD membranes into permeate. In this work, air gap (AGMD) and water gap (WGMD) were utilized to study HA behavior in MD using seawater and synthetic water over a range of typical MD temperatures, flow rates and membrane types. HA diffusion was first shown with seawater feed then on synthetic solutions at all process conditions. While electrical conductivity rejection was always above than 99%, HA rejection showed values of 33% and 90% for AGMD and 68% and 93% for WGMD with seawater and synthetic water, respectively. Analytical techniques were used to perform a preliminary organic matter characterization in permeate, obtaining clear differences between the feed and permeate HA property. Compared to hydrophobic membranes, uniquely oleophobic membranes inhibit HA diffusion suggesting hydrophobic surface diffusion of HA through the membrane. HA flux as well as potential undesirable effects of the organic matter in permeate should be considered for MD applications.
Keywords: humic acid, air gap membrane distillation, water gap membrane distillation, organic matter, diffusion, seawater.

1. Introduction

Water shortages and the loss in water quality are one of the main common global problems humanity faces (Anand et al., 2018; Voulvoulis, 2018). In addition, many anthropogenic compounds that cannot be treated with conventional wastewater treatments can be found in natural waters, posing a significant risk to the environment and to human health (Biel-Maeso et al., 2018; Han et al., 2017; Herce-Sesa et al., 2018; Wagner et al., 2016).

Of particular interest in water quality are natural organic matter (NOM) compounds which is present in natural water systems. NOM compounds are derived from the degradation of plants, animals, and microorganisms by chemical, biological and photochemical reactions. Among the compounds making up NOM, humic substances (HS) are important since they are the major carbon pool in the biosphere. Of the NOM presents in natural waters, up to 50% consist of HS and they are the main organic compounds in seawater (Lipczynska-Kochany, 2018; Naidu et al., 2015; Rodríguez et al., 2014).

HS are complex and heterogeneous mixtures of a wide range of molecular weight species. The two main categories of HS are fulvic acids (FA) and humic acids (HA), and can be distinguished in function of their solubility at pH 1 where the latter often form colloids because of their large size (Rodríguez et al., 2014; Wagner et al., 2016). Although HS do not cause any known adverse effects for human health, they are undesirable substances in water treatment and they can play a fundamental role as indicators of water quality. HS contributes to odor, color, taste and acidity problems in water supplies. Furthermore, HS, and especially HA, lead to a greater spending on disinfection when chlorination is used as they are precursors of toxic disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Liu et al., 2008; Roccaro et al., 2009). Finally, HS have been identified as one of the major compounds responsible for fouling in membrane processes as well as the complexes formation...
with a multitude of metal ions and organic pollutants promoting the formation of biofilm in water pipes (Bond et al., 2012; Chowdhury et al., 2016; Jermann et al., 2007; Liu et al., 2008; Roccaro et al., 2009). Therefore, HA and its behavior through a new proposed water treatment technology is important to be investigated.

Water desalination and reuse technologies have great potential to address the problems associated with water shortages and water quality by use of non-conventional water sources. These desalination technologies are mainly based on membrane and/or thermal processes, or a combination of both in a process train while reuse technologies are mainly based on membrane processes. Some of these technologies are reverse osmosis (RO), electrodialysis, nanofiltration (NF), multiple-effect distillation (MED) and multi-stage flash distillation (MSF). An alternative process combining membranes with thermal desalination is membrane distillation (MD) (Criscuoli and Carnevale, 2015; Ghaffour et al., 2013; Kim and Hong, 2018; Prisciandaro et al., 2016; Ziolkowska and Reyes, 2016). MD is a thermally driven separation using a membrane as a barrier for saline liquid water, while being permeable to fresh water vapor. In this way, the vapor pressure between both sides of this membrane, being microporous and hydrophobic in order to fulfill the liquid barrier and vapor permeable requirement, is the driving force in this separation process.

The advantages of MD proposed include the use of small and compact equipment and very low working pressures which could lead to lower material costs and greater process safety compared to other conventional technologies (Alkhudhiri et al., 2012a; Essalhi and Khayet, 2015; Khalifa, 2015). Additionally, MD can use low-grade and waste heat as well as alternative energy sources, increasing energy efficiency. In terms of membrane performance, the fouling of the membranes can be lower than in other membrane processes while a very high water quality is produced because of the 100% theoretical rejection of non-volatile components (Alkhudhiri and Hilal, 2017; Guillen-Burrieza et al., 2014). Among MD configurations, commonly investigated modes include direct contact MD (DCMD), air gap MD (AGMD) and water gap MD (WGMD). In DCMD, feed and cooling water are in contact with the membrane surfaces. In this way, the
transmembrane flow (membrane flux) is high but there are also high heat losses by conduction. As a result of this setup, obtaining an isolated distillate is not possible, since it is mixed with the cooling water. This is avoided with the AGMD setup as the distillate can be obtained separately from the cooling water, however the drawback is membrane flux is lower than in DCMD.

Another configuration, WGMD, emerged as an improvement over these limitations of DCMD and AGMD. In WGMD, the gap is filled with distilled water. This configuration offers an improvement in the permeate flow in comparison with AGMD and it allows a separate distillate to be obtained, unlike DCMD (Francis et al., 2013; González et al., 2017).

