UNIVERSITÀ DELLA CALABRIA
DIPARTIMENTO DI **INGEGNERIA DELL'AMBIENTE**

Preparation of Nanocomposite Membranes based on Metal-Organic Frameworks for selective recovery of Valuable Metals and Minerals from seawater brine.

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Introduction

Valuable Metals and Minerals (M&M) mining is an industrial process with a considerable environmental impact; therefore, in the last few years, the need for exploring new mining techniques and alternative sources of raw materials emerged. In this scenario, seawater desalination brines, the byproducts of Reverse Osmosis plants, have gained more attention for selective extraction of M&M, being rich of soluble salts.
On these basis, it has been proved that Metal Organic Frameworks (MOFs) - an emerging class of crystalline materials with a topological porous structure consisting of the coordination of metal ions or clusters with organic ligands [1] - can guarantee selectivity towards specific metal ions, ensuring their recovery form complex solutions [2].

Objective

- Development of functional coating incorporating MOFs sprayed on the surface of commercial Polyvinylidene Fluoride (PVDF) membranes;
- Heterogeneous Nucleation and crystallization under sunlight irradiation of sodium chloride solutions.

Materials and Methods

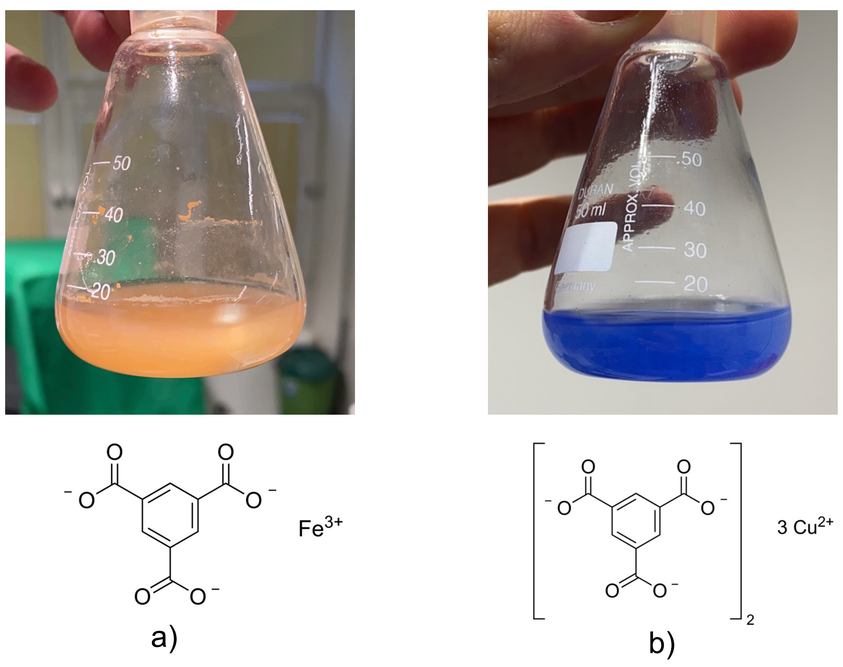
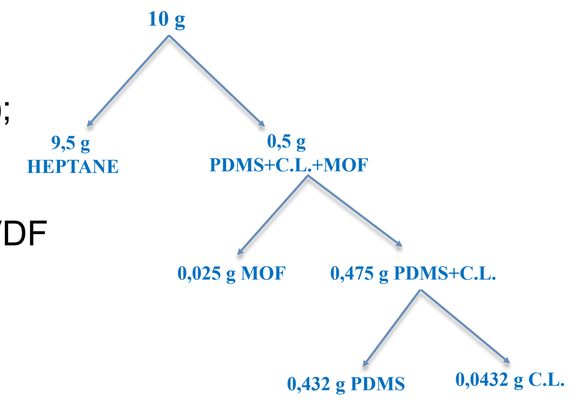


Figure 1. Mixture and corresponding chemical structure of: a) Basolite F300 and b) Basolite C300. Solvent: n-Heptane.

