Supporting information

Improvement of nanostructured electrospun membranes for desalination by membrane distillation technology

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Content

1. DSC thermograms of the PVDF polymer and ENMs

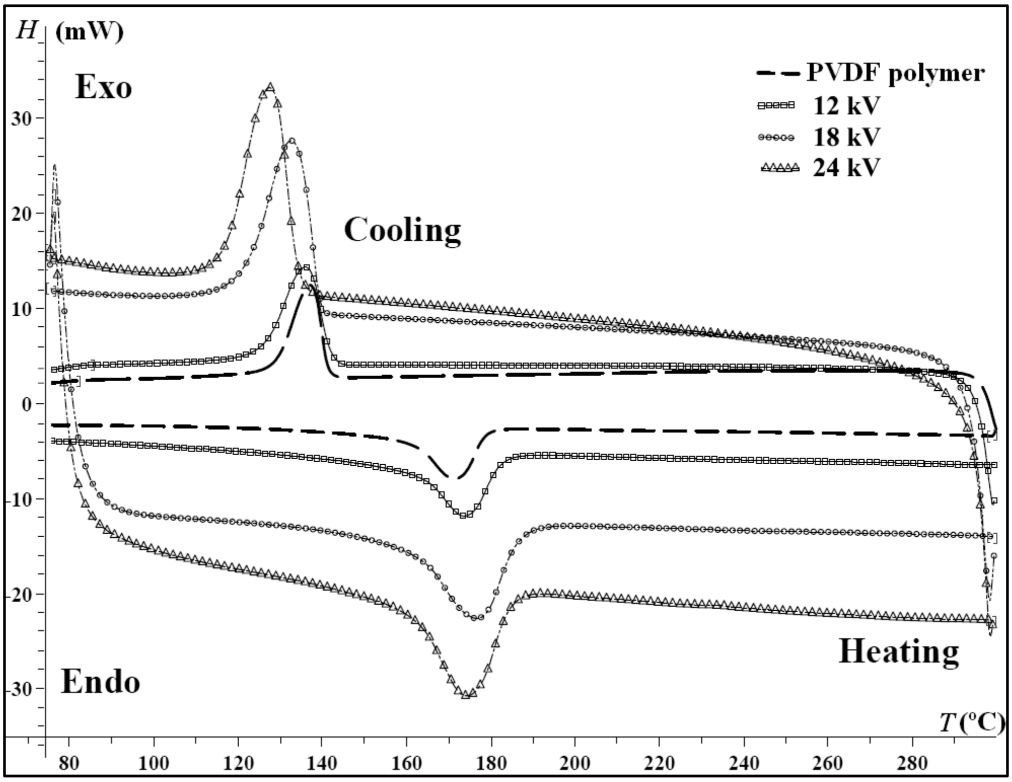


Figure S1. DSC exothermic and endothermic thermograms of the PVDF polymer and ENMs prepared with different electrospinning electric voltages.