These MD advantages make it a promising alternative to conventional desalination and water reuse technologies for many environmental and industrial applications (Amaya-Vías et al., 2018; Cui et al., 2018; Silva et al., 2018). Nevertheless, MD is not fully commercialized and implemented by industry (Khayet, 2011; Qtaishat et al., 2009), since many aspects have still not been studied in detail; for example, the effect of organic matter (OM) and HA in the MD process. Many authors have focused their studies on the MD fouling and the HA influence in the rejection of different substances. However, the permeation of HA through the membrane into the permeate has so far only been observed as a side result in these DCMD fouling studies (Han et al., 2017; Khayet et al., 2004; Meng et al., 2014; Naidu et al., 2015, 2014; Wijekoon et al., 2014).

In view of their importance and consequences of HA presence in treated water supplies, the reason for the diffusion of this non-volatile molecule of large size into the treated MD permeate is clearly of interest to scientists and engineers. This work is therefore dedicated to explore the behavior of HA through the membrane in AGMD and WGMD configurations with the view to understand its diffusion mechanisms. Studies have been carried out in order to analyze the pure permeate and evaluate the behavior of the HA for different membranes, operating temperatures and flow rates. Different conditions have been studied with synthetic water as well as real seawater from a local seawater source.

2. Materials and methods
2.1. Reagents and membranes

Synthetic water composition used in this study was set at 1 g L\(^{-1}\) sodium chloride (NaCl) EMSURE® (Merck, Germany), 8 mM (~0.88 g L\(^{-1}\)) calcium chloride ≥96% anhydrous (CaCl\(_2\), Sigma-Aldrich), 100 mg L\(^{-1}\) humic acid sodium salt (H16752 Sigma-Aldrich) and deionized water, in order to simulate surface water with a typical OM model, according to Han et al (Han et al., 2017). In addition, real seawater was obtained from Port Phillip (Melbourne, Australia) to study NOM behavior in MD.

A hydrophobic, microporous membrane from Ningbo Changqi Porous Membrane Technology Co., Ltd. (Ningbo, China) was used in the MD tests. The membrane consisted of a thin polytetrafluoroethylene (PTFE) active layer (40 µm) on top of a polypropylene (PP) support layer, with a nominal pore size and total thickness of 0.5 µm and 106 µm, respectively. Although this PTFE membrane was used as a reference throughout the study, another three membranes were used in order to study the HA behavior with different materials and membrane characteristics.

In this way, a hydrophobic polyethylene (PE) membrane and omniphobic PE membrane without support layer from Aquastill were used, featuring both a nominal pore size of 0.2 µm and thickness of 63 µm and 67 µm, respectively. In addition, a hydrophilic polyurethane (PU) coated hydrophobic PTFE membrane from Australian Textile Mills (ATM) was used. PU layer has a pore size less than 2 nm and the PTFE layer, 0.35 µm with a total membrane thickness of 164 µm. Some additional membrane characteristics used in this study are reported elsewhere (Mostafa et al., 2017; Qin et al., 2018; Villalobos García et al., 2018).

2.2. Experimental MD setup

MD testing was conducted in a laboratory system in AGMD and WGMD modes using a similar setup reported elsewhere (Amaya-Vías et al., 2018; Francis et al., 2013; Khalifa, 2015). Briefly, MD system consisted of a co-current flat sheet acrylic membrane module with an effective membrane area of 0.018 m\(^2\), a feed tank, a cooling tank and two peristaltic pumps (Masterflex®
L/S 77800-62, Cole-Parmer). One spacer (thickness = 0.8 mm, porosity = 0.87) was placed on feed side to enhance the turbulence of the feed stream. In addition, for both MD configurations a 3 mm gap made with a perforated plate was used to support the membrane and prevent the membrane from possible deformation or damage (Alkhudhiri et al., 2012b; Attia et al., 2017b, 2017a; Duong et al., 2016; Khalifa, 2015; Khalifa and Alawad, 2018; Pal and Manna, 2010; Xu et al., 2016). Both tanks were covered to minimize losses by evaporation and a mass balance was calculated for all experiments. A heater (Thermo Scientific Neslab RTE7) and a chiller (PolyScience®) maintained the temperatures configured in the feed and cooling tanks, respectively. The permeate was collected in a measuring cylinder and the permeate flow was measured by the volumetric method, as described by Dow et al. (Dow et al., 2016). A simplified schematic flowsheet is shown in Fig.1.

Several parameters were calculated based on experimental measurements. The first is the permeate flow rate (L h$^{-1}$) used to determine total flux, $J$ (L h$^{-1}$ m$^{-2}$) by Eq. (1):

$$J = \frac{V_{perm}}{A \cdot \Delta t}$$

Where $V_{perm}$ is the permeate volume produced in the time interval (L), $A$ is the membrane area (m$^2$) and $\Delta t$ is the time interval (h).

HA flux, $J_{HA}$ (mg$_{HA}$ h$^{-1}$ m$^{-2}$), with respect to total flux in both MD configurations was also calculated as in Eq. (2), where $[HA]$ is the HA concentration (mg$_{HA}$ L$^{-1}$) in permeate collected over time interval $\Delta t$, using the TOC calibration equation to specify the $[HA]$. Limits of detection (LOD) were calculated as $3\sigma_b/m$ where $\sigma_b$ is the standard deviation of ten blank samples and $m$ the slope of the calibration curve. Additionally, limit of quantification (LOQ) was calculated as $10\sigma_b/m$ (Miller et al., 2002).
Finally, rejection factor (RF) for a variable was calculated by Eq. (3):

\[ J_{HA} = [HA] \cdot J \]  

(2)

\[ RF(\%) = \left( \frac{C_{\text{feed}} - C_{\text{perm}}}{C_{\text{feed}}} \right) \cdot 100 \]  

(3)

Where \( C_{\text{feed}} \) and \( C_{\text{perm}} \) are values in the feed and permeate, respectively. This equation was used to calculate the EC rejection factor \( RF_{EC} \) and Non Purgeable Organic Carbon (NPOC) rejection factor \( RF_{NPOC} \) using experimentally obtained EC and NPOC values respectively.

