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Multi-walled carbon nanotube/PVDF blended membranes with sponge- and finger-like pores for direct contact membrane distillation

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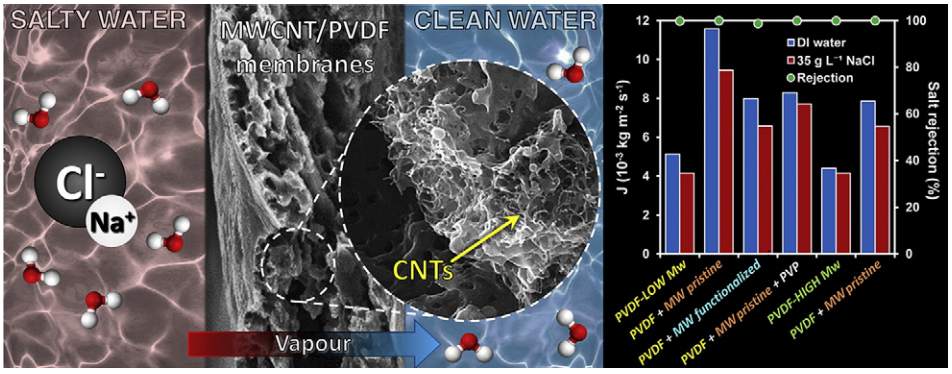
HIGHLIGHTS

- MWCNT/PVDF blended membranes prepared by phase inversion method
- Membranes tested in direct contact membrane distillation (DCMD) of salty water
- Large sponge-like pores and small membrane thickness allow complete salt rejection.
- Functionalization of MWCNTs and PVP addition are not recommended.
- The membrane with 0.2 wt.% of pristine MWCNTs exhibited the best performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Polyvinylidene fluoride (PVDF) flat sheet membranes were blended with multi-walled carbon nanotubes (MWCNTs) by the phase inversion method for direct contact membrane distillation (DCMD) of salty water (35 g L^{-1} NaCl). The membrane properties and performances depended markedly on the synthesis parameters such as MWCNT loading, polyvinylpyrrolidone (PVP) addition and MWCNT surface chemistry. MWCNT/PVDF membranes prepared with functionalized MWCNTs have a smaller pore size (determined by bubble point measurements) and lower contact angles, thus, functionalization of MWCNTs is not recommended for this application. For membranes presenting the same pore size, the pore morphology and the membrane thickness are crucial for efficient salt rejection. Sponge-like pores and the smallest possible thickness (i.e., membranes prepared without PVP) allow complete salt rejection (i.e., 100%), in contrast with larger thickness and elongated finger-like pores (resulting from PVP addition) whose salt exclusion ranged from 88.8 to 98.6%. Overall, the MWCNT/PVDF blended membrane prepared with 0.2 wt.% optimal content of pristine MWCNTs (without adding PVP) exhibited the best performance in DCMD, presenting total salt rejection and a higher permeate flux (9.5×10^{-3} kg m^{-2} s^{-1}) than that obtained with a commercial PVDF membrane (7.8×10^{-3} kg m^{-2} s^{-1}).

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1. Introduction

Water scarcity is among the main concerns to be faced by humankind in the 21st century. Growing population and economic expansion are the major factors affecting the availability of freshwater resources. Changes in production, consumption patterns, markets and policies

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have led to increasing domestic, industrial and agricultural water requirements [1]. Food security, industrial productivity, public health and environmental sustainability might be compromised if no technological improvements or policy changes are met. The adoption of technologies based on desalination can contribute for the development of alternative water sources and risk minimization.

Water desalination can be performed by several processes generally based on interactions with selective membranes, thermal distillation and/or application of electric fields [2]. Some of the conventional technologies include reverse osmosis (RO), electrodialysis (ED) or primary thermal distillation (TD) processes (such as multi-stage flash distillation, multi-effect distillation and thermal vapour compression), but RO is still the main route for water desalination. In particular, separation processes driven by improved membranes have received increasing attention from researchers, motivated by the needs in the industrial sectors. New technologies, such as membrane distillation (MD) and forward osmosis (FO), are seen as potential alternatives to the currently leading RO desalination technology. MD presents several advantages such as high rejection rates, theoretically total exclusion (100%) of non-volatile solutes, low operating temperature and hydrostatic pressure and, thus, less demanding mechanical resistance for the membrane applied [3].

MD is a non-isothermal process based on the vapour pressure difference (driving force) resulting from the thermal gradient generated at both sides of a porous hydrophobic membrane, which prevents liquid water to enter into the pores until overcoming a specific pressure difference, known as the liquid entry pressure (LEP). Thus, the membrane acts as a barrier through which only vapour molecules pass and then condensate on the permeate side. For this reason, low thermal conductivity (to avoid heat losses), high chemical resistance, good thermal stability, as well as appropriate pore size, thickness, surface roughness, hydrophobicity and porosity, are properties determining the membrane efficiency. Besides the membrane intrinsic characteristics, various operating parameters, such as feed temperature, flow rates, feed concentration, module design and respective hydrodynamic conditions, also determine the performance in MD processes [4–6]. For instance, Shirazi et al. [4] observed a higher permeate flux by increasing the flow rate of hot stream, the module depth on the cold side and the feed temperature, the last being the most important parameter in their study.

Direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), vacuum membrane distillation (VMD) and air gap membrane distillation (AGMD) are the main MD configurations [3] and, among them, DCMD is the most frequently applied in lab-scale experiments, since it allows a better assessment of the membrane properties [7]. However, this technology has not yet been widely implemented at the industrial level due to challenges related with the module design, cost effectiveness, flux decay, permeate flow rate, possible membrane pore wetting, and energy efficiency when the process is not assisted using renewable sources of energy [8].

New research paradigms, involving the combination of nanotechnology and separation sciences, have resulted in promising solutions to overcome some of the membrane engineering issues. For instance, carbon nanotubes (CNTs) are an interesting option to improve the membrane performances due to their mechanical properties [9–11]. Compared to conventional MD membranes, the immobilization of CNTs in polymeric matrices (e.g., polyvinylidene fluoride — PVDF), resulting in the so-called mixed matrix membranes (MMMs), can reduce the required operating temperature of the MD process while increasing the water fluxes [12]. For instance, the beneficial effect of CNTs on MMMs has been reported for polyamide membranes, and ascribed to the improved mechanical resistance of the membrane (toughness and tensile strength) and both salt and organic matter rejection [13]. Other studies dealing with self-supporting and supported CNT membranes, known as buckypapers, have already demonstrated the successful application of CNT membranes in DCMD for synthetic water desalination [14–17]. The CNT membranes can have improved properties (i.e., high contact angle, high porosity and relatively low conductivity) when compared with most of the commercially available polymeric membranes applied in MD. Despite their remarkable properties, the CNT tendency to form bundles by means of strong intrinsic van der Waals forces between the tubes [18], as well as their inert graphitic surface, may result in a poor interaction with the polymer when composites are prepared, in some cases limiting the CNTs effective dispersion.

In order to address this issue, CNT edges and sidewalls can be functionalized, enhancing the durability and stability of the membrane structure. Chemical functionalization of CNTs, by using treatments in gas or liquid phases, allows controlling the CNT surface chemistry, some functional groups turning the surface more hydrophilic and, as consequence, improving their dispersion in specific solvents. This will also affect the membrane properties, promoting attractive or repulsive interactions depending on the target solute [19]. In our previous work [16], multi-walled carbon nanotubes (MWCNTs) were used to prepare buckypapers over a polytetrafluoroethylene (PTFE) commercial membrane. The resulting membranes were tested in DCMD under salinity conditions, a significant enhancement on the permeate flux and a total rejection of chloride ions being observed when using functionalized CNTs instead of the pristine ones. In addition, a correlation between the permeate flux and the amount of oxygen functional groups of the MWCNTs was obtained.

In the present work, MWCNTs are used to prepare PVDF blended membranes, instead of buckypapers, studying different synthesis parameters such as the loading and surface chemistry of the MWCNTs, pore former loading and PVDF molecular weight (M_W). The resulting MWCNT/PVDF blended membranes are tested in DCMD of salty water and the membrane properties correlated with the performance obtained in terms of water permeation and salt rejection.

2. Experimental

2.1. Materials

Two different polyvinylidene fluoride (PVDF) polymers were used to prepare the membranes, one purchased from Alfa Aesar (Alfa Aesar® 44080, labelled as "A") and another kindly supplied by Solvay (Solef® 1015, labelled as "S"). Polyvinylpyrrolidone (PVP or P) was used as a pore former agent and 1-methyl-2-pyrrolidinone (NMP, anhydrous, 99.5% and density of 1.03 g mL^{-1}) as solvent; both reagents were purchased from Sigma-Aldrich. Some physical properties of the PVP and PVDF polymers are collected in Table 1. NMP was used as a solvent since it allows dissolving the PVDF polymer at a relative low temperature and because the CNT dispersion (functionalized or pristine) was more effective in NMP than in other solvents, like *N*,*N*-dimethylformamide (DMF). In addition, the NMP toxicity is relatively lower than that of DMF. Pristine MWCNTs prepared by CVD were supplied by Nanocyl™ (NC3100 series). MWCNTs presented a carbon purity of >95 wt.%, outer diameter of 9.5 nm, average length of 1.5 μm and an ash content of <5 wt.%. Commercial PVDF membranes (GVHP Durapore® with 0.22 μm pore size, 125 μm thickness and 25 mm diameter) were purchased from Millipore and employed as reference.

Table 1
Properties of used polymers supplied by the manufacturers.

Nomenclature	Type of polymer	M_w (kDa)	Viscosity[a] (Pa s)	Density (g cm^{-3})	Melting point (°C)
"P"	Polyvinylpyrrolidone	10	NA	1.20	>130
"A"	Alfa Aesar® 44080	~350	2350–2950	1.78	155–160
"S"	Solef® 1015	573	2800–3800	1.78	171–175

NA — not available.
[a] Determined at 230 °C and 100/s.

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