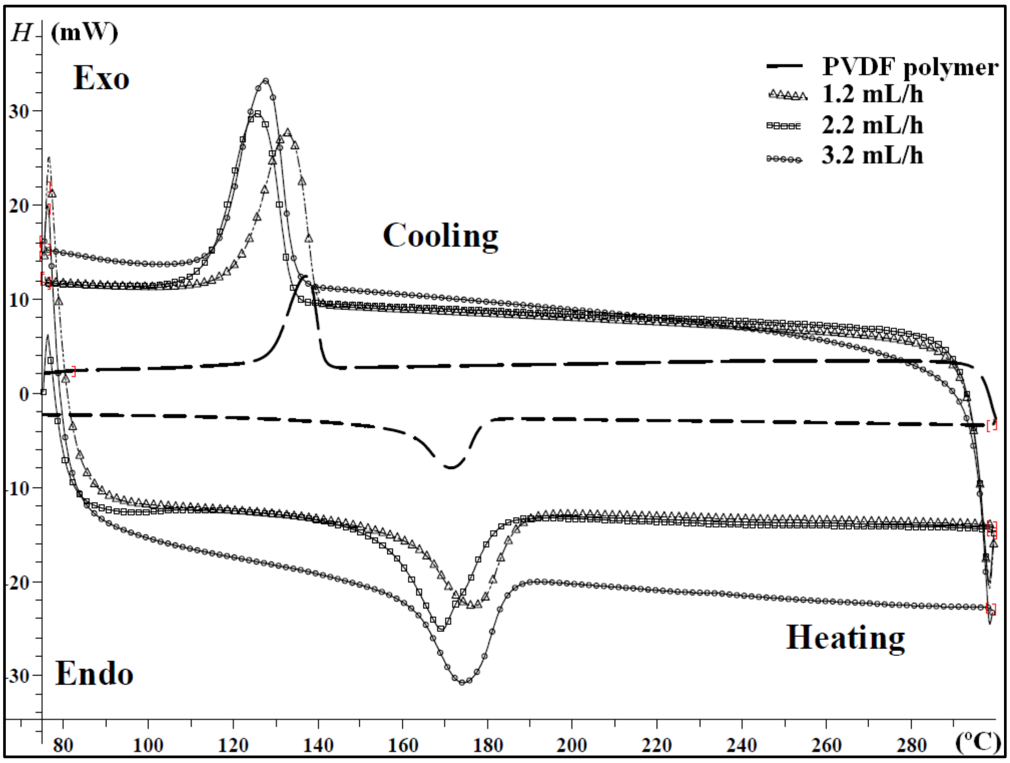


Figure S2. DSC exothermic and endothermic thermograms of the PVDF polymer and ENMs prepared with different polymer solution flow rates.

