Supplementary information

Innovations in Water Desalination: Enhancing Air Gap Membrane Distillation Performance by the Incorporation of Clay Nanoparticles into PVDF Matrix Membranes

Roberto Navarro-Tovar [a], Patricia Gorgojo [b,c], Megan Jobson [a], Peter Martin [a], Maria Perez-Page [a,*]

[a] *Department of Chemical Engineering, The University of Manchester, Manchester M13 9PL, United Kingdom.*
[b] *Instituto de Nanociencia y Materiales de Aragón (INMA), CSIC-Universidad de Zaragoza, Zaragoza, 50018, Spain.*
[c] *Departamento de Ingeniería Química y Tecnologías del Medio Ambiente, Universidad de Zaragoza, Zaragoza, 50018, Spain.*

Structure of the clay materials

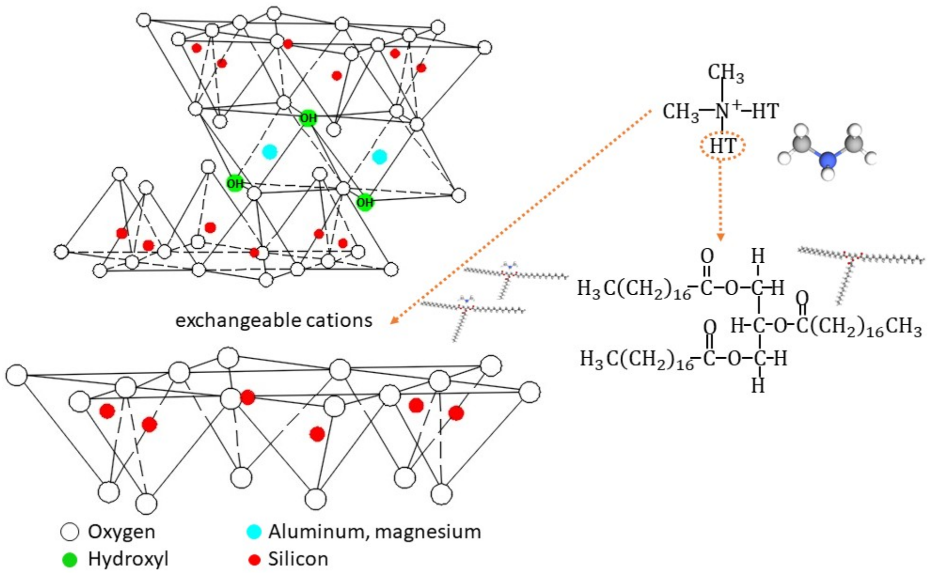


Fig. S1 Structure of natural MMT and dimethyl dehydrogenated tallow quaternary ammonium organic modifier. Modified from Mokhtar et al. [24] with permission from the RSC.

