Hydrophobic Phase Inverted Polyethersulfone Mixed Matrix Membrane for Water-in-Oil Emulsion Separation

Abuhasheesh Y. H.[1], Hegab H. M.[1], Wadi V. S.[1], Naddeo, V.[2], Al Marzooqi F.[1], Banat F.[1], Aljundi H. I.[3,4], Hasan, S. W.[1,*]

[1]Center for Membranes and Advanced Water Technology (CMAT), Department of Chemical Engineering, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates
[2]Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno - Via Giovanni Paolo II #132, 84084 Fisciano (SA), Italy
[3]Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia
[4]Interdisciplinary Research Center for Membranes and Water Security, King Fahd University of Petroleum and Minerals, Saudi Arabia

*corresponding author:
e-mail: shadi.hasan@ku.ac.ae

Abstract. The limited access to clean water sources and the severe consequences of oil spills on the environment are of significant concern. Membrane technology showed superior performance to the other conventional techniques due to its higher performance, lower cost, ability to separate emulsions, and being more environmentally friendly. Emulsified water/oil emulsions are highly stable and have a small droplet size, hence are more challenging to separate than water/oil mixtures. Herein, hydrophobic iron oxide-oleylamine (Fe-Ol) nanomaterial was prepared and used to fabricate polyethersulfone (PES) mixed matrix membranes (MMMs) using non-solvent induced phase separation (NIPS). A similar procedure was used to fabricate pristine PES. The performance of the membranes in emulsion separation was tested using a dead-end vacuum filtration setup and a 1 vol.% water-in-n-hexane surfactant stabilized emulsion. The use of the hydrophobic Fe-Ol nanomaterial enhanced the separation efficiency of the membranes. The 1.5 wt.% PES/Fe-Ol MMM exhibited a 97.4% separation efficiency and a high filtrate flux of 1020 L/m^{2}h (LMH), hence, showing great potential in the application of water-in-oil separation.

Keywords: Membrane technology, Fe-Ol nanomaterial, hydrophobicity, oil-water, separation.

1. Introduction

The formation of oil layers on the water surface caused by oil spills can lead to harsh repercussions on the environment (Buskey, White, & Esbaugh, 2016). It highly affects marine creatures as they can get poisoned by this carcinogenic compound (Putatunda, Bhattacharya, Sen, & Bhattacharjee, 2019). Even though the number of oil spill accidents has decreased drastically in the past decade, we still face about 6 to 7 accidents annually (Galieriková & Materna, 2020). The implementation of membrane technology as a replacement for conventional methods to treat oil spills was widely studied by testing it on the separation of water/oil mixtures and water-in-oil emulsions. These emulsions are known for their lower-sized particles compared to water/oil mixtures, which makes them more stable and more challenging to separate (Esmaeili, Esmaeilzadeh, & Mowla, 2014).

The preparation of mixed matrix membranes (MMM) by the incorporation of a nanomaterial into a polymer matrix can form a more efficient membrane for such application. The addition of the nanomaterial alters the properties of the membrane to become more compatible with the application. For instance, the incorporation of a hydrophobic/superhydrophobic nanomaterial increases the surface roughness of the membrane and enhances its ability to repel water and pass the oil through its pores. In this work, a hydrophobic polyethersulfone (PES) MMM was prepared by blending iron oxide-oleylamine (Fe-Ol) nanoparticles in the polymeric dope solutions and fabricated via the non-solvent-induced phase separation (NIPS) method.

2. Materials and methods

Iron oxide (Fe_2O_3) nanoparticles functionalized with oleylamine were synthesized using a typical method of thermolytic decomposition of iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) in hot alkylamine (Tzitzios et al., 2007). A schematic representation of the Fe-Ol nanomaterial is represented in Figure 1. The amine group of oleylamine is attached to the Fe_2O_3 nanoparticles via hydrogen bonding, making the hydrophobic long alkyl chain exposed. This hydrocarbon chain strongly repels the water and improves the interaction with organic solvents and oils.