For the experimental design, real seawater was tested with the purpose of checking the presence of NOM in MD permeate. It was decided to use seawater for two main reasons. Firstly, seawater desalination is one of the main applications in which MD can be potentially used. Secondly, taking into account that HS are the main component of the NOM in seawater (Naidu et al., 2015; Rodríguez et al., 2014), HA flux can be evaluated easily, assuming that all NOM in seawater samples was HA. Therefore, HA flux is estimated by the TOC-HA calibration curves used for synthetic water. Then to ensure tests with a consistent feed, the seawater was replaced with a synthetic saline water in order to study the influence of the both sides (feed and cooling) temperatures, operation flow rates and the different membranes described previously. The initial feed volume was 2.5 L and the operation time for each test was 4 h being sufficient time to show steady state performance. Permeate samples were taken every hour, while feed side was monitored taking a sample at the start and at the end of the test. New membranes were used for each operating condition.

Firstly, AGMD and WGMD tests were performed at different temperatures, flow rates and cross flow velocity (CFV) using four different MD membranes as indicated in Table 1.
Table 1. Operating conditions (temperatures, flow rates, CFV and MD membranes) studied in AGMD and WGMD tests.

<table>
<thead>
<tr>
<th>Feed temperature (°C) / Cooling temperature (°C)</th>
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<tbody>
<tr>
<td>50 / 18</td>
</tr>
<tr>
<td>60 / 18</td>
</tr>
<tr>
<td>70 / 18</td>
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<tr>
<td>70 / 35</td>
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</tbody>
</table>

Flow rate tests at 70°C (feed) and 18°C (permeate) using PTFE membrane

<table>
<thead>
<tr>
<th>Flow rate (L h^{-1}) / CFV (m s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>60 / 0.023</td>
</tr>
<tr>
<td>75 / 0.029</td>
</tr>
<tr>
<td>90 / 0.034</td>
</tr>
<tr>
<td>105 / 0.04</td>
</tr>
<tr>
<td>120 / 0.046</td>
</tr>
</tbody>
</table>

Membrane tests at 70°C (feed), 18°C (permeate) and 90 L h^{-1} (0.034 m s^{-1}) cross flow

<table>
<thead>
<tr>
<th>PTFE</th>
<th>PTFE-PU</th>
<th>PE-hydrophobic</th>
<th>PE-omniphobic</th>
</tr>
</thead>
</table>

Further experiments were conducted to better understand the behavior of HA in AGMD, by implementing a double gap width (total thickness of 6 mm) into the module. In this case, feed water was slightly changed using deionized water and 50 mg L^{-1} of HA to avoid saline interferences and a high HA concentration. This mode was compared to AGMD and WGMD keeping the same feed water and the experimental conditions.

Finally, Naidu et al (Naidu et al., 2015) reported thermal degradation of HA where lower molecular sized HS and other organics were observed. Hence, tests using a rotary evaporator (Tokyo Rikakikai SB-650 N-N, Japan) were carried out, recreating MD tests with seawater and synthetic water in order to determine if HA presence in the permeate was because of the MD process or to a greater volatility of HA thermal degradation byproducts.
Fig. 1. Schematic co-current AGMD/WGMD setup used in this work and MD module details.

2.3. Analytical techniques

The concentration of HA in the feed and permeate was measured mainly by total organic carbon analyser (TOC-V CSH, Shimadzu, Kyoto, Japan), as suggest Meng et al (Meng et al., 2014). NPOC method was used for all organic carbon measurements. Complementary measurements
using a UV spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan) at the wavelength of 254 nm were used, according to Han and Myat et al (Han et al., 2017; Myat et al., 2012). Both instruments were calibrated, resulting in a linear relationship in the HA concentration range of 0-100 mg L\(^{-1}\), with a regression coefficient of 0.999 and 0.998, respectively. Furthermore, fluorescence excitation-emission spectra (EEM) were recorded on a fluorescence spectrophotometer (Horiba Scientific Aqualog, Kyoto, Japan). These spectra were compared with previous studies related to HA and OM (Rodríguez et al., 2014; Wang et al., 2009).

Contact angle with deionized water and with HA solution was examined for each membrane, using a Contact Angle Analyser (Kruss DSA25). An average of four measurements at different locations of the membrane were taken by the static sessile drop method and the average value is reported.

Finally, the various MD tests and sample measurements were carried out at least in triplicate, in order to demonstrate the confidence of the results obtained. In addition, all results were verified with calibration curves, as well as TOC and HA flow data were found above with LOD (0.30 mg L\(^{-1}\)) and LOQ (0.44 mg L\(^{-1}\)) in all cases.

3. Results and discussion

3.1. MD performance with real seawater and synthetic saline water with HA

Results for all experiments performed with both MD configurations and feed solutions are shown in Table 2. In all cases, the saline rejection factor, \(RF_{EC}\), (based on EC measurement) was above 99%. This shows that membrane wetting has likely not taken place and membranes were intact during the experiments. Meanwhile \(RF_{NPOC}\) showed lower values, reaching a minimum value of 33 ± 11 % and no higher than 93% in all cases. Seawater tended to show lower \(RF_{NPOC}\) values suggesting a different property of the organics. The carbon and representative HA flux are shown in Table 3. However the lower rejection of organics compared to EC shows that even for synthetic saline water, organic material is diffusing through the membrane. In the case of
synthetic water where the only organic material added was HA, it confirms that this diffusion is by HA molecules.

