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# AN EXPLORATIVE STUDY ON THE POTENTIAL OF 2D MATERIALS-BASED MEMBRANES FOR ENHANCED WATER DESALINATION PROCESSES

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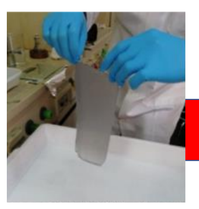
## Aim of the Work

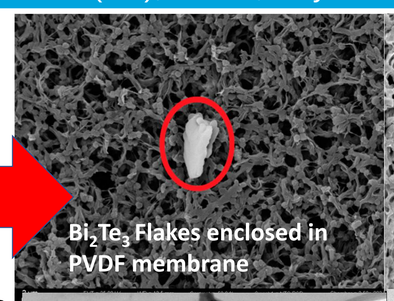
Water scarcity forces the science to find the most environmentally friendly propulsion technology for supplying plentiful freshwater at low energy costs. Membrane distillation (MD) and membrane crystallization (MCr) well meet criteria of eco-friendly management of natural resources such as seawater. However they are not yet competitive on scale due to the low availability of membranes enabling fruitful purification processes. Production of freshwater and energy consumption are still somewhat distant from the desired targets. So, there is insistence to identify frontier materials, which can make membrane distillation and crystallization processes breakthrough for productivity of freshwater at high energy efficiency and recovery of reusable products. Herein, new 2D materials engineered membranes are proposed for enhanced water desalination. These membranes are used to equip MD and MCr devices, leading to high productivity-efficiency trade-offs.

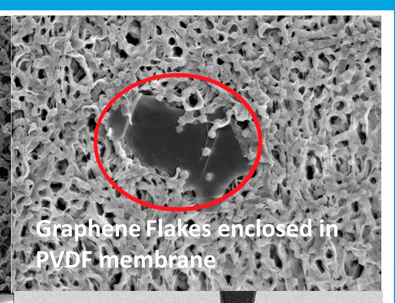
**MD AND MCR PROCESSES REPRESENT AN ECO-SUSTAINABLE SOLUTION FOR FRESHWATER AND REUSABLE SALTS RECOVERY**

## Membrane Fabrication

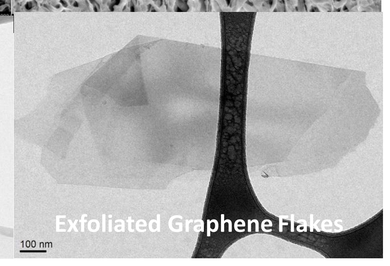


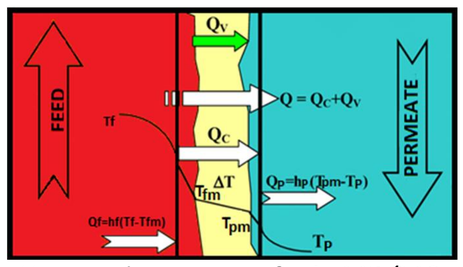
Graphene and Bismuth Telluride were exfoliated via wet-jet milling (WJM) technique and were added with PVDF under controlled thermal conditions. After a mechanical stirring of 24 h, the mixtures were cast and coagulated in a soft bath containing 2-propanol. In this way, phase separation was induced and porous membranes entrapping few layers 2D materials were formed.







