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Preparation and Characterisation of Polyethersulfone/ Hydrous Ferric Oxide Mixed Matrix Membranes with Improved Hydrophilicity for Treatment of Oily Waste Water

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The rapid growth in oil and gas industry has led to the large production of oily wastewater. The massive amount of oily wastewater derived from the industry has raised concerns in community especially its adverse impact to the environment. Membrane technology has been in the spotlight in recent advancement to treat the oily wastewater. The major obstacle regarding the membrane technology is fouling due to surfactant adsorption and/or oil droplets plugging the pore, which would lead to a severe decline of the flux and rejection rate. HFO nanoparticles are incorporated into the PES membrane matrix with the aim to improve the hydrophilicity, water permeability as well as the antifouling properties of the membrane. HFO is abundant and easily obtained making it the perfect candidate in developing economical and energy saving membrane operation. Hydrous ferric dioxide (HFO) nanoparticles were synthesised via chemical precipitation method and incorporated in polyethersulfone (PES) to fabricate nanocomposite mixed matrix membranes (MMMs) for ultrafiltration (UF). The resulting membranes were characterised by SEM, FTIR, contact angle goniometer, before further subjected to water permeation test. It was found that contact angle of membrane decreased remarkably with an increase in HMO nanoparticle loading (state the value/ percentage decrement). The pore size at the skin layer however decreased as observed by SEM. As for the UF experiments, pure water permeation rate increased remarkably with increasing nanoparticle loading.

1. Introduction

In these modern millennia, the advancement of technology has been the force that builds the rapid growth of many industries, especially oil and gas industry. The oil and gas industry has been a key player in keeping the world economy in fast pace and has been one of the biggest industry that attract a lot of attention. With growth of this industry it has raised concerns especially to environment as some oil and gas industry operations have been in charge of water contamination through by-results of refining and oil slicks (Ahmed et al., 2007). Oily wastewater pollution can be manifested in different way such as affecting drinking water and groundwater resources besides endangering aquatic resources and human health. Numerous techniques have been adapted to separate oil/water mixture which includes air flotation, gravity separation, oil-adsorbing materials, coagulation and flocculation (Liu et al., 2011). These methods are ineffective in treating emulsified oil/water mixtures (Fakhru'l-Razi et al., 2010). The permit limits for oil and gas industry for treated produced water according to the United States Environmental Protection Agency regulatory limits are 29 mg/L for monthly average and 42 mg/L for daily maximum. Oily wastewaters are characterised by a high content of salts and oil, which makes mandatory to draw a specifically purposed treatment train, different, for example, from those commonly used for municipal wastewaters treatment.

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Membrane technology coupled with filtration method has attracting attention in effort to separate various emulsions especially surfactant stabilised emulsions. It has excellent discharge quality and yet a very simple process. Polymeric membrane has advanced seamlessly for the past few years and it has grown steadily with vast utilisations especially in water treatment. The utilisation of membrane technology has brought about attention due to its excellent selectivity and low energy requirement. It is effective in separating the oils, emulsions, and silts. It has challenged many researches for its fouling tendency. This is due to the fact that surfactant adsorption and/or pore plugging by oil droplets will cause a severe decline of the flux and rejection rate. Hence there are need to reduce the fouling in order to enhance separation performance. One of the effective ways in increasing the antifouling property of the membrane is by surface modification.
The main objective of this study is to develop a new mix-matrix membrane that has excellent selectivity and permeability with enhanced performance in separation of oily emulsions besides having improved antifouling ability. The main concern in fabrication of the said MMMs is its ability to eliminate membrane fouling and enhance its overall performance. In this study, flat sheet PES-HFO ultrafiltration membrane has been fabricated using different loading of HFO. The fabricated membrane has been evaluated for its performance and reusability of fabricated membrane on separation of oily wastewater as well as its morphological characterisation.

2. Materials and Method

2.1 Chemicals

Commercial PES pellets (Ultrason®E) purchased from BASF SE Germany is the main component in membrane formation. NMP and polyvinylpyrolidone (PVP) (MW = 24,000 g/mol) supplied by Merck is utilised as polymer solution and pore forming agent. Ferric chloride hexahydrate ($FeCl.6H_2O$), hydrochloric acid (HCl) and ammonia solution (NH_3) and is used for synthesising HFO.