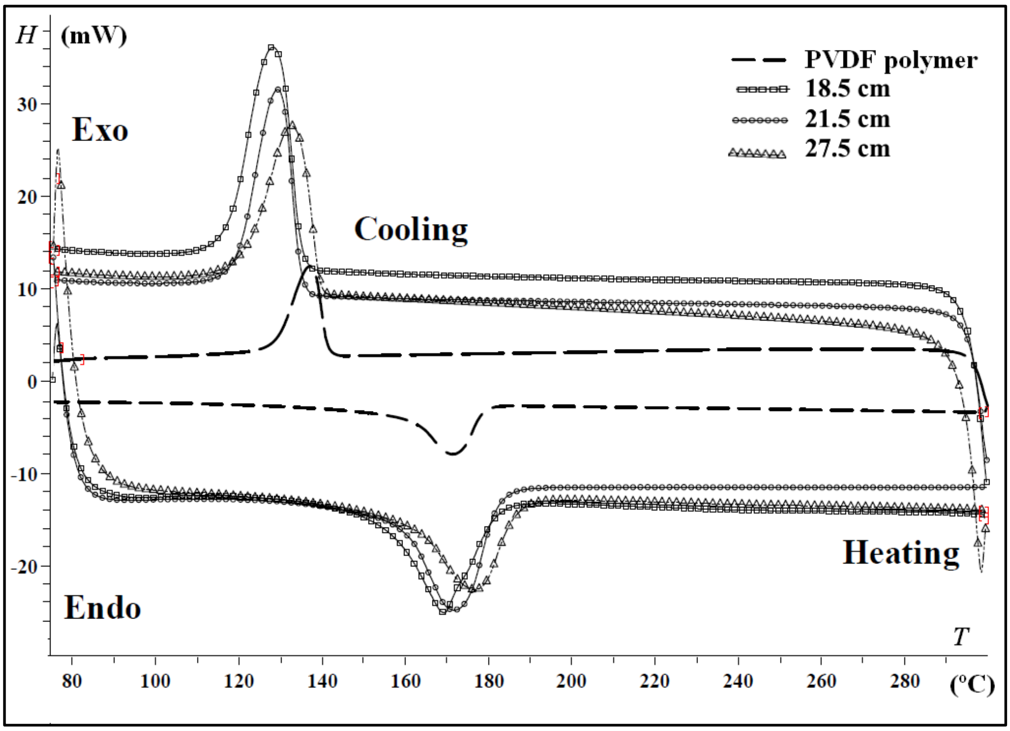
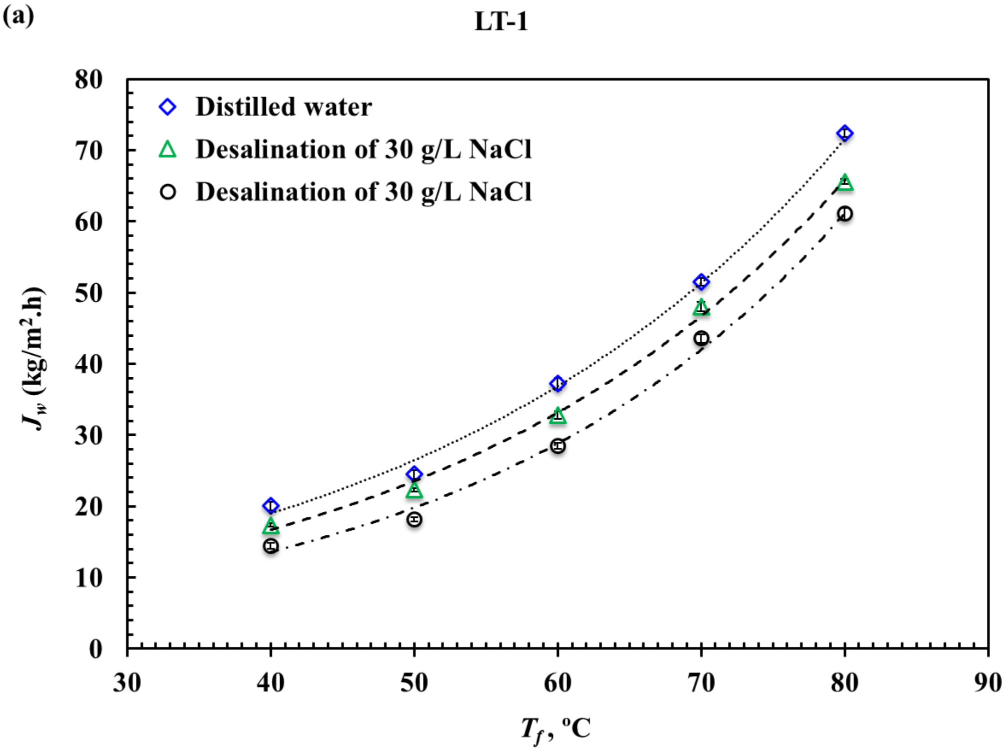


Figure S3. DSC exothermic and endothermic thermograms of the PVDF polymer and ENMs prepared with different air gap distances.