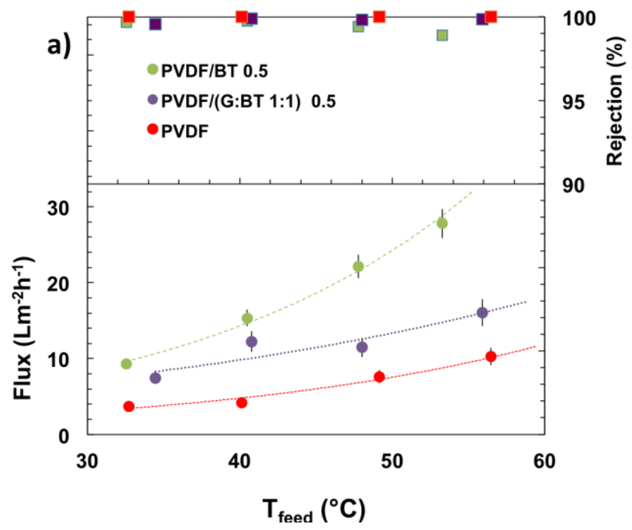

*Heat and mass transfer in MD/MCr*

Morphological parameters estimated for pristine and PVDF/2D materials membranes

| Membrane | Filler | Contact Angle (°) | Thickness (μm) | Mean pore size (μm) | Porosity (%) |
|---|---|---|---|---|---|
| **PVDF** | No filler | 139±3 | 71±3 | 0.52±0.05 | 82±4 |
| **PVDF/BT(7%)** | $Bi_2Te_3$ | 130±2 | 100±5 | 0.50±0.08 | 77±1 |
| **PVDF/BT(0.5%)** | $Bi_2Te_3$ | 128±8 | 68±1 | 0.5±0.2 | 75±1 |
| **PVDF/G (0.5%)** | Graphene | 136±1 | 62±3 | 0.24±0.05 | 56±7 |
| **PVDF/(G:BT)(1:1)** | $Bi_2Te_3$/graphene | 135 ± 2 | 65±5 | 0.40±0.06 | 55±3 |

## Membrane Distillation (MD)

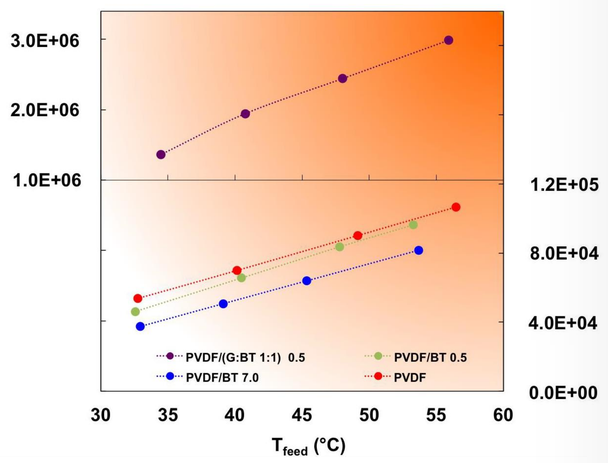
MD experiments were executed accordingly with the Membrane Direct Contact (DC) configuration using NaCl solutions 0.6 M (35 g/L, synthetic seawater) – flow rate = 100 to 300 mL/min; $T_{feed}$ = 33 to 58.8°C and $T_{perm}$ ~11°C.



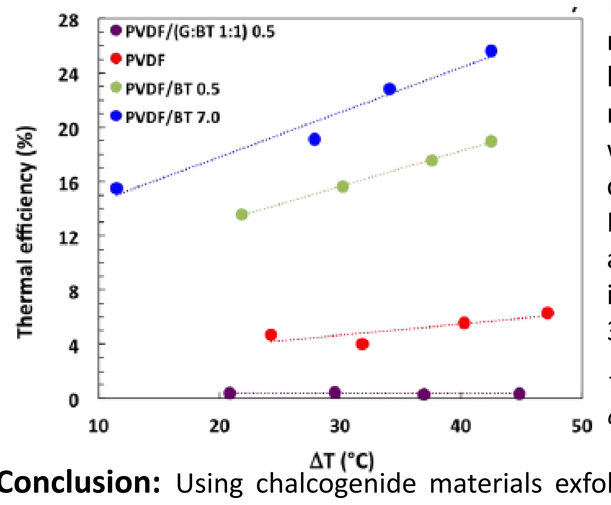

*Flux and rejection values estimated for PVDF, PVDF/(BT:G 0.5) (1:1) and PVDF/BT 0.5 membranes: Tfeed, 32-55 °C*

Lessening of heat dissipation around 190% at 32°C and 170% at 53°C is obtained with the PVDF/BT 7 membrane. $Bi_2Te_3$ is one of the best thermoelectric materials with the highest thermoelectric figure of merit, ZT (~1.1-1.2). Synergistic effects may reasonably enhance the ability of $Bi_2Te_3$-enabled membranes to restore the driving force thus maximizing the productivity. This beneficial effect is contrasted in PVDF/(BT:G) 0.5. Few layer graphene causes a heat loss higher than one order of magnitude as compared with the other membrane-types, sacrificing the driving force.

