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# Preparation and Characterization of Flat Sheet Polymeric Membranes: Application to the Removal of Humic Acids from Mediterranean Seawater

Z. Tigrine <sup>1\*</sup>, S. Hout<sup>1</sup>, O. Benhabiles<sup>1</sup>, L. Merabti<sup>1</sup>, S. Mahidine<sup>1</sup>, F.K. Benabdelaziz<sup>1</sup>, Z. Belgroun<sup>1</sup>, F.Z. Yahiaoui<sup>1</sup>, C. Torki<sup>1</sup>, D. Tassalit<sup>1</sup>

<sup>1</sup>Unité de Développement des Equipements Solaires, UDES/Centre de Développement des Energies Renouvelables, CDER, Bou-Ismaïl 42415, W. Tipaza, Algeria.

\*Corresponding author's email: phyzahia@yahoo.fr

## ABSTRACT

Membrane separation is an effective and versatile technology widely used for water purification. Organic membranes are increasingly emerging as a sustainable and potentially cost-effective alternative to inorganic membranes used for water treatment and other separation processes. They can exhibit good selectivity and permeability for specific applications. The membrane fabrication technique depends on several factors, including desired membrane properties, material selection, cost and environmental impact. In this work, organic flat-sheet membranes have been prepared for water pretreatment. Polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF) porous membranes were prepared by non-solvent-induced phase separation method (NIPS). The membranes were made by different compositions of solvent. The prepared membranes were characterized using spectroscopic methods (SEM, XRD, FTIR) in order to determine the morphology and size of the pores, the thickness, the permeability and the retention of certain compounds. The results obtained from the SEM showed that the membranes developed are ultrafiltration membranes with specific morphological shapes and porous surfaces. Micrographs of samples present morphologies that corroborate with the efficiency. The results indicate that PVDF porous membrane show good performance for the application of humic acid elimination. Moreover, the performance of the prepared membranes was determined by PWF and humic acid rejection.

**Keywords:** Polymers, Membrane elaboration, Phase separation, Hydrophilic membrane, Ultrafiltration, Membrane characterization, Humic acid.

## 1 Introduction

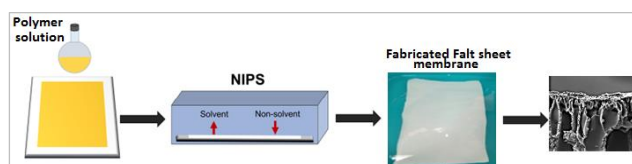
Various polymers are selected as membrane materials during membrane manufacturing based on their good physical and chemical characteristics such as high filtration performance, good fouling resistance, environmental tolerance as well as easy processing [1-3]. The fabrication of organic membranes holds great promise for sustainable and efficient separation processes. With continued research and development, this technology is set to play an increasingly important role in solving the world's water and environmental problems. To determine the type of membrane, it is necessary to characterize the different membranes according to their physical and structural properties. In fact, measurements of water contact angle and surface charge provide information on the hydrophilicity/hydrophobicity and surface charge of the membrane, which has an impact on its resistance to fouling and its interaction with contaminants [4]. By evaluating parameters such as permeability, selectivity and rejection rate under controlled conditions, we can assess the membrane's efficiency in separating specific components from a mixture. Characterization therefore plays a key role in determining the type of membrane and its successful application in various fields, including water treatment, desalination, bioprocessing and gas separation [5-7]. In this study, various organic membranes were prepared for water pretreatment. Membranes based on polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF) were prepared using the non-solvent-induced phase separation (NIPS) method. The water content and pure water permeability tests were carried out. The performance of the prepared membranes was evaluated using different types of water to be treated. In addition, conventional



filtration combined with prepared membranes provided better results in terms of reducing turbidity, conductivity and salinity.

## 2 Method and materials

Membrane films were manufactured by spreading a solvent/polymer solution on a glass substrate, previously cleaned with acetone. A cast polymer solution film was instantly immersed in a coagulation bath containing osmosis water at ambient temperature. This phase is crucial for promoting solvent-non-solvent exchange (fast mass transfer), which leads to solidification and film formation creating a porous structure within the membrane film.



**Figure 1.** Scheme of the membrane preparation using NIPS technique

The performance of a membrane is assessed using a parameter called permeable water flux (PWF). It is a critical parameter because it directly relates to the membrane's efficiency in terms of water transport. Before the permeation tests, the membranes undergo compaction by applying 2.5 bar pressure with pure water until the water flux become stable. Compacting the membrane reduces its porosity and its structure can become slightly denser, which can lead to more consistent permeation behavior and reduce the risk of rapid initial changes in water flow during the actual test. The PWF was then measured for different pressure values. The permeate water was collected and weighed over a given period and the PWF was calculated using the formula  $PWF = J / (S \cdot t)$  where  $J$  is the mass of permeate water (kg),  $S$  is the effective membrane surface area (m<sup>2</sup>), and  $t$  is the permeate water collection time (h). The developed membranes were tested in a cross-flow membrane filtration system whose active surface area used is 17.34 cm<sup>2</sup>, Fig 2.