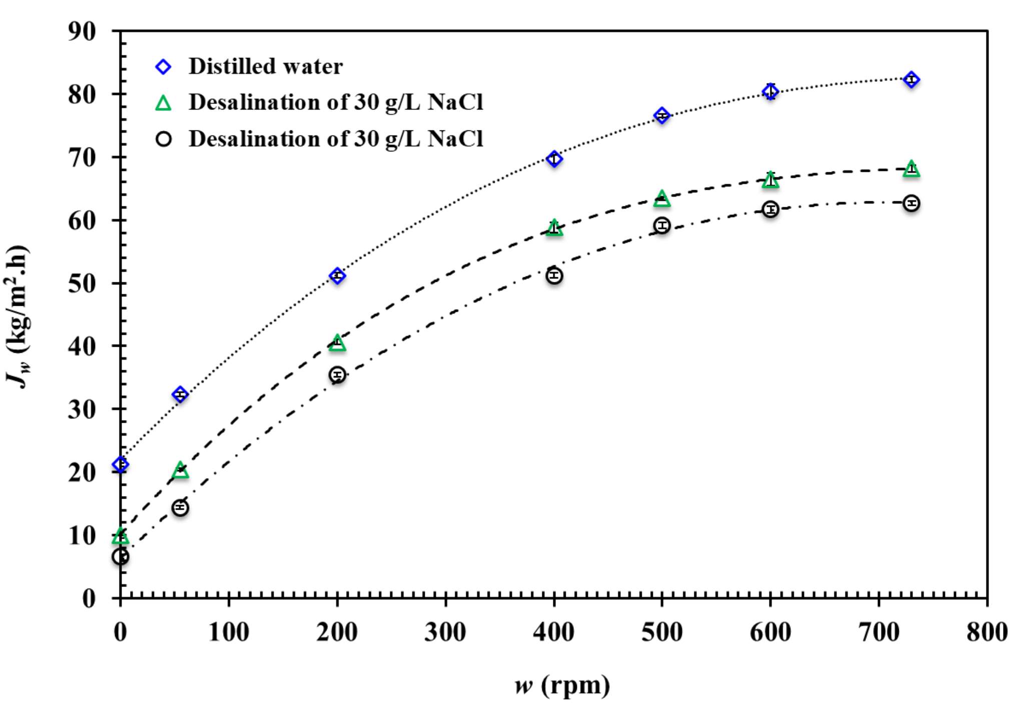
The effects of the electrospinning parameters on the DSC exothermic and endothermic curves of the ENMs are shown in the above figures together with those of the PVDF polymer for sake of comparison. A slight enhancement of the crystallinity of the ENMs was detected by increasing the applied voltage and decreasing the air gap length or the polymer flow rate. The determined data are reported in Table 3.

2. DCMD permeate fluxes of LT-1 and HT-1 ENMs at different feed temperatures, stirring rates and NaCl salt concentrations

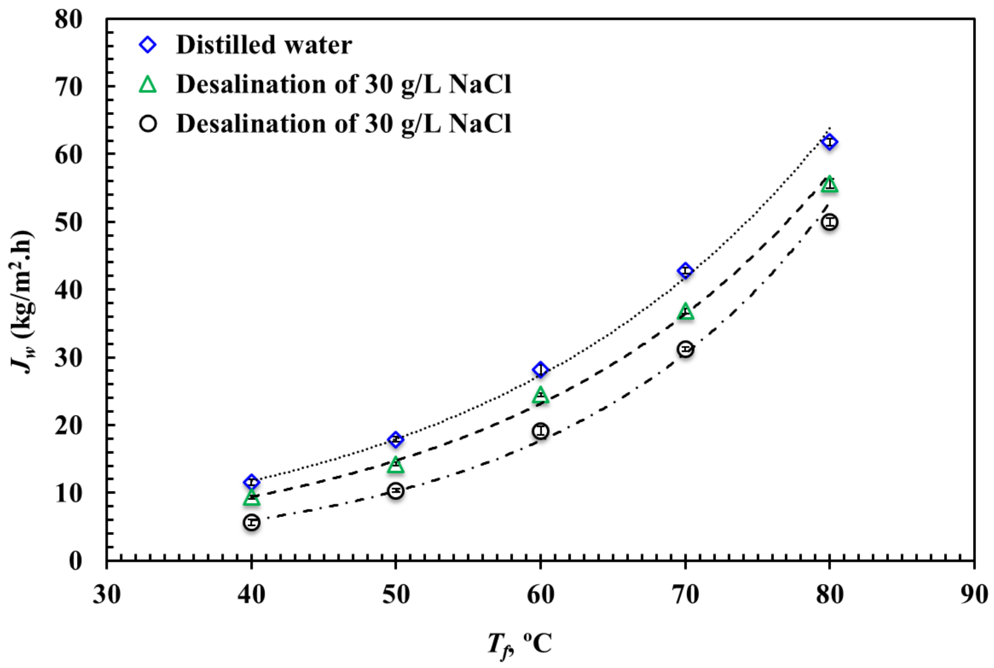
(a)



(b)