2.2 Preparation of dope solution

A predetermined amount of PVP was first dissolved in NMP solvent. HFO inorganic particle were then added into the solution and dispersed sufficient well with stirring, followed by sonication at 50 °C for several hours. Dried PES polymer pellets were then added into the mixture and stirred at 500 rpm for 24 h until a homogenous suspension was obtained. The dope solution for the pristine PES membrane was prepared in the same way without adding HFO particles. The composition of dope solution is depicted in Table 1.

Table 1: Composition of dope solution

Membrane	HFO-HNT/PES Ratio	PES (wt%)	PVP (wt%)	NMP (wt%)	HFO-HNT (wt%)
PES	0	15.00	1.5	83.5	-
PES/HFO 0.5	0.5	13.95	1.30	80.59	6.98
PES/HFO 1	1	13.04	1.22	72.60	13.04

2.3 Preparation of Flat Sheet Membrane

The uniform suspension above prepared was poured onto a smooth glass plate and cast by a casting blade at a speed of 5 cm/s to form a film of 250 mm thickness. The cast film together with the glass plate was then immersed into a DI water bath for a few minutes for phase inversion to take place. Once the membrane was peeled off naturally from the glass plate, it was transferred to another water bath where it was kept for another 3 days to completely remove residual solvent and PVP. The membrane was then dried at room temperature (with humidity between 60 and 70 %) prior to use.

2.4 Membrane Characterisation

Transmission electron microscope (TEM) (Model: HT 7,700, Hitachi) was used to analyse the morphology of the synthesised HFO nanoparticles. Fourier-transform infrared spectroscopy (FTIR) was then used to analyse the functional group in the HFO nanoparticles. The membrane surface morphology and cross-area were inspected utilising a field emission scanning electron microscope (FESEM, ZEISS SUPRA 35VP)

2.5 Pure Water Flux Analysis

Pure water permeation flux (PWP) of membranes was obtained using dead-end tubular UF using method proposed by Tseng et al. (2012). Prior to pure water flux estimation, the cut layer inside the cell was at first pressurised with refined water at 101.32 kPa for 30 min and was then utilised as a part of ensuing immaculate water flux estimation tests at 68.95 kPa for 2 h.

The pure water flux will be measured under steady state flow and then governed using the following Eq(1) (Tseng et al., 2012):

$$J_w = Q/(A \times \Delta T) \quad (1)$$

Where J_w is denoted as pure water flux ($L/m^2/h$), Q is the quantity of permeate (L), A is the membrane area (m^2), and ΔT the sampling time (h).

2.6 Membrane Hydrophilicity

To determine membrane surface hydrophilicity, the water contact angle of the membranes was measured by sessile drop method using an automated contact angle goniometer (Model: OCA 15plus, DataPhysics). A droplet of DI water with a volume of 0.5 mL was carefully formed at ten spots randomly chosen on the membrane surface using a motor-driven microsyringe and the average value was reported.

3. Result and Discussion

3.1 Morphological Analysis of Membrane

The SEM micrographs of the cross-section and surface of the PES membrane and the MMMs are shown in Figure 1. The formation of asymmetric structure, which made up of a porous skin layer and undergirded by a sub layer with finger-like consistency, is the usual depiction of process adopted in this work for membrane fabrication which is the phase inversion method. As the magnification of the micrographs increased, it is observed that there's integration of HFO on the modified membrane as shown in Figure 2. It is observed that PES-HFO membrane 0.5 has roughest surface compared to the other. All membranes were observed to possess thin or selective layer based on the cross sectional micrograph. It is observed that the pristine PES membrane (PES-HFO 0) has observable formation of macrovoids whereby the modified membranes (PES-HFO 0.5 and 1.0) shows lesser formation of macrovoids. This is due to the increased viscosity of the dope solution of the modified membrane. The lesser macrovoids formation will lead to more selective membrane and the formation decrease as the loading of HFO increased. It is also observed that the finger-like formation of the modified membranes is longer compared to the pristine membrane. Theoretically, HFO exists as spherical shape and this is confirmed as TEM analysis as shown in Figure 2(c) is done to the fabricated HFO nanoparticles. The integration of HFO into the membrane is shown as the spherical dots on the SEM micrographs as shown in Figure 2(b) as the magnification increased. The even distribution of HFO is enhanced as agglomeration is decreased with increased aging of the nanoparticles.