Table 2. Average permeate EC, NPOC, $RF_{EC}$ and $RF_{NPOC}$ for different MD configuration and feed water. Initial conditions for feed seawater: EC: 44057 ± 1858 $\mu$S cm$^{-1}$, NPOC: 2.6 ± 0.2 mg L$^{-1}$. Initial conditions for feed synthetic water: EC: 3340 ± 180 $\mu$S cm$^{-1}$, NPOC: 16.3 ± 1.8 mg L$^{-1}$. TOC LOD: 0.30 mg L$^{-1}$; TOC LOQ: 0.44 mg L$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>EC</th>
<th>NPOC</th>
<th>$RF_{EC}$</th>
<th>$RF_{NPOC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu$S cm$^{-1}$</td>
<td>mg L$^{-1}$</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>AGMD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seawater</td>
<td>40 ± 21</td>
<td>1.7 ± 0.3</td>
<td>99.9 ± 0.1</td>
<td>33 ± 11</td>
</tr>
<tr>
<td>Synthetic water</td>
<td>14 ± 1</td>
<td>1.7 ± 0.7</td>
<td>99.6 ± 0.0</td>
<td>90 ± 4</td>
</tr>
<tr>
<td>WGMD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Seawater</td>
<td>51 ± 20</td>
<td>0.8 ± 0.2</td>
<td>99.9 ± 0.0</td>
<td>68 ± 7</td>
</tr>
<tr>
<td>Synthetic water</td>
<td>3 ± 0</td>
<td>1.2 ± 0.3</td>
<td>99.9 ± 0.0</td>
<td>93 ± 2</td>
</tr>
</tbody>
</table>

Table 3. Carbon and representative HA flux for MD test using real seawater and average results (all operating conditions) for MD test using synthetic saline water with HA. Feed and cooling temperatures for seawater: 70°C and 18°C, respectively. Steady state fluxes for seawater tests: 3.3 ± 0.2 L h$^{-1}$ m$^{-2}$ for AGMD and 8.1 ± 1.0 L h$^{-1}$ m$^{-2}$ for WGMD.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Seawater Carbon Flux mgC h$^{-1}$ m$^{-2}$</th>
<th>Seawater HA Flux mgHA h$^{-1}$ m$^{-2}$</th>
<th>Synthetic water Carbon Flux mgC h$^{-1}$ m$^{-2}$</th>
<th>Synthetic water HA Flux mgHA h$^{-1}$ m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGMD</td>
<td>5.9 ± 1.4</td>
<td>21.5 ± 5.4</td>
<td>6.0 ± 2.5</td>
<td>21.6 ± 9.7</td>
</tr>
<tr>
<td>WGMD</td>
<td>6.4 ± 1.0</td>
<td>19.7 ± 4.4</td>
<td>8.2 ± 2.7</td>
<td>27.9 ± 10.3</td>
</tr>
</tbody>
</table>

3.2. Rotary evaporator tests with real seawater and synthetic saline water with HA

Results obtained in the rotary evaporator tests are shown in Table 4. The experiments were carried out under the same conditions as in MD for convenient comparison. EC was measured in some permeate samples, where EC values below 3 $\mu$S cm$^{-1}$ were obtained in all cases. The $RF_{EC}$ therefore reached where >99% and compared well with the MD tests shown in Table 2. However a major difference was to NPOC rejection, where the distillate concentrations were very similar to the blank (deionized water) in all cases showing that HA compounds and OM contained in both synthetic water and seawater are not volatile. In addition, it is verified that HS
thermal degradation byproducts do not pass into the vapor phase. In this sense, HA diffusion process through the membrane is inherent to the MD process. Therefore the next part of this work will be to explore the effect of typical MD operating conditions on the diffusion of HA.

Table 4. NPOC values for seawater and synthetic water using rotary evaporator.

<table>
<thead>
<tr>
<th></th>
<th>Seawater</th>
<th></th>
<th>Synthetic water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NPOC mg L⁻¹</td>
<td>Feed</td>
<td>Condensate</td>
<td>Blank</td>
<td>Feed</td>
</tr>
<tr>
<td></td>
<td>2.6 ± 0.2</td>
<td>0.4 ± 0.2</td>
<td>0.4 ± 0.2</td>
<td>16.3 ± 1.8</td>
</tr>
</tbody>
</table>

3.3. Effect of MD operating conditions on HA diffusion

3.3.1. Effect of operating temperatures

Fig. 2 shows the influence of different operating temperatures on the HA flux through the membrane. As it can be seen, HA flux was increased (from 15.6 to 37.1 mg h⁻¹ m⁻² for AGMD and 13.1 to 38.1 mg h⁻¹ m⁻² for WGMD) with higher feed temperatures in the same manner as the total flux (from 1.7 to 3.9 L h⁻¹ m⁻² for AGMD and 3.8 to 7.6 L h⁻¹ m⁻² for WGMD). Nevertheless, when the cooling temperature set to 35°C keeping feed temperature at 70°C, total flux decreased (3.1 L h⁻¹ m⁻² and 4.7 L h⁻¹ m⁻² for AGMD and WGMD, respectively) since there was a lower vapor pressure across the membrane. Likewise, HA flux decreased to 18.0 mg h⁻¹ m⁻² for AGMD and 16.0 mg h⁻¹ m⁻² for WGMD. Based on this result, it appears that HA flux generally follows total flux, supporting the concept that HA is entrained through the membrane with water following the model proposed by Meng et al (Meng et al., 2014). However it is not a direct correlation since there was little or no increase in HA flux from 50°C to 60°C, but a large increase occurred from 60°C to 70°C. Meanwhile water flux increase was proportionately similar at each temperature step (cases of 18°C permeate cycle temperatures). This is evidence that water and HA diffusion are not entirely connected which will be further explored later in this paper. Comparing the HA flux obtained for AGMD and WGMD, both MD configurations showed a similar behavior where it should be expected no non-volatile HA would be present at all in AGMD permeate. In this way, several types of condensation may occur in AGMD...
systems as is suggested by Warsinger et al (Warsinger et al., 2018) and therefore, the presence of HA flux in AGMD suggests liquid contact between the membrane and condensing plate. Additionally, in Figure 2 a discrepancy of HA fluxes for AGMD and WGMD in the test at a temperature of 60°C is reported. This performance could be also attributed to liquid contact between membrane and condensing plate (water bridging) in AGMD. Thus, water bridging could be different as the flux is lower, but when more water flux occurs, the risk of bridging increases rapidly, potentially due to rapid coalescence of condensed water clusters. This is potentially a reason why it rose suddenly for AGMD when water flux is higher.