PVDF optimization

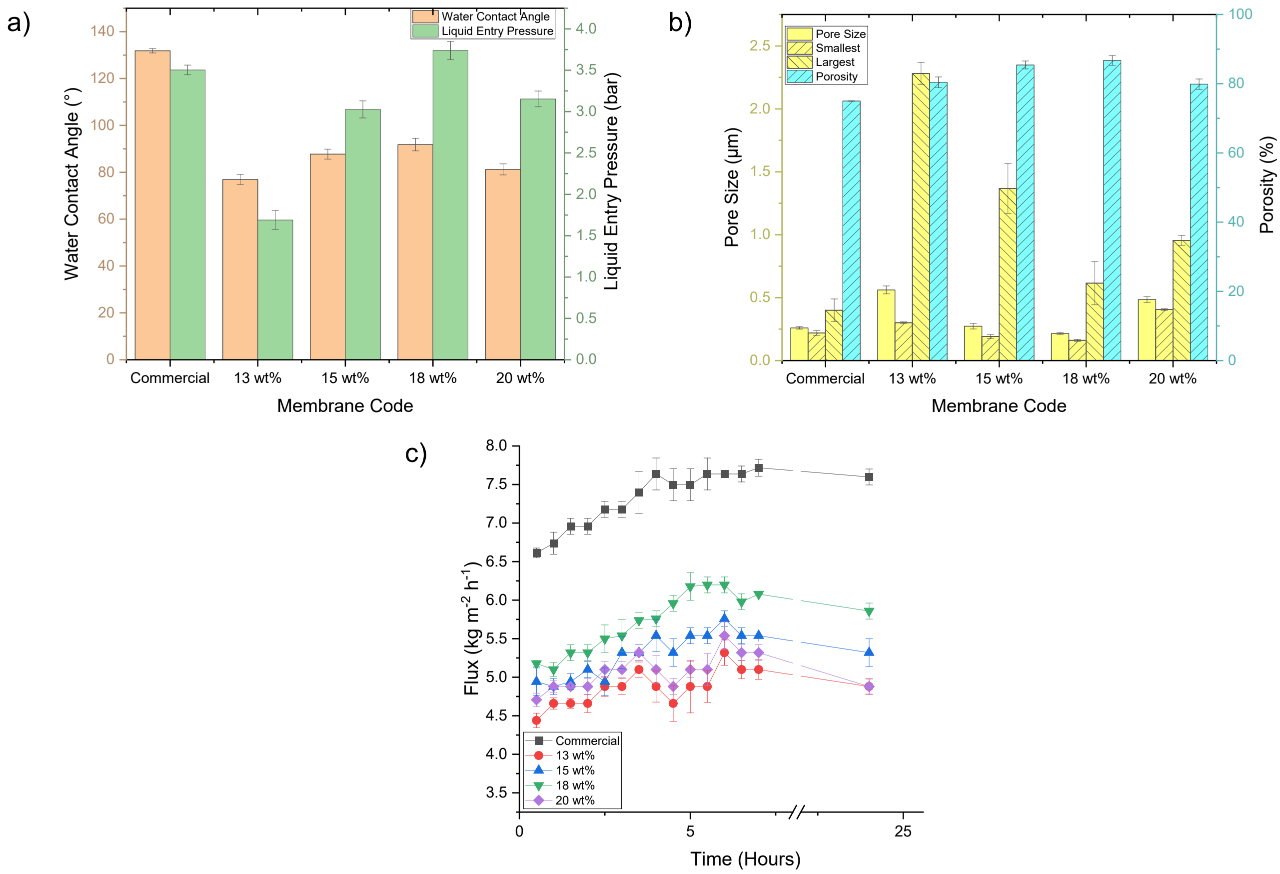


Fig. S2 PVDF optimization analysis for a) LEP and water contact angle, b) porosity and pore size, and c) permeate flux.

Polymer dope solution compostions

Table S1. Polymer dope composition. PVDF represents 18 wt% of the total casting solution. Membrane codes were generated as the name of the filler used followed by the weight % of the filler.

Membrane Code	DMSO weight (g)	MT/OMT weight (g)
Pristine PVDF	8.200	0
MT0.5	8.191	0.009
MT4	8.128	0.072
MT8	8.056	0.144
OMT0.5	8.191	0.009
OMT2	8.164	0.036
OMT4	8.128	0.072
OMT6	8.092	0.108
OMT8	8.056	0.144

SEM images and EDX results

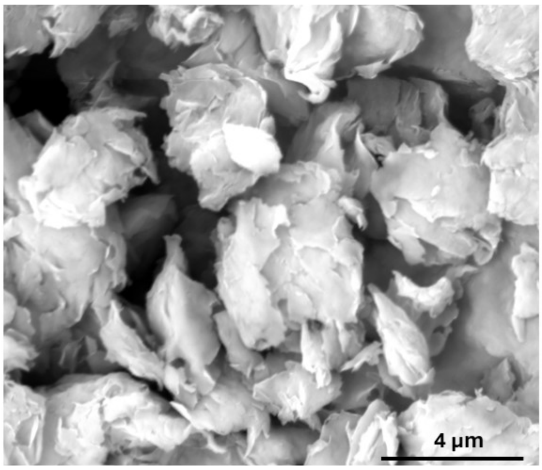
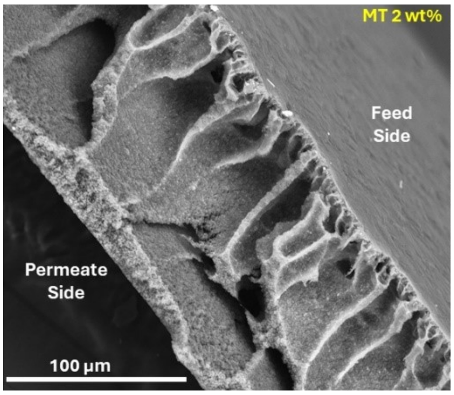