Several dope solutions with different concentrations of Fe-Ol nanomaterial were prepared to optimize the membrane's performance. The preparation of the dope solution started by dispersing the nanomaterial in N-Methyl-2-pyrrolidone (NMP) solvent, followed by the addition of polyvinylpyrrolidone (PVP) powder to it. PVP acts as a pore-forming and binding agent. Finally, PES pellets were dispersed in the dope solution and kept under stirring until a homogeneous solution was obtained. A degassing process was performed to remove the excess bubbles by placing the solutions in a vacuum oven for an hour. Afterwards, the membranes were cast on a glass plate with a casting knife set at 250 µm. The plates holding the cast solutions were directly immersed in a DI water bath for 24 h, then left to dry. Table 1 shows the content details of each of the dope solutions prepared.

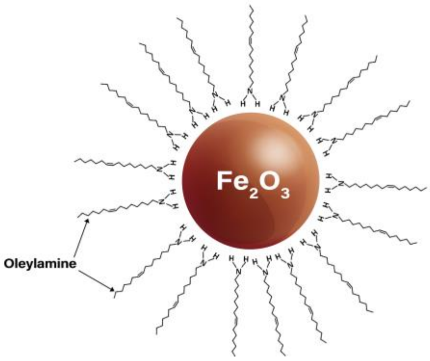

Figure 1. A schematic representation of Fe-Ol nanoparticle.

Table 1. The weight percentages of the dope solution's contents.

Membrane	PES (wt%)	PVP (wt%)	Fe-Ol (wt%)*	NMP (wt%)
PES	16	2	0	82
PF-1	16	2	0.75	81.88
PF-2	16	2	1.5	81.76
PF-3	16	2	3	81.52
PF-4	16	2	6	81.04

*The percentage is calculated with respect to the total mass of PES.

3. Results and discussions

The hydrophobicity of the Fe-Ol nanomaterial was examined by testing its water contact angle (WCA) via Goniometer, DSA25, Kruss. The WCA of Fe-Ol was 137.2 ± 2.8°, as shown in Figure 2, representing its highly hydrophobic nature.

Figure 2. WCA image for Fe-Ol nanomaterial.

The surface morphology and structure of the pristine membrane and the MMMs were studied using scanning electron microscopy (SEM). A 10 nm coating layer of gold-palladium was used to coat all the samples to enhance their conductivity and reduce sample charging. The top and bottom surfaces SEM images of the membranes are shown in Figure 3. The top surface was presented as a defect-free dense layer. Furthermore, the prepared membranes can be categorized as ultrafiltration membranes due to the formation of nanosized pores. The smoothness of the membranes' surface was found to decrease with the increase of the nanomaterial's content. Hence, the surface roughness of the membranes was improved with the addition of Fe-Ol nanoparticles. The bottom surface images show the increase in the number of pores and their size for the modified membranes at low loadings of the nanomaterial compared to the pristine PES membrane. However, with the excessive use of Fe-Ol, they decreased due to particle agglomeration.