Looking more closely at the chemistry, pH is known to play an important role in the behavior and solubility of HA (Khayet et al., 2004). However no large differences in pH were observed in the experiments carried out using synthetic water. The pH on average for AGMD was 6.39 ± 0.26 while for WGMD was 6.66 ± 0.21. Feed pH was 6.81 ± 0.31. According to the results obtained, it can be assumed that HA behavior is not attributed to pH changes between feed and permeate. In terms of EC rejection, AGMD was slightly less effective than WGMD but both were >99%. The salinity may also play a role in the HA diffusion, where future work could consider the effect of total dissolved solids concentration, including effects of other trace minerals including calcium and iron.
Fig. 2. HA flux obtained for PTFE membrane and both MD configurations at different operating temperatures. Total flux is represented by lines graphed on the secondary axis. Feed and cooling cycle flow rate: 90 L h\(^{-1}\). Feed water: 1 g L\(^{-1}\) NaCl, 0.88 g L\(^{-1}\) CaCl\(_2\) and 100 mg L\(^{-1}\) HA. PTFE membrane with effective area of 0.018 m\(^2\). Due to low errors on some points, error bars cannot be seen.

3.3.2. Effect of cross flow rate

Figure 3 shows the total flux and HA flux from MD testing on synthetic saline water with HA at varied cross flows with fixed feed and permeate temperature conditions. AGMD total flux was mostly constant (3.9 L m\(^{-2}\) h\(^{-1}\)) for flow rates of 90, 105 and 120 L h\(^{-1}\) but slightly increase by 7.75% over the entire range. WGMD showed large variations in total flux for flow rates of 60 and 75 L h\(^{-1}\) but was generally higher than AGMD with flux values between (7 L m\(^{-2}\) h\(^{-1}\) and 9 L m\(^{-2}\) h\(^{-1}\)). These total flux and HA flux variations in WGMD could be caused by the specific operational features. For example, in WGMD, permeate is collected by overflow of the water gap while AGMD is collected by gravity. Therefore, as a possible effect, WGMD permeate is affected by the feed flow pushing on the membrane surface and in turn, membrane movement generates a pulse effect in the gap. In this sense, flow rates greater than 75 L h\(^{-1}\) generated a constant total flux in all experiments. Nevertheless, for the studied flow rates of 60 L h\(^{-1}\) and 75 L h\(^{-1}\), the membrane pulse was lower, and consequently, total flux was more variable over time. In any case, errors in WGMD did not show a discernible trend, and the total flux overall trend for both MD configurations indicated a low sensitivity of the total flux to CFV within the range studied. However, considering this more carefully, temperature must also be considered with varying cross flow as it is a key factor for MD process. In all cases, high EC rejections were obtained (99.9% for WGMD and 99.6% for AGMD) and pH values (6.5 and 6.4 for WGMD and AGMD, respectively) were similar and comparable to temperature tests. In the studied range, a change in flow rates keeping temperatures constant does not significantly affect the vapor pressure difference across the membrane and consequently, total fluxes are almost constant. This does not mean that in other flow rate conditions, the reduced polarization effects and a higher temperature profile uniformity, added to a thermal energy increase by higher CFV, would in turn substantially increase the total flux.
Looking at HA fluxes the behavior was independent to that of total flux and showed a unique effect. Therefore, it has been further shown that HA can diffuse independently of water, where effects of cross flow will impact its diffusion. The functional effect cross flow has on HA diffusion may be its effect on the fluid-membrane interface (i.e. boundary layer).

**Fig. 3.** HA flux obtained for PTFE membrane and both MD configurations at different flow rates and CFV. Total flux is represented by lines graph on a secondary axis. Feed and cooling temperatures: 70°C and 18°C, respectively. Feed water: 1 g L⁻¹ NaCl, 0.88 g L⁻¹ CaCl₂ and 100 mg L⁻¹ HA. PTFE membrane with effective area of 0.018 m². Due to low errors on some points, error bars cannot be seen.