Fig. S3 SEM micrograph of OMT particles (x10000 magnification).

a)



b)

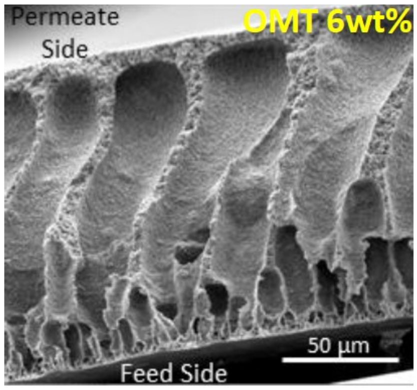


Fig. S4 SEM cross-section micrograph of PVDF MMMs of a) MT at 2wt% and b) OMT at 6wt%.

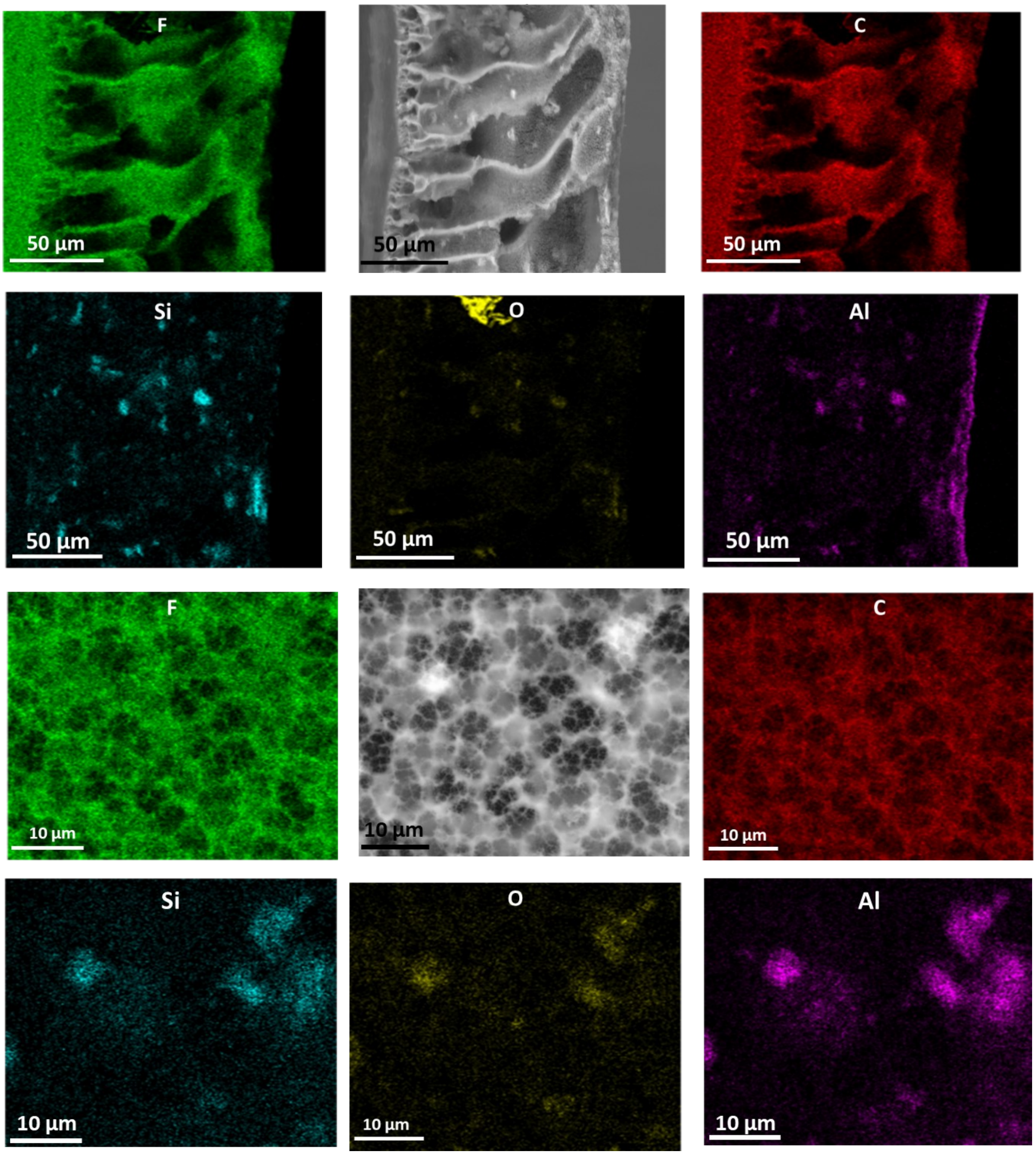
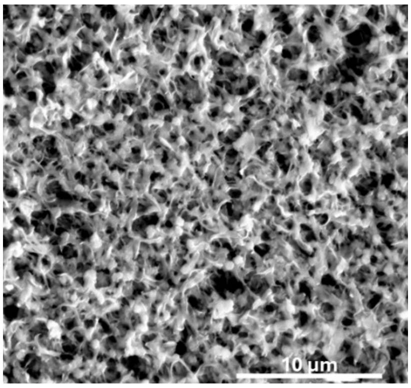