It is interesting to observe how the PVDF/BT 0.5 membrane has higher ability to transfer water vapor when a difference of temperature is applied across the matrix. Exponential intensification in the flux is targeted up to 27.8 LMH at 53°C. The membrane containing BT in mixture with G (1:1) continues to exhibit a constant increase in the mass transfer when compared to the pristine PVDF membrane. It is however important to remark that membranes filled with BT shows the highest trans-membrane fluxes with a pronounced exponential trend at higher temperature.
The salt rejection ranging from 99.99 to 100 %




*Heat flow estimated for all membranes within the overall range of temperature and at flow rate of 100 mL/min*



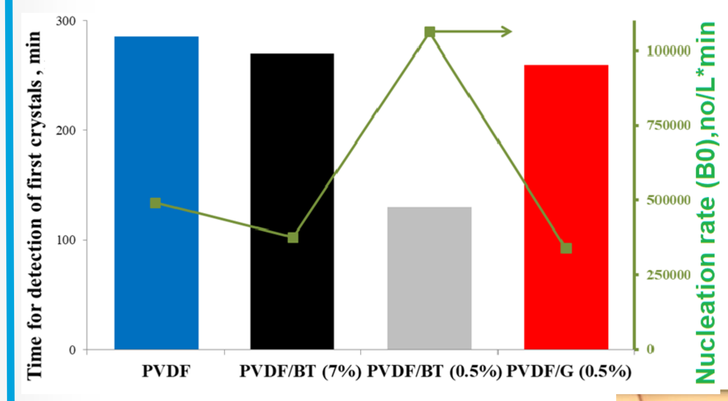

The thermal efficiency in MD can be specified as the ratio of latent heat of vaporization to the total - latent and conduction - heat. BT-enabled membranes show the best capability to promote water vapor transfer while contrasting heat conduction. An increase of 65% is estimated for PVDF/BT 7 when the difference of the temperature across the membrane is increased; the intensification is of 40% for PVDF/BT 0.5 against the 34% for the pristine PVDF membrane.

*Thermal efficiency estimated for all membranes within the overall range of temperature at flow rate of 100 mLm/min*

## Membrane Crystallization (MCr)

MCr experiments were executed in Direct Contact (DC) configuration using high concentrated NaCl solution (5 M) as feed and distillate water as permeate. Feed and permeate flow rate= 250 and 100mL/min respectively; $T_{feed}$ = 33 to 58.8°C and $T_{perm}$ ~11 °C.

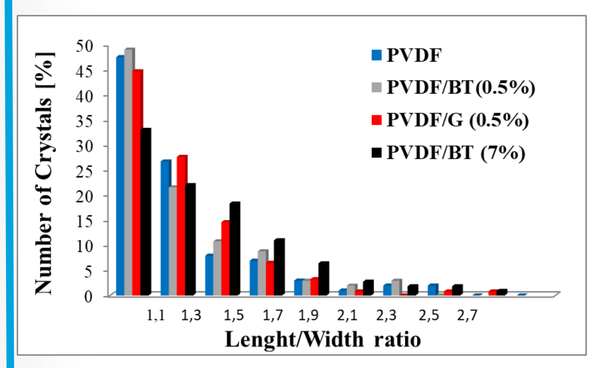
Under the same operating conditions, PVDF/BT (7%) membrane exhibited flux higher than the other 2D enabled membranes, (3.9 $L{\cdot}m^{-2}h^{-1}$) while PVDF/BT (0.5%) and PVDF/G (0.5%) showed an average flux of 2.7 LMH and 1.6 LMH, respectively. The confinement of graphene and bismuth telluride in polymeric hydrophobic matrices has produced a more uniform NaCl crystals dispersion (especially in the case of PVDF/G (0.5%) membrane) and reduced the time for detection of the first clearly visible crystals (from 285 minutes in the case of PVDF-pristine membrane to 140 minutes in the case of PVDF/BT (0.5%)).



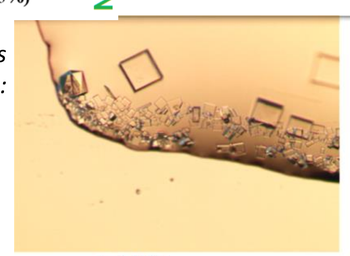

The most part of achieved crystals showed the characteristic cubic block-like form in accordance with the expected geometry of the NaCl crystals, particularly in the case of PVDF/BT (0.5%).