(c) HT-1



(d) HT-1

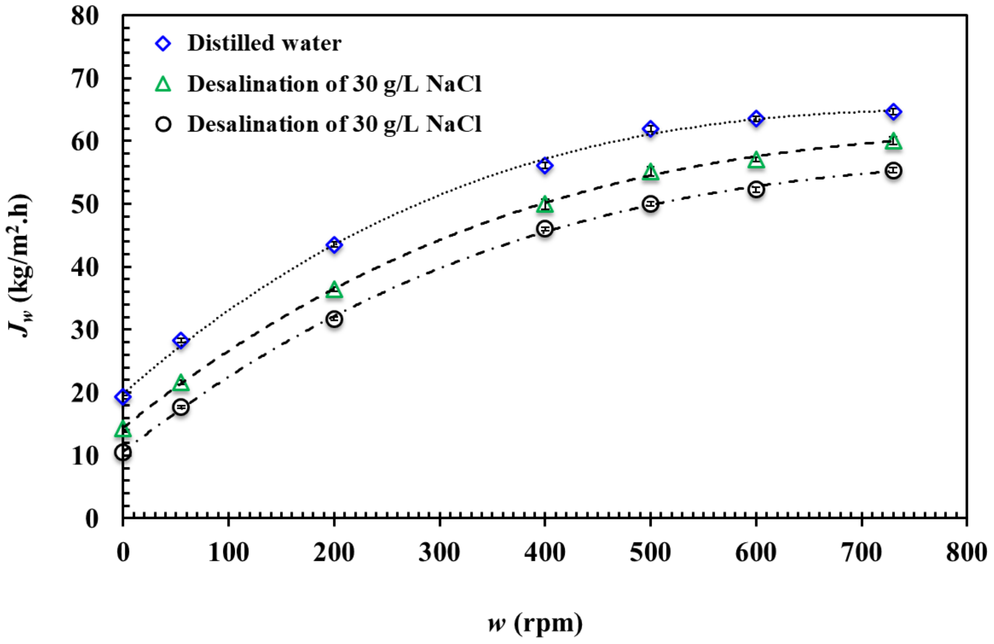


Figure S4. Permeate flux (J_w) of the ENMs (LT-1 and HT-1): (a and c) for different feed temperatures (T_f) and (b and d) for different stirring rates (w) in both feed and permeate, using distilled water, 30 and 60 g/L NaCl aqueous solutions as feed and a permeate temperature, $T_p = 20$ °C.

Figure S4 shows the relationship between the feed temperature (40 to 80 °C) and the DCMD permeate flux at different concentrations of NaCl aqueous solutions (0, 30, 60 g/L). For both ENMs, LT-1 and HT-1, The permeate flux increases with the feed temperature following an exponential trend type of dependence due to the increase of the vapor pressure at the feed/ENM interface [1]. The corresponding NaCl salt rejection factors were found to be greater than 99.86% and 99.95% for the ENMs LT-1 and HT-1, respectively.

The permeate flux decreases with the increase of the salt concentration in the aqueous feed solution due to the reduction of the water vapor pressure at the feed/ENM interface and the coupled effect of the concentration polarization [2]. The obtained salt rejection factor was found to be higher than 99.76% and 99.96% for LT-1 and HT-1, respectively.

The increase of the stirring rate reduces both the temperature and concentration polarization effects [3] and improves the DCMD permeate flux of both ENMs LT-1 and HT-1 (Figure S4. b and d). For these experiments, the salt rejection factors were found to be greater than 99.91% and 99.93%, for the ENMS LT-1 and HT-1, respectively.

3. Calculation of the temperature polarization coefficient

During steady state conditions, heat transfer through the DCMD system is summarized by the following equation [4]:

$$h_f\left(T_{f,b}-T_{f,m}\right)=\frac{k_m}{\delta}\left(T_{f,m}-T_{p,m}\right)+J_w\Delta H_v=h_p\left(T_{p,m}-T_{p,b}\right) \qquad \text{Eq. S1}$$

where, $T_{f,m}$ and $T_{p,m}$ are the temperatures at the feed-membrane interface and at the membrane-permeate interface, respectively; k_m is the thermal conductivity of the membrane; h_f and h_p are the heat transfer coefficients in the feed and permeate boundary layers, respectively; δ is the thickness of the membrane; J_w is the water permeate flux, and ΔH_v is the water heat of evaporation.