Fig. S5 EDX surface and cross-section micrographs of PVDF-OMT 4 wt% membrane.

Table S2. EDX quantitative analysis of PVDF (18 wt%) and PVDF-OMT composite membranes.

Surface elements (wt%)	Pristine PVDF (18 wt%)	PVDF-OMT (0.5 wt%)	PVDF-OMT (2 wt%)	PVDF-OMT (4 wt%)	PVDF-OMT (6 wt%)	PVDF-OMT (8 wt%)
F	58.44	56.18	53.30	52.30	49.80	49.00
C	40.54	39.37	40.02	36.19	34.62	31.91
O	1.02	3.62	4.29	4.05	4.01	3.88
Si		0.45	1.49	4.29	7.15	9.73
Al		0.23	0.74	2.85	4.11	5.03
Mg		0.15	0.16	0.32	0.31	0.45
Total elements	100	100	100	100	100	100

a) 

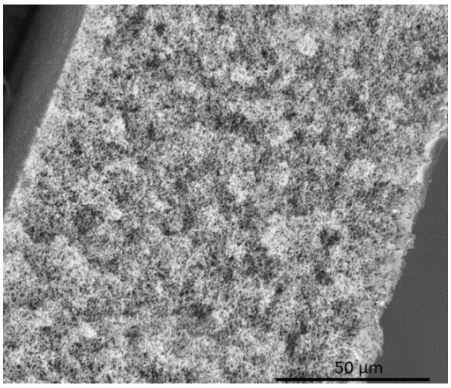
b) 

Fig. S6 SEM a) surface and b) cross-section micrograph of a PVDF commercial membrane.

Clausius–Clapeyron equation:

$$h_{vap}(C,T) = RT^2\left(\frac{d\ ln\left(P_S^0(T)\right)}{dT} + \frac{d\ ln\left(a_S(C,T)\right)}{dT}\right) \quad \text{(S1)}$$

where R is the ideal gas constant, T is the absolute temperature, $P_S^0(T)$ is the equilibrium partial vapour pressure of the pure solvent at temperature T, and a_S is the activity of the solvent in an NaCl solution of concentration C at temperature T.

Properties of membranes

Table S3. Summary of membrane properties and performance characteristics.