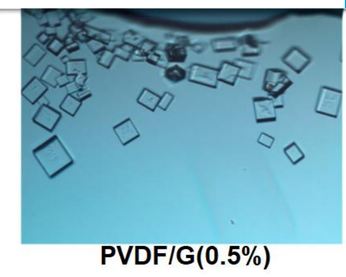
*Time for detection of the first crystals and nucleation rate for the PVDF-pristine membrane and PVDF functionalized membrane*

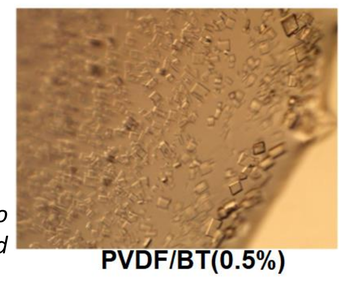
*Pictures collected on the first sample of NaCl crystals obtained with the different analysed membranes: PVDF, PVDF/G (0.5%), PVDF/BT (0.5%), PVDF/BT(7%)*

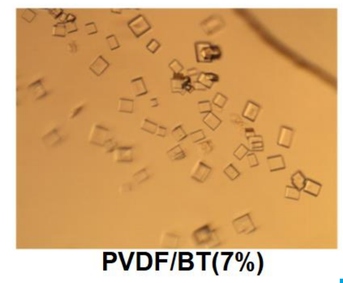


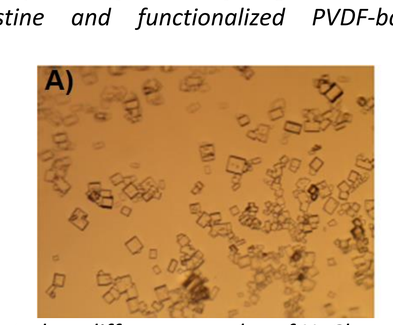

*Percentage of crystals in function of length/width ratio for the pristine and functionalized PVDF-based membranes*

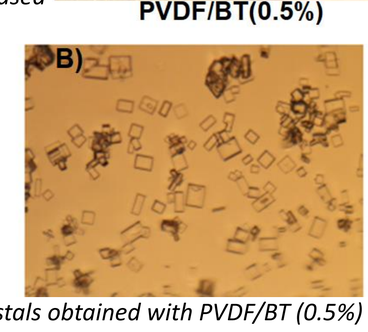

PVDF

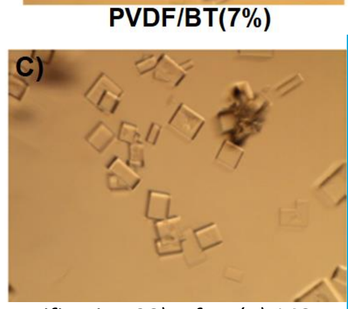

PVDF/G(0.5%)


PVDF/BT(0.5%)


PVDF/BT(7%)




*Pictures collected on different samples of NaCl crystals obtained with PVDF/BT (0.5%) (magnification 20): after (**a**) 140, (**b**) 170 and (**c**) 200 min.*

**Conclusion:** Using chalcogenide materials exfoliated in dispersant liquid phase, we demonstrate $Bi_2Te_3$- enabled membranes for ultrafast and energy-saving recovery of freshwater. We show that MD technology can change its own performance when topological compounds are confined in membranes for water desalination purposes. Our experiments provide clear evidence about the capability of BT-enabled membranes to increase effectively mass transfer reducing heat loss simultaneously. High-quality freshwater can be produced reducing energy and working in more eco-sustainable way. The experimental evidence reported in this work makes the combination of chalcogenides materials and membrane technology more realistic for water desalination purpose. We also demonstrate that the confinement of graphene and bismuth telluride in polymeric hydrophobic matrices produces a more uniform NaCl crystals dispersion (especially in the case of PVDF/G (0.5%)) at reduced detection time for the first clearly visible. The achieved results confirm the effectiveness of 2D materials as frontier materials for new-concept water desalination through breakthrough thermally-driven membrane distillation and crystallization, which are regarded as new low-energy and sustainable solutions to address the growing demand for access to freshwater and recovery of salt crystals to reuse in agricultue and industry cycles.

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