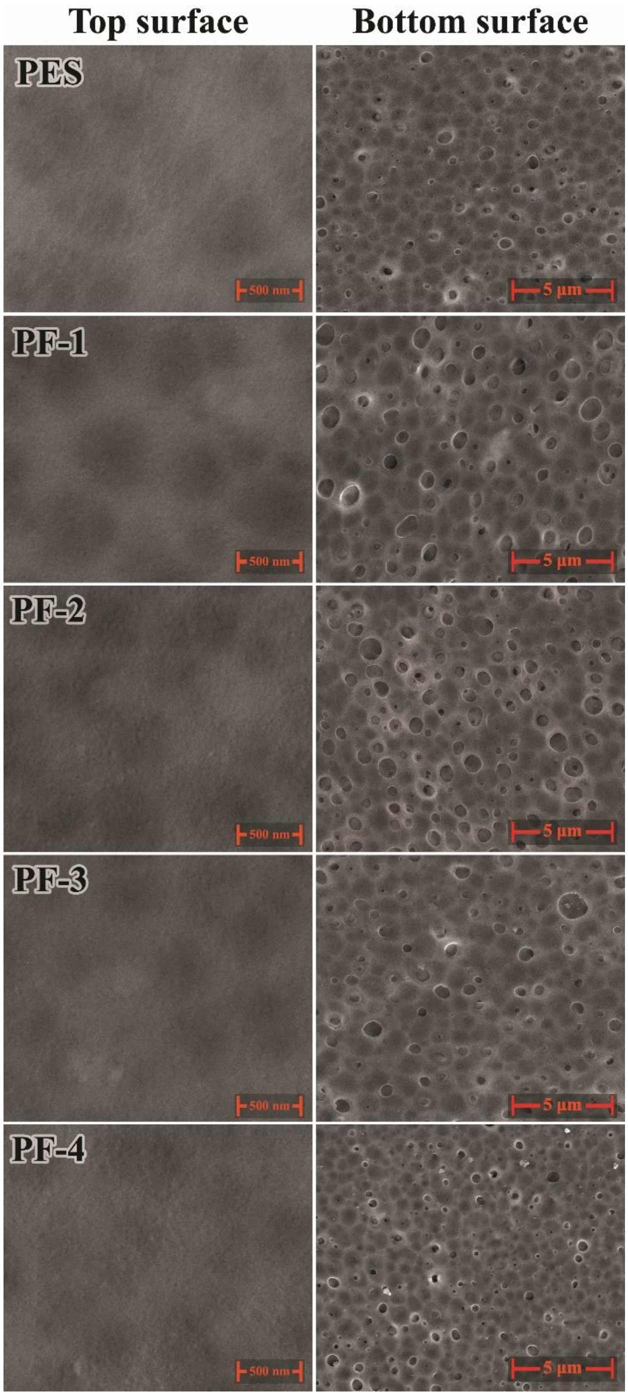

Figure 3. Top and bottom surfaces SEM images of the prepared membranes.

Table 2 shows the effect of the incorporation of Fe-Ol into the matrix of the membranes on the surface hydrophobicity. The WCA of the membranes has increased from 71.0 ± 1.9° for the pristine PES membrane to 98.4 ± 1.8°, 100.4 ± 1.3°, 102.8 ± 1.8°, and 101.2 ± 1.3° for PF-1, PF-2, PF-3, and PF-4, respectively. Furthermore, the surface free energy of the membranes decreased for the modified membranes, which also supports the increase in the hydrophobicity of the MMMs compared to the pristine membrane.

Table 2. The static WCA and surface free energy of the pristine PES and PES/Fe-Ol MMMs.

Membrane	**WCA (°)**	**Surface free energy (mJ/m^2)**
PES	71.0 ± 1.9	96.5 ± 2.2
PF-1	98.4 ± 1.8	60.4 ± 2.2
PF-2	100.4 ± 1.3	59.7 ± 1.6
PF-3	102.8 ± 1.8	56.7 ± 2.2
PF-4	101.2 ± 1.3	58.6 ± 1.7

The performance of the fabricated membranes in the separation of water-in-oil emulsions was tested using a Span 80 surfactant stabilized water-in-n-hexane emulsion. Figure 4 shows the water rejection efficiency and filtration flux of the pristine PES and the MMMs. Generally, the incorporation of the nanomaterial improved both the separation efficacy and the flux. Membrane PF-2 showed the best performance in the filtration of the stabilized water-in-n-hexane emulsion. It achieved a 97.4% rejection efficiency and 1020 LMH filtration flux compared to 91.5% and 307 LMH for the pristine PES membrane.

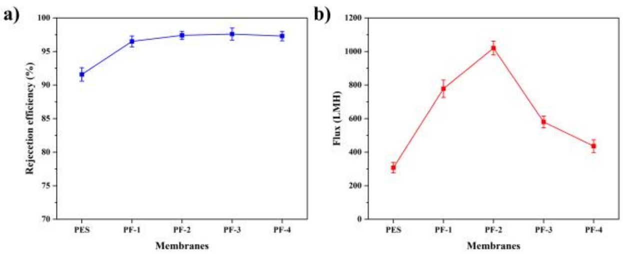

Figure 4. a) Water rejection efficiency and b) filtration flux of the pristine and MMMs.

4. Conclusions

The occurrence of oil spill accidents during offshore drilling leads to adverse effects on the environment. Herein, a hydrophobic PES MMM was fabricated using phase inversion. The incorporation of Fe-Ol nanomaterial into the polymer matrix enhanced the hydrophobicity of the membranes. A surfactant-stabilized water-in-n-hexane emulsion was used to test the membranes' performance. The 1.5 wt% MMM showed an excellent water rejection ability with 97.4% efficiency and a high flux of 1020 LMH. Hence, proving its potential in the application of water-in-oil separation.

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