In these tests, HA flux showed a clear trend. At lower CFVs, 2.28 and 2.86 cm s⁻¹, HA flux for AGMD showed low values. The explanation could be related to a higher mass transfer resistance of the AGMD, as will be discussed in section 3.4. However, it peaks considerably at the middle range CFV at 3.43 cm s⁻¹. Meanwhile, HA flux for WGMD showed a similar peak at this CFV but gave higher initial values at the lower CFVs tested. For higher CFVs to 3.43 cm s⁻¹, a clearly descending trend can be observed for HA flux in both MD configurations, reaching a minimum HA flux by WGMD at CFV of 4.57 cm s⁻¹. A mechanisms of HA diffusion related to the flow across the membrane surface has become evident, which will be discussed later. The next section will consider the membrane surface chemistry to further explore the effect of the liquid-membrane surface interactions on HA flux.
3.3.3. Effect of membrane chemistry

Fig. 4 shows the results for tests on the standard hydrophobic PTFE membrane compared to other membrane types to explore the influence of different materials on the HA flux in permeate. PU-PTFE (hydrophilic PU coated hydrophobic PFTE), hydrophobic PE and omniphobic PE showed similar results to the standard PTFE membranes in terms of total flux. EC rejection (99.6% AGMD and 99.9% for WGMD) and pH of AGMD and WGMD permeates (6.4 and 6.5, respectively) were similar in all cases and behavior similar to both temperature and flow rate cases. However difference were observed between the membrane chemistries for HA flux. HA flux through the PTFE membrane is highest in both AGMD and WGMD, and similar to PU-PTFE within error. Meanwhile PE hydrophobic was only similar in HA flux for WGMD mode, while AGMD mode showed HA flux was about 50% of any of these higher values. This small value was similar for PE omniphobic, uniquely in both AGMD and WGMD.

**Fig. 4.** HA flux obtained for different membranes and both MD configurations. Total flux is represented by lines graph on a secondary axis. Feed and cooling temperatures: 70°C and 18°C, respectively. Feed and cooling cycle flow rate: 90 L h⁻¹. Feed water: 1 g L⁻¹ NaCl, 0.88 g L⁻¹ CaCl₂ and 100 mg L⁻¹ HA. Each membrane has an effective area of 0.018 m². Due to low errors on some points, error bars cannot be seen.

In relation with other membranes tested, omniphobic PE membrane with about 50% of the HA flux through PTFE in both AGMD and WGMD while at the same time as maintaining a similar
level of total flux. Clearly membrane chemistry is influencing the HA flux, where a
hydrophobic chemistry favours HA diffusion in the liquid-liquid feed-permeate contact WGMD
mode. This is also true for PU-PTFE where despite the hydrophilic PU coating facing the feed
solution, HA still diffused into the permeate through the underlying hydrophobic PTFE layer.
The omniphobic membrane possessed also the ability to repel hydrophobic interactions
indicating the HA diffusion through MD membranes is due to hydrophobic interactions between
the membrane and the HA molecule. The outstanding result was for the hydrophobic PE
membrane which gave HA fluxes for WGMD similar to the PTFE membranes, but gave lower
HA flux in AGMD similar to the omniphobic PE membrane. This result cannot be fully
explained based on the present data, and may be due to differences in the hydrophobicity of the
PE material compared to PTFE that yielded differences between the MD modes where AGMD
may have had less water bridging and in turn reduced HA flux.

Contact angle (CA) was measured on virgin membranes using synthetic water (1 g L\(^{-1}\) NaCl,
0.88 g L\(^{-1}\) CaCl\(_2\) and 100 mg L\(^{-1}\) HA) and deionized water measurement in order to confirm the
hydrophobicity of the membrane surfaces. A MD membrane with a water contact angle above
90º is considered hydrophobic (García-Fernández et al., 2015). In this way, according to water
CA measured, PTFE (97º) and both PE membranes (106º for hydrophobic and 122º for
omniphobic) exhibited hydrophobic surfaces, while hydrophilic PU-PTFE membrane showed a
water CA around 69º showing a hydrophilic surface, due to the PU coating on the underlying
hydrophobic PTFE that blocks liquid water.

Furthermore, CA measurements using synthetic water supported the same theory explained
previously using deionized water. In this way, synthetic water CA measured for each membrane
was 88º for PTFE, 72º for PTFE-PU, 114º for PE hydrophobic and 127º for PE omniphobic.
Although HA interaction with the membrane surface cannot be completely explained only by
the CA analysis, a trend is observed among the CA and the HA flux using synthetic water, even
for the PTFE-PU membrane, which is a composite membrane where only its surface facing the
liquid is hydrophilic.
In this sense, it is important to highlight the CA analysis to omniphobic PE membrane, which presents the lowest values of HA flux and, in turn, the highest CA values (122° and 127° for deionized water and synthetic water, respectively). These results suggest that modified membranes could play an important role in OM rejection and other elements with the same features. Meanwhile, the unusual result for the hydrophobic PE membrane in Figure 4 observed earlier may be explained by the relatively higher CA. When the gap is filled with water in the case of WGMD, HA may freely diffuse from the membrane surface into the permeate liquid. On the other hand, for AGMD the more hydrophobic surface could have assisted in repelling the bridging of liquid water from the permeate membrane surface across the gap to the condensing plate sufficiently more than both PTFE membranes. The more intact air gap therefore acted as a barrier to HA flux being more like the rotary evaporator test where HA could not be entrained into the distillate through the vapour phase. Furthermore, the study of other membrane properties such as thickness, porosity and tortuosity would play a role, so a detailed analysis of such properties on these membranes is needed to extend our current study to explore means to understand and control HA diffusion through MD membranes.

In conclusion, even though there are no large changes in the total flux, a clear decrease in the HA flux was obtained for omniphobic PE membrane and for the high CA hydrophobic membrane in AGMD mode. Therefore, according with works from other authors (Damtie et al., 2018; Duong et al., 2018; Wang et al., 2018; Woo et al., 2016; Zheng et al., 2018) and the results obtained in this study, we conclude that MD membranes play an important role in the quality of the permeated water.