3.2 Membrane Hydrophilicity

Surface hydrophilicity of membrane is the key role in defining the pure water flux and antifouling property. Membranes in an aqueous environment will naturally possessed attractive or repulsive response to water. The composition of the membrane and its corresponding surface chemistry has effects especially in the water interaction that indigenously relate to its wettability. Hydrophilic membranes are typically distinguished by the presence of active groups with ability in forming "hydrogen-bonds" with water.

The contact angle of PES neat membrane and the modified membranes has significant difference that is depicted in Figure 4. It is observed that the angle of neat PES (PES:HFO 0) is 70°, PES-HFO 0.5 is at 59° and PES-HFO 1.0 is 38°. The decrease in contact angle naturally depicted the increase in hydrophilicity of the membrane. The results showed that the increasing of HFO loading has obviously increased the wettability of the membrane. The hydroxyl groups of HFO nanoparticles are found to be able to interact with water molecules seamlessly by bonding of hydrogen as well as the van der Waals force that attributes to the increment of water permeability hence led to increased membrane hydrophilicity. The addition of HFO has increased the –OH group in the membranes which increased the water interaction thus enhance the water permeability. The FTIR analysis of the HFO nanoparticles has depicted the nanoparticles spectrum of O–H stretching vibration band at around 3,236.55 cm^{-1} as shown in Figure 3.

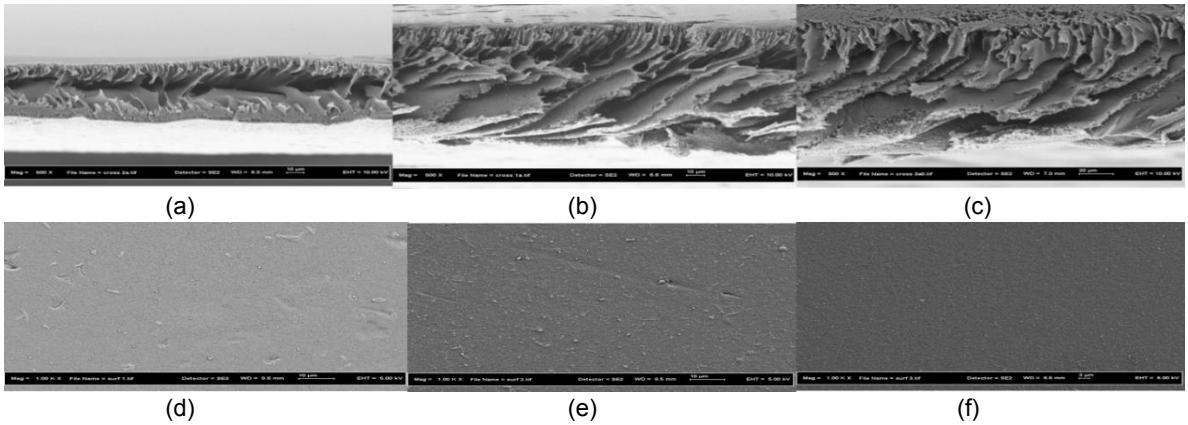

Figure 1: SEM micrographs of cross sections and surface of membranes at 1,000x magnification; Cross section (a) PES-HFO 0, (b) PES-HFO 0.5, (c) PES-HFO 1.0; Surface (d) PES-HFO 0, (e) PES-HFO 0.5, (f) PES-HFO 1.0