Membrane code	Thickness (µm)	Pore size: smallest; mean; largest (µm)	Porosity (%)	Contact angle (°)	LEP (bar)	Permeate flux (*kg m⁻² h⁻¹*)
PVDF Commercial	124 (±1.5)	0.22 (±0.02); 0.26 (±0.01); 0.40 (±0.09)	75 (±0.10)	131.9 (±0.94)	3.5 (±0.06)	7.6 (±0.23)
Pristine PVDF 18 wt%	198 (±7.4)	0.16 (±0.01); 0.21 (±0.01); 0.62 (±0.17)	85 (±1.40)	91.8 (±1.88)	3.7 (±0.13)	6.1 (±0.24)
MT 0.5 wt%	208 (±6.5)	0.39 (±0.07); 0.43 (±0.08); 2.93 (±0.15)	75 (±1.87)	69.4 (±1.47)	2.4 (±0.05)	4.6 (±0.25)
MT 4 wt%	213 (±8.4)	0.55 (±0.07); 0.77 (±0.08); 2.90 (±0.13)	75 (±1.35)	71.9 (±2.30)	2.3 (±0.03)	5.3 (±0.30)
MT 8 wt%	201 (±5.0)	0.48 (±0.08); 0.66 (±0.10); 2.54 (±0.12)	74 (±1.83)	73.8 (±2.59)	2.5 (±0.02)	5.9 (±0.31)
OMT 0.5 wt%	208 (±1.9)	0.22 (±0.05); 0.27 (±0.03); 0.83 (±0.13)	79 (±2.21)	93.3 (±2.25)	3.5 (±0.05)	6.1 (±0.30)
OMT 2 wt%	204 (±5.7)	0.21 (±0.06); 0.26 (±0.02); 0.82 (±0.10)	84 (±1.83)	96.3 (±2.15)	3.6 (±0.08)	8.1 (±0.33)
OMT 4 wt%	206 (±14.8)	0.15 (±0.02); 0.21 (±0.04); 0.52 (±0.09)	86 (±1.99)	104.5 (±2.48)	4.6 (±0.04)	8.6 (±0.26)
OMT 6 wt%	201 (±11.9)	0.14 (±0.01); 0.19 (±0.09); 0.49 (±0.09)	87 (±1.73)	110.5 (±2.10)	4.6 (±0.03)	8.5 (±0.31)
OMT 8 wt%	205 (±3.4)	0.18 (±0.08); 0.24 (±0.08); 0.91 (±0.09)	82 (±1.91)	102.4 (±1.95)	3.9 (±0.06)	7.9 (±0.26)

Rating chart

Table S4. Rating table for Fig. 9* [44, 47-49].

Variable	Alumina	GO	MOFs	OMT	TiO_2
Permeate flux ($kg\ m^{-2}\ h^{-2}$)	0.4 / 1.5	0.9 / 3.6	0.8 / 3.0	0.9 / 3.6	0.3 / 1.1
Liquid entry pressure (bar)	0.1 / 1.0	0.5 / 4.6	0.5 / 4.6	0.5 / 4.6	1 / 10
Contact angle (°)	0.9 / 145	0.5 / 73	0.5 / 81	0.7 / 111	0.9 / 136
Wetting Resistance	0.2	0.8	0.8	0.8	1
Cost ($/kg)	0.5 / 10.4	0.2 / 17.1	0.5 / 10.0	0.9 / 1.6	0.8 / 3.2
Availability	1	0.6	0.8	0.8	1

* The actual values used to derive the scores for the quantitative criteria (permeate flux, LEP, CA and cost) are shown in the bottom right-hand corner. The scores were derived qualitatively using the authors' judgement for the availability criteria.

The performance of five different material fillers was evaluated in Fig. 9 of the main article using a rating table. The evaluation was based on five performance criteria, with a score from 0 to 1 assigned to each material filler. A score of 1 was assigned to the best-performing material, and all criteria were equally important. Higher scores were preferred.

'Permeate flux' scores are based on the rate at which water vapour passes through the membrane ($kg\ m^{-2}\ h^{-1}$). In this case, a corrected flux was utilized, given by the temperature correction from the Arrhenius equation, to make a more fair comparison of the fluxes for different temperatures. The equation is used as follows: $F_c = F * \left(T_{ref}/T\right)^{\beta}$; where F_c is the corrected flux ($kg\ m^{-2}\ h^{-1}$), F is the actual permeate flux ($kg\ m^{-2}\ h^{-1}$), T_{ref} is the reference temperature (25 °C), T is the temperature in which the experiment was performed (°C), and β is the temperature correction exponent (equal to 1). 'Liquid entry pressure' scores are based on the pressure at which liquid begins to penetrate the membrane pores (bar). 'Contact angle' scores depend on the angle formed between the liquid and solid surface of the membrane (°). 'Wetting resistance' scores are based on a combination of values of the LEP and contact angle, as follows: 1 for LEP >4 bar and CA >150 °, 0.8 for LEP >4 bar and CA <150 °, 0.6 for LEP >2 bar and CA <110 °, 0.4 for LEP >2 bar and CA <90 °, 0.2 for LEP <2 bar and CA >90 °, and 0 for LEP <2 bar and CA <90 °. 'Cost' scores are based on the monetary expense of acquiring the raw material ($USD/kg). 'Availability' scores are based on the extent to which the necessary raw materials are accessible or obtainable.