3.4. HA diffusion models

According to results obtained for MD tests using synthetic water, HA diffusion models can now be proposed based on the key operating conditions of temperature and flow rate. Experimental data suggest that the HA diffusion as a function of temperature can be explained by Fick's Law. Thus, the diffusivity of HA within the membrane and the HA driving force
across the membrane surfaces are the main phenomena that could affect the flux. Hence, it is observed that the increase in feed temperature increased the HA flux and therefore, the temperature influences the HA diffusivity. However, the increase in permeate temperature showed a considerable decrease in HA flux, so it seems to be strongly related to the HA driving force based on the surface concentrations of HA. Taking the latter into account as well as the results obtained for flux and membranes tests, it is suggested that the increase in feed temperature raised the concentration of HA on the membrane surface by increasing its access from the bulk to the surface, potentially from increased diffusion through the boundary layer. So, when permeate temperature increased, total flux decreased and the concentration polarization of HA from water flux on the feed declined. Figure 5 shows the proposed model for the HA diffusion because of temperature.

In addition, another phenomenon could affect in a complementary way to overall HA flux, by which, the adsorption of HA on the surface of the membrane decreases with the increase in temperature, while the diffusivity of HA increases.

In this sense, the discrepancy obtained for the HA flux in AGMD at 60ºC (Figure 2) could be explained both to the effect of the water bridges, to the diffusion models, discussed above, and to small structural changes of the HA with temperature. In the latter case, some authors (Giovanela et al., 2010, 2004; Kolokassidou et al., 2007) reported that there are small changes in the structure of HA resulting in a loss of mass in the temperature range of 40ºC to 80ºC. These changes are related to the reversible and irreversible losses of different types of water molecules contained in the HA. Thus, reversible structural changes occur at around 60ºC, while irreversible changes become important at 70ºC (formation of more condensed and hydrophobic polyaromatic structures) (Giovanela et al., 2010, 2004; Kolokassidou et al., 2007). Based on these studies, in MD tests at temperatures of 60ºC, it is suggested that HA molecules loaded with water coexist with HA molecules with more condensed reversible structures. Therefore, while for WGMD both types of molecules could be diffused without high resistance to permeate, the heavier HA molecules would have lower diffusion because of the higher mass
transfer resistance of AGMD due to the air gap (Alkhudhiri et al., 2012a). In addition, the effect of less water bridges in AGMD at lower fluxes (section 3.3.1) could be considerable. For these reasons, the HA flux in the AGMD is lower than the WGMD under these experimental conditions. However, there is not enough evidence to conclude if the sudden rise in HA flux at 70°C is due to altered HA chemistry or an accelerated water bridging effect.

**Fig. 5.** HA diffusion in AGMD and WGMD because of temperature. Low temperatures imply a low particle speed and therefore, less diffusivity through the boundary layer (a). Higher temperatures assisted HA flux by improving diffusion of accumulated HA at the membrane surface (b). Permeate side temperature increase implies a HA concentration polarization decrease (c).

HA flux trend for flow rates tests can be explained by three different processes as is illustrated in Fig. 6. Firstly, at lower flow rate and cross flow velocity (2.28 cm s⁻¹), concentration polarization and boundary layer phenomena are significant leading to high HA concentration at the surface under relatively quiescent conditions. In this way, most of molecules and colloids of HA were deposited on the membrane surface, inhibiting HA diffusion through the membrane. For AGMD, at lower CFV (2.28 and 2.86 cm s⁻¹), lower HA flux compared to WGMD was obtained, as it was shown in Figure 3. These results suggested a CFV influence by concentration polarization and boundary layer phenomena. Thus, at low CFV, the residence time of HA on the membrane surface is longer. Therefore, with low velocity, higher concentration polarization, as well as a higher AGMD resistance to mass transfer, this resulted in a lower HA diffusion in this
MD configuration. Nevertheless, in WGMD, as a result of lower mass resistance, the HA diffuses more easily to permeate under the same experimental conditions.

As the flow and CFV increased, the feed water mixture was increasingly homogeneous. For this reason, the concentration polarization and associated boundary layer and HA fouling layer phenomena were weakened, and HA diffusion to permeate reached a maximum at 90 L h$^{-1}$. From this point, although the mixture is homogeneous at higher flow rates, HA flux dropped noticeably at CFV of 4.00 and 4.57 cm s$^{-1}$. The latter process suggests the influence of shear forces, which complicate HA transport to the membrane surface. It appears some accumulation within the boundary layer is needed for HA flux to occur. With too much mixing and the surface condition approaching the bulk solution, HA flux becomes reduced.

![Fig. 6. Influence of the flow rates in HA diffusion for AGMD and WGMD. Predominance of boundary layer phenomena and concentration by polarization (a). Complete mixture of feed cycle, reaching the maximum diffusion (b). Shear forces play an important role at higher flow rates (c).](image)

To date, only a few studies have detected HA in permeate and their migration through the membrane in DCMD. According to Meng et al (Meng et al., 2014), the process involves HA adsorption-desorption onto the membrane surface, because of amphiphilic nature of HA. Thus, HA migrates through the membrane pores by hydrogen bonding between water vapor and humic molecules. This process suggests a dependence between migration mechanism and vapor pressure and therefore, with the total flux for DCMD.
According to the results obtained for all tests carried out in this work and diffusion models suggested, HA behavior based on diffusion is proposed for AGMD and WGMD. The diffusion mechanism is independent of total flux and consequently, vapor pressure as well. AGMD and WGMD have been used with the purpose of analyzing an isolated permeate, avoiding the dilution effect in DCMD and therefore, not underestimating the amount of HA or NOM present in permeate.

