The Improved Oil Removal Using Polysulfone Membranes Containing Al_2O_3 Nanoparticles

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Abstract: Oil-intensive industries produce environmentally problematic wastewaters and their treatment is more difficult because of their high stability in aqueous solutions. Although conventional separation methods are used for the removal of oily compounds, these processes cannot satisfy environmental regulations. Therefore membrane separation processes such as microfiltration (MF) and ultrafiltration (UF) have gained attention to separate micron sized oily compounds. Many researchers have studied to increase the oil removal performance of membrane filtration by incorporating nanoparticles to the membrane matrix. In this study, the flat-sheet PSF/PEI/Al_2O_3 nanocomposite membranes were prepared by a phase inversion method for oil removal. The oil removal performances of the membranes were evaluated with 1,800 mg/L synthetic wastewater. 20 nm Al_2O_3 nanoparticles was added to the membrane matrix with three different weight percentages of 0.2 wt%, 1 wt% and 5 wt%. The effect of Al_2O_3 nanoparticles on the structural properties and filtration performance of the membranes were investigated. Prepared membranes were characterized in terms of SEM, contact angle, water flux, porosity, ATR-FTIR, porosity and tensile strength. The highest oil removal efficiency was obtained by 15 wt% PSF, 1 wt% PEI and 0.2% wt Al_2O_3 nanoparticles blended nanocomposite membrane with an oil rejection of 99 %.

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INTRODUCTION

Oily wastewaters are mainly produced from the food, leather, metallurgical, petrochemical and cosmetic industries, and petroleum refineries (Ghandashtani et al. 2015, Kajitvichyanukul et al. 2011, Lotfiyan et al. 2014, Mueller et al. 1997), it needs to be reduced to the environmental standards of 10–15 mg/L for safely discharge to receiving water bodies (Gohari et al. 2015, Um et al. 2001, Way et al. 1992). Conventional technologies used to remove oil from wastewaters, however, these methods cannot treat stable oil/water (O/W) emulsions (size≤20 μm) effectively (Chakrabarty et al. 2010, Srijaroonrat et al. 1999). Ultrafiltration (UF) process, which has pore sizes of 2–100 nm range, has gradually become an attractive technology for oil removal (Jamshidi Gohari et al. 2014, Yi et al. 2011, Zhang et al. 2009). Polymeric UF membranes were widely used for oily water treatment and PSF is the most commonly used polymer to fabricate membranes and preferred due to its mechanical robustness, structural and chemical stability, large range of solubility, and thermal resistance (Maximous et al. 2009, Yunos et al. 2014). PSF needs to be modified to reduce its hydrophobic characteristics and increase its permeability and antifouling capacity for treating oily wastewaters (Fenu et al. 2010, Kumar et al. 2013, Li and Chu 2003, van Reis and Zydney 2007). To enhance antifouling property, hydrophilic additives such as hydrophilic polymers and inorganic nanoparticles have been performed.

This study focuses on fabricating PSF/PEI nanocomposite membranes using Al_2O_3 nanoparticles (20 nm) via the phase inversion method. To the best of our knowledge, there are no reported data on using a PSF/PEI/Al_2O_3 blended substrate to fabricate polymeric nanocomposite membranes for treating oily wastewater, and the effect of the Al_2O_3 nanoparticles on PSF/PEI membranes has not been examined. The effects of the nanoparticle concentration on the performance of membranes were thus investigated. The membrane properties were evaluated by scanning electron microscopy (SEM), contact angle, porosity, water flux and BSA rejection. To examine the membrane permeability performance and antifouling properties towards O/W emulsion separation experiments were also carried out accordingly. The findings provide new insight that may contribute to the development of better nanocomposite membranes for water-based filtration applications.

EXPERIMENTAL

Materials

PSF (MW: 60,000) was purchased from Acros Organics. PEI (MW: 25,000) was obtained from Sigma-Aldrich and used as a modifying agent. DMF (Merck, anhydrous, 99.8%) and NMP (Merck) were used as solvents. Hydrophilic Al_2O_3 nanoparticles (20 nm) were supplied from Nanografi, Turkey, BSA was used as a foulant and supplied from Amresco Inc. (USA). Sodium dodecylsulfate (SDS) was used as an emulsifier and was purchased from Serva. Vacuum pump oil (G-19) was purchased from Edwards (UK).

Preparation of membranes

Al_2O_3 nanoparticles were first dissolved in an NMP solution at three different concentrations of 0.2, 1 and 5 wt% Al_2O_3 (M201, M202, M203). The mixture was then sonicated for 2 hours. Next, the Al_2O_3 nanoparticles were dissolved with 15 wt% PSF and 1 wt% PEI in DMF and NMP mixture to form casting solutions. The final solution was than mixed for one day at 400 rpm using a magnetic stirrer to make the solution homogeneous. The polymer suspension was then sonicated for at least 2 hours and then cast on a glass plate to form flat sheet membranes.

Membrane Characterization

SEM: The top-surface and cross-section morphologies of the membranes were observed using a Zeiss Evo LS10 scanning electron microscope. The membranes were carefully sectioned with an average 0.5 mm width and 3 mm length and then mounted onto the SEM grid. Before the analysis, each sample was coated with platinum, and the samples were analyzed at 10 kV.