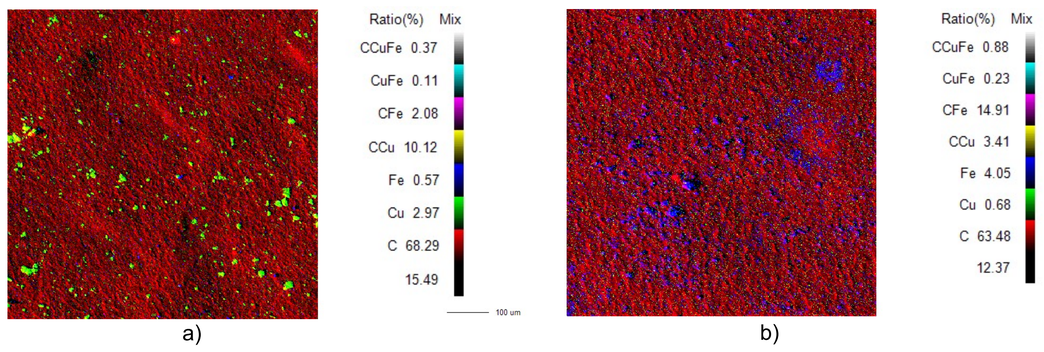
Commercial Basolite F 300 (Iron 1,3,5 benzenetricarboxylate) and C 300 (Copper benzene-1,3,5-tricarboxylate) were:

- ✓ Dispersed in n-Heptane via sonication (Figure 1);
- ✓ Mixed with a solution of Polydimethyl siloxane (PDMS) and appropriate cross-linker;
- ✓ Spray coated on the surface of a commercial PVDF membrane kindly supplied by GVS Spa (Italy);
- ✓ Cured in oven for 1 hr at 60°C.



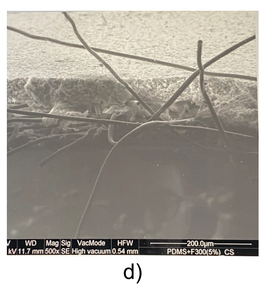
MOFs concentration was varied from 2,5% to 5,0% with respect to the polymer mass. For the crystallization tests, membranes were inserted in Polylactic Acid (PLA) tailor-made modules produced with a 3D printer. Experiments were conducted under sunlight exposure (30°C, 35% RH).

Membrane Characterization



Membrane	Porosity (%)	Bubble Point (bar)	Mean Pore size (μm)
PVDF	58,57	0,759	0,28
C300 2,5%	56,05	0,742	0,272
C300 5%	59,31	0,718	0,295
F300 2,5%	55,23	0,765	0,281
F300 5%	58,15	0,778	0,275

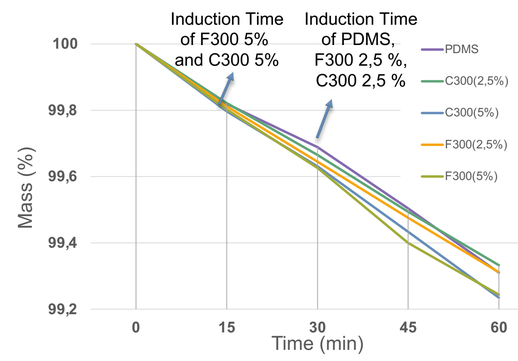
c)



d)

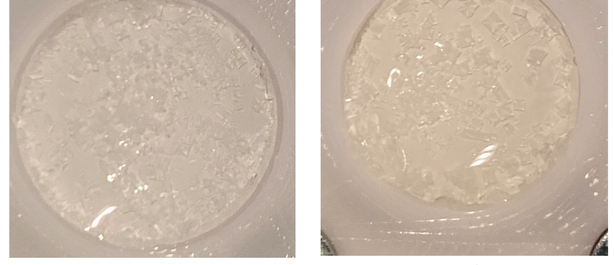
As from EDX analysis, Copper (a) and Iron (b) are spread nearly homogeneously on the surface of PVDF membranes. Morphological properties of the functionalized membranes are not affected by the coating (Table c) a membrane characterization with the main parameters to compare the Spray coated membranes with PVDF not treated.
A SEM micrograph of the cross-section of a PVDF membrane loaded with F300 5% is shown in Figure d.

Crystallization



Crystals grown on the surface of the F300 membranes at different loads: 2.5% (a), 5% (b).

The graph on the left shows the trend of saline solution mass versus time during the sunlight crystallization experiments. Induction times show a higher nucleation rate on the F300 5% and C300 5% membranes.



Conclusions

1) Deposition of the MOFs based coating didn't affect significantly the porosity and mean pore size of PVDF membranes;

2) the presence of MOFs on the membrane surface facilitate the nucleation of NaCl crystals.

Bibliography: [1] H.Mao et al. Journal of Membrane Science 573 (2018) 344–358.
[2] D.T. Sun et al. ACS Central Science 4 (2018) 349–356.

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