Development of Fenton-Type Catalytic Membrane for Membrane Distillation

POSTER
Ph.D. Student: Y/N
Journal: XXX

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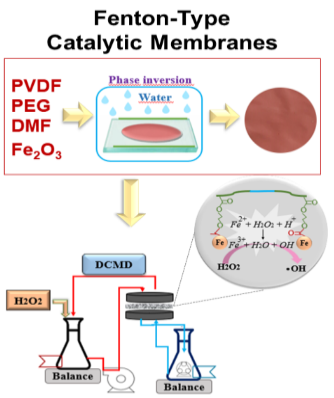

This study developed and evaluated an innovative Fenton-type catalytic membrane for application in Membrane Distillation (MD), using Fe_2O_3 as a catalyst and PVDF as a polymeric matrix. The phase inversion technique was employed in the membrane fabrication, resulting in a porous structure with uniformly distributed Fe_2O_3 nanoparticles. The addition of Fe_2O_3 increased the hydrophobicity and roughness of the membranes, reducing fouling. The Fenton-type catalytic membrane showed higher permeate flux compared to conventional membranes, both for water and acid dye treatment, due to its greater efficiency in mass and heat transfer and oxidation of organic contaminants. These characteristics highlight the importance of Fenton-type catalytic membranes in MD, offering high efficiency, selectivity, and fouling resistance.

Introduction

In recent years, Membrane Distillation (MD) has emerged as a promising solution for water treatment, leveraging its high efficiency and selective separation capacity [1]. Despite the advantages of MD, operational challenges such as temperature polarization and membrane fouling have limited its industrial application [2]. Recently, catalytic membranes have been developed as an innovative solution, integrating catalysis and membrane filtration. These membranes offer advantages in efficiency, selectivity, and energy savings, providing a high-performance treatment and recovery system [3].

This study aimed to develop and evaluate a Fenton-type catalytic membrane for application in MD, using Fe_2O_3 (Iron Oxide) as a catalyst and polyvinylidene fluoride (PVDF) as a polymeric matrix. The physicochemical properties, water permeability, and catalytic performance of the membranes were investigated. It is important to highlight that, to the best of our knowledge, there are no reports in the literature on catalytic membranes developed with iron oxide-based catalysts specifically for membrane distillation applications.

Material and Methods

The Fenton-type catalytic membrane was prepared by the phase inversion process, in which a solution containing PVDF (15% w/w), polyethylene glycol 400 (PEG) (1% w/w), dimethylformamide (DMF) (81% w/w), and the Fe_2O_3 catalyst (3% w/w) was prepared by dissolving the components at 60°C for 4 h. After stirring, the solution was subjected to ultrasonic bath for 30 min and then allowed to cool for an additional 30 min to reach room temperature. The membranes were then immersed in a coagulation bath with distilled water for 24 h and dried for 24 h at room temperature. The membranes were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), Attenuated Total Reflectance Infrared spectroscopy (ATR-FTIR), Contact Angle (CA), Liquid Entry Pressure (LEP), thickness, and roughness. To validate the catalytic membranes in an MD operation, tests were conducted using distilled water and the textile dye Acid Black (AB) (Trimacid, CP 194) with a concentration of 1000 $mg.L^{-1}$, with a total time of 8 h for each experiment. The permeate flux J ($kg\cdot m^{-2}\cdot h^{-1}$) was calculated according to Equation 1, where ΔM is the mass of permeate (kg) at time Δt (h) of the process, and A is the effective area of the membrane (m^2).

$$J = \Delta M/(A\Delta t) \qquad (1)$$

For comparison purposes, the PVDF membrane was also synthesized without the addition of catalysts, identified as PV0, and the Fenton-type catalytic membrane as PTPI-Fe_2O_3.