3.5. Complementary studies

3.5.1. Double gap width for AGMD

Following our finding earlier where HA flux occurred in AGMD as well as WGMD, water bridges have been proposed by which HA could diffuse into permeate. These water bridges can play an important role in this phenomenon, because of an additional sweeping effect of the membrane cold side (Warsinger et al., 2018).

In relation to this suggestion, an additional frame was installed in order to double the gap size to 6 mm. Thus, a significant decrease in both total and HA fluxes could be expected. In this regard, as it can be seen in Fig.7, while the total flux dropped noticeably, the HA flux detected was greater (around 36%) than that obtained for 3 mm gap. Although a wider gap implied less water bridging as well as total flux drop, slightly increased HA flux was obtained. These results suggest that HA flux is not relying on total flux, and HA diffuses through the membrane in any case. In addition, HA flux increase may be due to new conditions for wider gap as for example, a favorable change in the temperature profile for HA diffusion. For example, at lower fluxes, temperature polarization will be lower leading to larger temperature differences over the membrane. As concluded earlier, the higher temperature on the feed side assisted HA flux by improving its ability to diffuse through boundary layers containing accumulated HA at the membrane surface which could also be eliminated by increasing cross flow (but only up to a certain point).
Fig. 7. HA flux obtained for different gap tests. Total flux is represented by the lines with the values indicated on the secondary axis. Feed and cooling temperatures: 70°C and 18°C, respectively. Feed and cooling cycle flow rate: 90 L h⁻¹. Feed water: Deionized water and 50 mg L⁻¹ HA to avoid influence of salts and high HA concentrations. PTFE membrane with an effective area of 0.018 m². Due to low errors on some points, error bars cannot be seen.

3.5.2. HA preliminary characterization

Using appropriate calibration curves for UV spectrometer and TOC analyzer, a good correlation was achieved for the synthetic water. This means that the absorbance could be known from the NPOC value and, therefore, the concentration of HA in the sample, indistinctly. Errors using the correlation between both techniques were less than 10%, with an average value of 7%. It is important to underline that different high and low range HA calibration curves were applied in order to cover the entire range of concentrations.

On the contrary, when these correlation equations were applied for UV spectrophotometer and TOC analyzer in permeate samples, errors obtained were above 87%. In addition, the absorbance values obtained in the permeate samples did not correspond to the absorbance that would have a feed water with the same concentration of HA measured with TOC analyzer. For
these reasons, a profile change in the HA molecule is suggested, since it seems that the HS found in permeate absorb UV differently and therefore, they have different properties to the original HS contained in the feed water.

The composition differences of HA in feed and permeate was also analyzed using fluorescence spectrophotometry. Nevertheless, Excitation – Emission Matrix (EEM) fluorescence spectra can be altered by pH and salt concentrations in the sample. In order to study the possible saline interferences and differences between feed and permeate EEM spectra (Fig.8), fluorescence measurements were made using different concentrations of HA in deionized water without salts, as well as synthetic water (MD feed water) at different concentrations of HA. In all these measurements, EEM spectra similar to each other were obtained. In Fig. 8a an EEM spectrum of HA in deionized water (without added salts) is shown.

In Fig.8.b, an EEM fluorescence spectrum obtained from a synthetic water feed sample is shown. This spectrum presents typical values for a standard HA, showing two Ex/Em peaks around 250-350/450 nm (Rodríguez et al., 2014). High similarities between the EEM spectra of synthetic water feed and HA with deionized water are observed. Both EEM spectra showed the same profile as well as the peaks related to HA. Additionally, EEM spectra for AGMD and WGMD permeate samples are shown in Fig. 8c and 8d, respectively. The spectra obtained for the permeate samples in both MD configurations are very similar to each other, showing a maximum Ex/Em peak around 250/350-400 nm. Although these permeate EEM spectra showed fluorescence characteristics corresponding to humic acid-like substances (Wang et al., 2009), clear differences in relation to the feed EEM spectrum and also, with HA in deionized water EEM spectrum were observed. These results suggest and confirm a change in the HA profile diffused through the membrane, as was previously proposed with the UV spectrometer measurements.
Fig. 8. a. EEM spectrum for HA in deionized water; b. EEM spectrum for synthetic feed water sample; c. EEM spectrum for AGMD permeate sample; d. EEM spectrum for WGMD permeate sample.

4. Conclusions

Tests with different operating temperatures, flow rates and MD membranes were performed in order to study HA behavior, using AGMD and WGMD configurations. Non-volatile compounds have been detected in permeate, and humic flux through the membrane was affected by feed and cooling temperatures, boundary layers phenomenon, polarization concentration and shear forces. In addition, omniphobic PE membrane showed better HA rejection than the other membranes tested. In this way, MD membrane could play an important role in MD, which suggests that MD membrane is not only a passive element in the process. The same HA or
NOM behavior was obtained using both seawater and synthetic water. Therefore, a HA and 
NOM diffusion mechanism is proposed for AGMD and WGMD configurations.

On the other hand, a sweeping effect on the membrane cold side was detected in AGMD 
because of the frame, which separates the membrane and the cooling plate, acts as an 
intermediate condenser. Humic flux in AGMD could be similar as in WGMD because of this 
sweeping effect of the membrane.

Finally, a preliminary characterization of HA in MD permeate was carried out. HA differences 
in permeate and feed were detected. In this way, it is necessary to go in depth with HA 
characterization of MD permeate in order to analyze the OM complexation capacity and the 
transport of undesired compounds through the membrane.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

*Conflict of Interest*