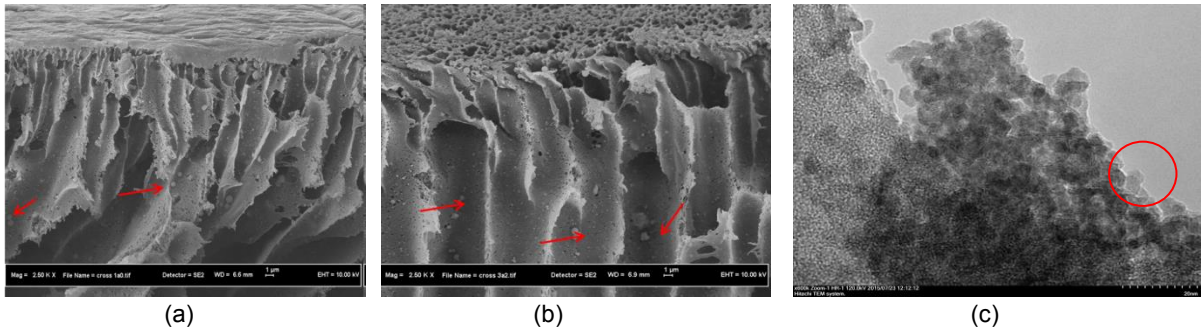

Figure 2: SEM micrographs of (a) PES-HFO 0.5, (b) PES-HFO 1.0, (c) TEM image of HFO

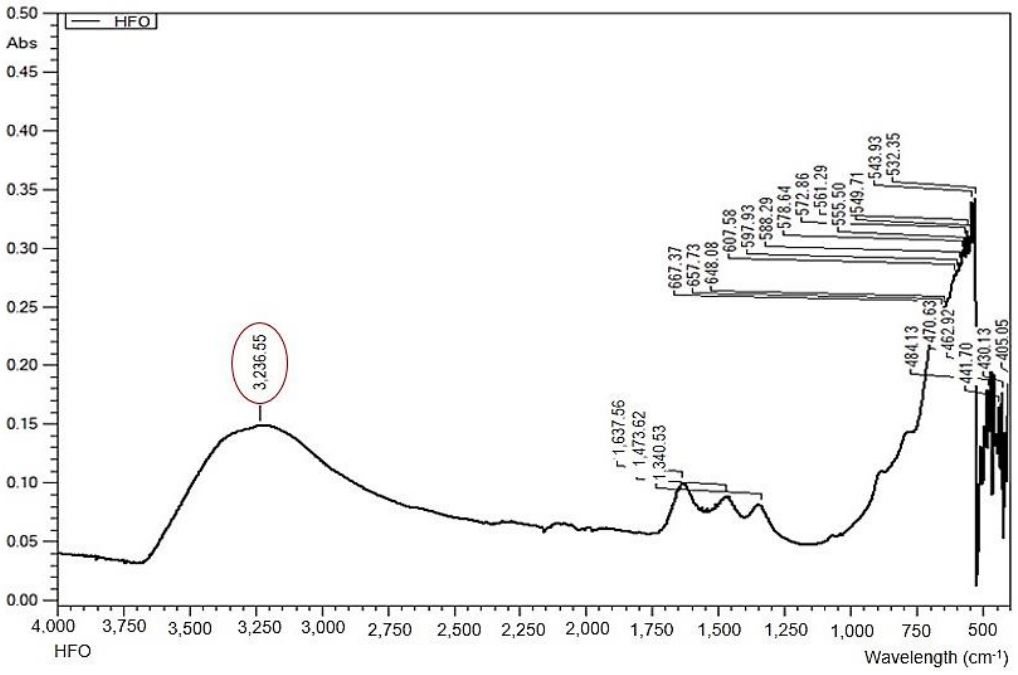

Figure 3: FTIR spectra of HFO

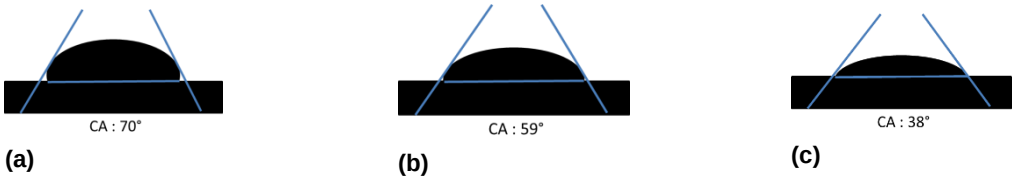

Figure 4: Water contact angle of membranes, (a) PES-HFO 0, (b) PES-HF0 0.5, (c) PES-HFO 1.0