Several equations to calculate the feed and permeate temperatures at the membrane surfaces have been presented in various MD papers [4-7]. Eq. (S2 and S3) can be used to determine the temperatures $T_{f,\mathrm{m}}$, and $T_{p,\mathrm{m}}$:

$$T_{f,m}=\frac{\frac{k_m}{\delta}\left(T_{p,b}+T_{f,b}\frac{h_f}{h_p}\right)+h_fT_{f,b}-J_w\Delta H_v}{\frac{k_m}{\delta}+h_f\left(1+\frac{k_m}{\delta h_p}\right)} \qquad \text{Eq. S2}$$

$$T_{p,m}=\frac{\frac{k_m}{\delta}\left(T_{f,b}+T_{p,b}\frac{h_f}{h_p}\right)+h_fT_{p,b}-J_w\Delta H_v}{\frac{k_m}{\delta}+h_p\left(1+\frac{k_m}{\delta h_f}\right)} \qquad \text{Eq. S3}$$

Additionally, the temperature polarization coefficient (TPC) is commonly utilized for quantifying the magnitude of the boundary layer resistances. It reflects the reduction of the driving force (i.e. the difference of the vapor pressure between both sides of the membrane), that negatively impacts on the DCMD permeate flux. It is defined as:

$$TPC = \frac{T_{f,m} - T_{p,m}}{T_{f,b} - T_{p,b}} \qquad \text{Eq. S4}$$

The thermal conductivity, k_m, of the membrane can be estimated from the following equation:

$$k_m = \varepsilon k_g + (1 - \varepsilon) k_p \qquad \text{Eq. S5}$$

where k_g is the thermal conductivity of the gas filling the membrane pores, k_p is the thermal conductivity of the membrane material and ε is the void volume fraction.

Because of membrane compaction, for the TPC estimation, it is assumed a linear compaction of the membrane in the first 30 h of 100 h DCMD long-term test and then the membrane thickness was taken constant (i.e. in the present case the thickness of the membrane LT-1 ENM decreased from 378.45 to 234.63 μm for the first 30 h and remained constant for the next 70 h).

In the previous equations (Eq. S2) and (Eq. S3), the heat transfer coefficients for the turbulent flow are determined using a semi-empirical correlation by assuming the Nusselt number is determined using the following correlations:

$$Nu = 0.027 Re^{4/5} Pr^{m} \left(\frac{\mu_b}{\mu_m}\right)^{0.14} \qquad \text{Eq.S6}$$

where Nu, Re, Pr are Nusselt, Reynolds and Prandtl numbers, respectively; $\mu_b$and μ_m are the water dynamic viscosity at the bulk and the membrane surface, respectively [7, 8]; the superscript m is 0.4 for the hot feed side and 0.3 for the cold permeate side, respectively [8].

The following steps were carried out in order to estimate the TPC and the temperatures at the membrane surfaces: First, a mean temperature is used to calculate the Re, Pr and Nu numbers. Next, the temperatures of the membrane surface ($T_{f,m}$ and $T_{f,p}$) are calculated by applying Eqs. (Eq. S2) and (Eq. S3). The mean temperature $(T_{f,m} + T_{f,p})/2$ is evaluated and Re; Pr and Nu numbers are recalculated. This procedure is repeated until the difference between two successive mean temperatures was below 10^{-15}. Finally, from the last value of $T_{f,m}$ and $T_{f,p}$, the temperature polarization coefficient is determined for the developed long-term experiment.