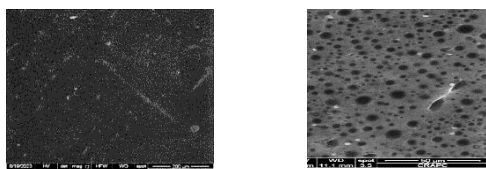


**Figure 2.** Photograph of the PVDF membrane in a filtration system before and after clogging (view of the active surface and the underside)

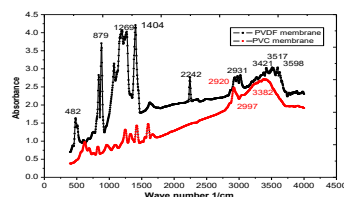
## 3 Results and discussion

Figure 3 shows SEM images of the active surface of the prepared membranes. The PVDF-based membrane had a porous structure of different sizes, while the PVC-based membrane had a porous but denser surface.

Figure 4 shows a comparison of the FTIR spectra of PVDF and PVC membranes, the results of which indicate a structural difference between them. We observe that the evolution of the spectrum of the membrane based on PVC is completely comparable to that of the membrane based on PVDF and this tells us about the similarity of their functional groups. According to these results, the spectra are divided into three regions: the region of simple bonds between (2750-4000 cm<sup>-1</sup>), the region of doubles and triples and bonds (1800-2750 cm<sup>-1</sup>) and the chemical fingerprint region (500-1750cm<sup>-1</sup>). In particular, seawater is contaminated with humic acid (HA), and its removal is essential during the pretreatment stage preceding desalination by reverse osmosis. For this reason, we have attempted to synthesize an organic membrane to remove traces of organic and inorganic elements such as HA, as the associated humic acid molecules have a complex structure that easily promotes clogging of reverse osmosis membranes and hence greater resistance to feedwater flow.



**Figure 3.** SEM images of the PVDF membrane (200 $\mu$ m, 50 $\mu$ m)



**Figure 4.** FTIR spectra of PVDF and PVC membranes

For each experiment, the PWF permeability of each membrane was measured at room temperature. The filtration results show that the PWF of the PVC membrane reaches 87.42 L/h.m<sup>2</sup>.bar compared with 171.069 L/h.m<sup>2</sup>.bar for the PVDF membrane at a pressure of 2 bar. The results of filtration of pure water containing humic acids at different concentrations using absorbance measured before and after membrane treatment are evaluated. We note that the humic acid removal rate (70%) becomes relatively constant from a concentration of 20 mg/L.

#### 4 Conclusion

The main objective of this work is the elaboration and characterization of flat organic membranes based on polymers (PVDF and PVC) using the phase inversion method for their application to the pretreatment of Mediterranean seawater (Bou Ismail region/Algeria). It was found that the type of material used significantly affected the membrane structure, which was supported by the filtration performance. Therefore, it is confirmed that the synthesized membranes are ultrafiltration membranes. The PVDF membrane demonstrated significantly improved properties and performance for humic acid rejection rate.

#### 5 Acknowledgements

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#### References

- [1] M. Ulbricht, Advanced functional polymer membranes, *Polymer*, 47 (2006) 2217-2262.
- [2] G. Kang, Y. Cao, Application and modification of poly(vinylidene fluoride) (PVDF) membranes – A review, *Journal of Membrane Science*, Volume 463, 2014, Pages 145-165, ISSN 0376-7388, <https://doi.org/10.1016/j.memsci.2014.03.055>.
- [3] M.B. Thürmer, P. Poletto, M. Marcolin, J. Duarte, M. Zeni, Effect of non-solvents used in the coagulation bath on morphology of PVDF membranes, *Mat. Res.* 15 (2012) 884–890.
- [4] R. Thomas, E. Guillen-Burrieza, H.A. Arafat, Pore structure control of PVDF membranes using a 2-stage coagulation bath phase inversion process for application in membrane distillation (MD), *J. Membr. Sci.* 452 (2014) 470–480. membranes – A review, *J. Membr. Sci.* 463 (2014) 145–165.
- [5] Lei Wang, Danxi Huang, Xudong Wang, Xiaorong Meng, Yongtao Lv, Xin Wang, Rui Miao. Preparation of PVDF membranes via the low-temperature TIPS method with diluent mixtures: The role of coagulation conditions and cooling rate. *Desalination*, Volume 361, 1 April 2015, Pages 25-37. <https://doi.org/10.1016/j.desal.2015.01.039>.