Results and Discussion

In Figure 1, SEM, ATR-FTIR and EDX of the produced membranes are shown. The micrographs show that the Fenton-type catalytic membrane has a porous structure, with Fe_2O_3 nanoparticles uniformly distributed. The phase inversion technique was effective in functionalizing the Fe_2O_3 nanoparticles in the PVDF membrane, and through EDX analysis, the homogeneous distribution of the catalysts on the surface and within the pores of the membrane was confirmed. ATR-FTIR spectra showed new bands in the Fenton-type catalytic membrane, indicating the presence of Fe-OH and Fe-O groups.

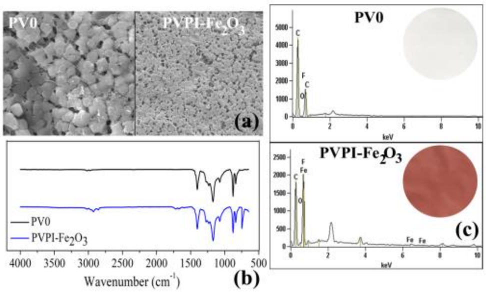

Figure 1. SEM (a), ATR-FTIR (b) and EDX (c) of intact membranes (PV0) and catalytic membrane (PVPI-Fe_2O_3).

Table 1 shows the results of contact angle, LEP, thickness, and roughness of intact and catalytic PVDF membrane. The addition of Fe_2O_3 catalyst increased the hydrophobicity of the membranes, as demonstrated by the increase in contact angle. Greater hydrophobicity contributes to the repulsion of solution droplets, hindering solute permeation. Additionally, increased surface roughness promoted the formation of air pockets between the membrane and the feed solution, reducing the effective contact area and improving the anti-fouling capacity of the membranes. The higher contact angle also resulted in a higher LEP, essential for maintaining MD process efficiency. The increased thickness of the catalytic membrane, within the ideal range for MD operation, provided additional benefits such as greater mechanical strength and efficiency in heat transfer.

The Fenton-type catalytic membrane exhibited higher permeate flux than the intact membrane for water permeability and in the treatment of acid dye from the textile industry. This was attributed to its greater hydrophobicity, roughness, LEP, and mechanical strength, which improved mass and heat transfer, positively affecting permeate flux. Additionally, specifically designed to optimize process efficiency, Fenton-type catalytic membranes provided high-quality permeate flux. The oxidation of organic contaminants by the Fenton catalyst reduced their concentration in the feed stream, resulting in increased permeate flux.

It was also observed that permeate fluxes for the acid dye were lower than for pure water, indicating a decrease in permeability due to the high load of organic contaminants. This reduction is attributed to the interaction between dye molecules and the chemical characteristics of the membranes. However, after 8h of continuous operation, all membranes achieved 100% dye rejection.

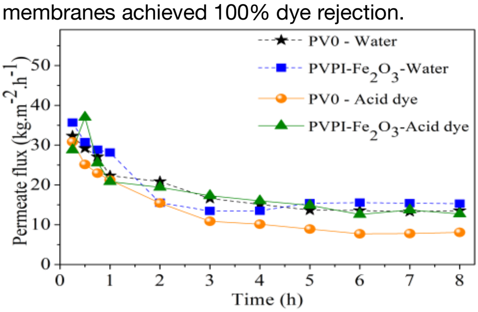

Figure 2. ATR-FTIR of the intact membranes (PV0) and the catalytic membrane (PVPI-Fe2O3).

Table 1. Contact angle, LEP and roughness of intact and catalytic PVDF membrane.

Membranes	Contact angle (°)	Roughness (nm)	LEP	Thickness
PV0	101.20 ± 0.01	27.00 ± 0.21	2.40 ± 0.02	140.00 ± 0.01
PVPI-Fe_2O_3	107.30 ± 0.66	60.00 ± 0.21	3.60 ± 0.01	140.00 ± 0.14

Conclusions

The Fenton-type catalytic membrane developed in this study represents a promising innovation for Membrane Distillation. With Fe_2O_3 as the catalyst and PVDF as the polymeric matrix, the membrane demonstrated effectiveness in reducing fouling and promoting efficient mass and heat transfer. Its ability to offer high efficiency, selectivity, and fouling resistance highlights its potential for industrial applications, providing a robust and effective solution for water treatment and recovery.

References

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