3.3 Pure Water Permeation Flux

Figure 5 shows the change in membrane flux over time. At the outset, the permeation fluxes dwindled gradually up to a point at which the flux remains in the same value. As the permeation take place in UF process, the fluxes of modified membranes PES-HFO 0.5 and PES-HFO 1.0 were always higher than those of neat PES-HFO 0, which was also contributed to the improved hydrophilicity of the membrane. This is due to the abundant –OH group from the HFO nanoparticles as confirmed by FTIR analysis depicted in Figure 3. This attribute to more water absorption hence increased hydrophilicity. It is also observed that the increasing loading of HFO has also increased the water permeation of the membrane at which PES-HFO 1.0 (with PES: HFO ratio is 1 : 1) is significantly higher than PES-HFO 0.5 (PES:HFO is 2 : 1) Stable flux of the PES-HFO 1.0 membrane is 168.06 L/(m^2.h), which is 1.61 times than that of the PES-HFO 0.5 membrane, 104.69 L/(m^2.h) and 2.64 times more than neat PES membrane, 63.67 L/(m^2.h). As time proceed, the permeation flux decrease and dropped consistently until flux stability reached.

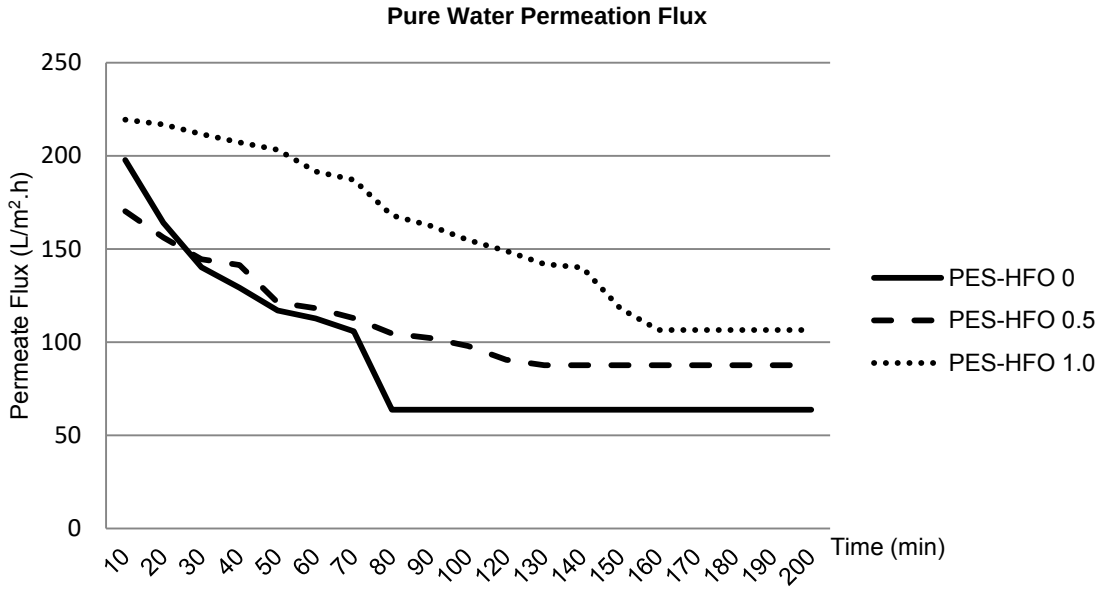

Figure 5: Pure water permeation flux of PES membrane with different loading of HFO

4. Conclusion

In this study, an investigation was made in water permeability of PES-HFO modified membrane for the purpose of oily wastewater treatment. The results revealed that the embedding of HFO has significantly increased the hydrophilicity of the membrane. It is also found that the integration of HFO not only increased the water permeability of the membrane but also greatly improved the selectivity of the membrane. The flux study showed that the flux decline is enhanced as the loading of HFO increased. With great improvement on the membrane hydrophilicity due to addition of HFO, the modified MMMs has shown robust potential to be further studied for oily wastewater purposes as wetting conduct is one of the vital roles in fabricating membrane with effective separation of oil-in-water emulsions.

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