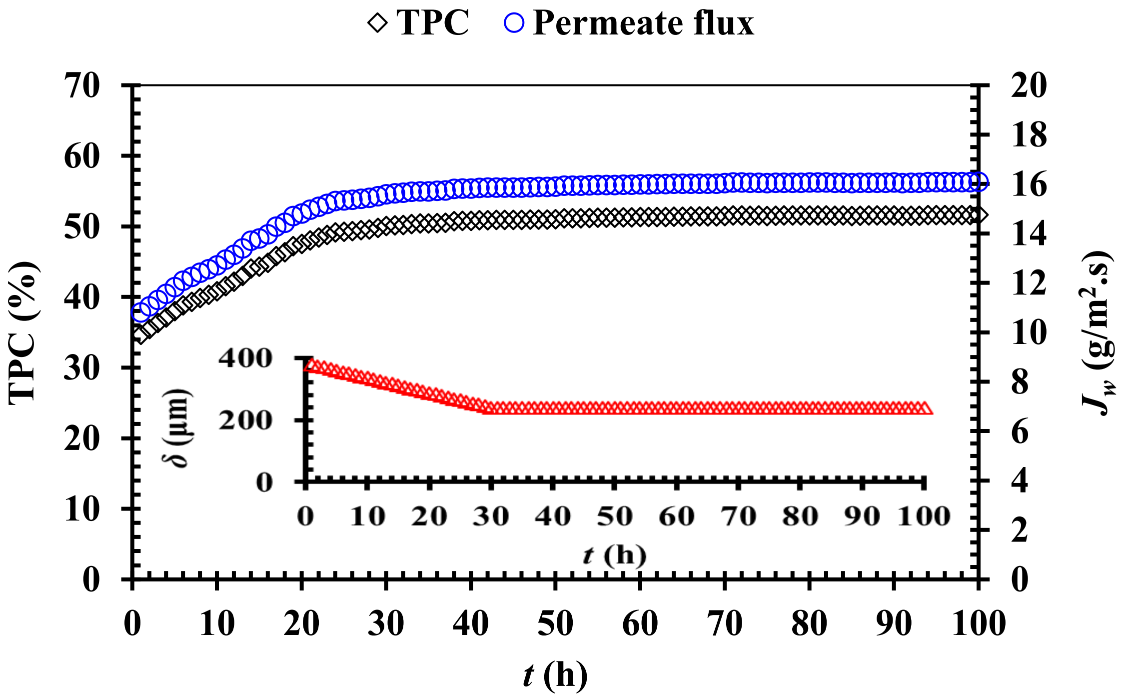


Figure S5. Variation of the temperature polarization coefficient and the measured permeate flux as a function of the DCMD operating time (t) using initially 30 g/L of NaCl aqueous solution in both the feed and permeate sides of the membrane (C_f = 30 g/L, T_f = 73.5 °C, T_p = 20 °C, feed and permeate stirring rates w = 500 rpm).

An increase of both the TPC and the permeate flux was observed during the first 30 h DCMD test before steady states were reached. Once these were reached, the heat transfer through the three regions (i.e. feed boundary layer, membrane and permeate boundary layer) must be the same ($Q_f = Q_m = Q_p$).

The following equation was used to determine the thermal conductivity (λ) of NaCl aqueous solutions as a function of temperature and concentration [9]:

$$Log_{10}(\lambda) = Log_{10}(240 + A.s) + 0.434\left(2.3 - \frac{343.5 + B.s}{T + 273.15}\right)\left(1 - \frac{T + 273.15}{647.3 + C.s}\right)^{1/3} \quad \text{Eq. S7}$$

being $\lambda\ in\ W/m\ K$, the salinity s in (g/kg) and the temperature T in ºC. The constants A, B and C are equal to 2x10^{-4}, 3.7x10^{-1}, and 3x10^{-2}, respectively.

The water vapor pressure is calculated using the following expression [10]:

$$P_{v,f}(x,T) = (1 - x)P_{v,w}^{0}(T) \quad \text{Eq. S8}$$

where x is the salt mole fraction; $T(K)$ is the temperature of feed solution and $P_{v,w}^{0}(Pa)$ is the vapor pressure of pure water calculated by Antoine equation:

$$P_{v,w}^{0}(T) = Exp\left(23.1964 - \frac{3816.44}{T - 46.13}\right) \quad \text{Eq. S9}$$

4. References

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