Membrane hydrophilicity

The surface hydrophilicity of the membranes was measured using a contact angle meter (Attention-Theta Lite, Biolin Scientific, Finland). For each measurement, at least three readings from different surface locations were taken, and the reported contact angles are the average values.

Porosity

For the porosity measurements, dry membranes were immersed in ethanol for 2 hours, and the liquid on the surfaces of the membranes was removed using filter paper. The membrane porosity (ε) was calculated using Eq. 1 (Lohokare et al. 2011):

$$\varepsilon = \frac{(\omega 1-\omega 2)/\mathrm{d}\omega}{\frac{\omega 1-\omega 2}{\mathrm{d}\omega}+\omega 2\,/\mathrm{dp}} \tag{1}$$

where ω_1 is the weight of the wet membrane (g), ω_2 the weight of the dry membrane (g), dω is the density of pure water (0.998 g/cm^3) ,and dp is the polymer density (1.24 g/cm^3).

Water filtration tests

A dead-end stirred cell filtration system (Sterlitech, HP4750) was used to determine the membranes' intrinsic separation properties. The effective membrane area for the system was 14.6 cm^2. The feed side of the system was pressurized by nitrogen gas. In the water filtration test, transmembrane pressures (TMP) were applied 4 bar constant TMP for PSF/PEI/Al_2O_3 membranes, and the temperature was kept at room temperature (25±3ºC). The water fluxes of the prepared membranes were calculated using Eq. 2:

$$\mathrm{J} = \frac{\mathrm{V}}{\mathrm{A}\times\mathrm{t}} \tag{2}$$

where, J is the water flux (L/m^{2}h), V is the permeate volume (L), A is the effective membrane area (m^2), and t is time (h).

BSA removal experiments

The rejection experiments were carried out at 2 bar TMP in the dead-end filtration module. The membranes' BSA rejection performance was determined using aqueous solutions containing 2.5 g/L of BSA (Jamal et al. 2014). The solutions were prepared using DI water at room temperature. BSA concentrations were analyzed using UV-visible spectrophotometry (UV-1800, Shimadzu, China) at a wavelength of 280 nm. The BSA and oil rejections (R) were calculated by Eq. 3:

$$\%R = 1 - \frac{\mathrm{Cp}}{\mathrm{Cf}} \times 100 \tag{3}$$

Oil removal experiments

The vacuum pump oil (G-19) was used for the preparation of synthetic O/W emulsion. The oil rejection tests were carried out at 2 bar TMP in the dead-end filtration module. The emulsion were combined with oil and surfactant SDS in a ratio of 9:1 (w/w), and then added to 500 mL DI water by mixing for 30. The emulsion was stored at room temperature. Oily water concentrations were analyzed using UV-visible spectroscopy (UV-1800, Shimadzu, China) at a wavelength of 283 nm.

The oil rejections (R) were calculated same as BSA rejection by Eq. 3. And where Cp is the concentration of oil in the permeate, and C_f is the concentration of oil in the feed solution.

RESULTS

Membrane morphology

Morphology analysis is a very important tool for the characterization of membranes. To investigate the morphological changes associated with the addition of PEI and Al_2O_3 nanoparticles, images of the top and cross sections of the membranes were obtained by SEM. Cross-section images of the PSF/PEI membranes with different concentrations of Al_2O_3 (0.2, 1, 5 wt%) are shown in Figure 1. As seen in Figure 1, the membrane morphology changed significantly with the increasing nanoparticle concentration in membrane matrix. Besides, with increasing content of Al_2O_3, the amount of finger-like pores enhanced, and the clear boundary between the sub-layer and center of the membrane disappeared for the 5 wt% Al_2O_3 added membranes (Fig. 1c) (Costa et al. 1999).

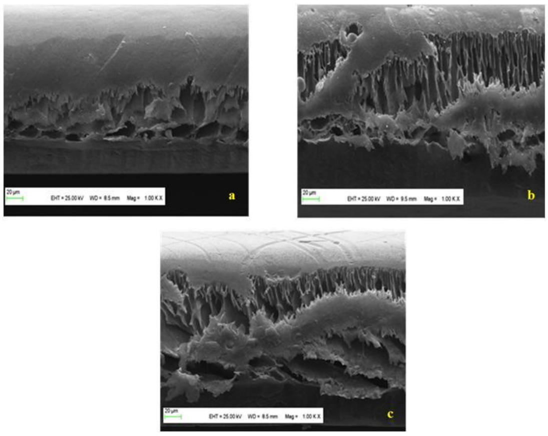

Figure 1: SEM images of PSF/PEI membranes cross-sections containing Al_2O_3 with different concentrations: (a) 0.2 wt%, (b) 1 wt%, (c) 5 wt%

Membrane hydrophilicity

Hydrophilicity is directly related to the flux and antifouling property of a membrane. The hydrophilicity of the PSF/PEI/Al_2O_3 nanocomposite membranes was evaluated by the contact angle measurements using the sessile drop method, as shown in Table 1. The pure PSF membrane's contact angle was 87°, but PEI addition decreased the contact angle to 67° (Table 1). The contact angles were 72°, 65°, and 56° for nanocomposite membranes including 0.2, 1, and 5 wt % Al_2O_3, respectively.

Table 1: Contact angle, pure water flux (at 4 bar), and porosity of membranes

Substrate	CA (°)	Flux (L/m^{2}h)	Porosity (%)
PSF	87±2	20.51	63±3
PSF/PEI	64±4	317.70	95±4
0.2 wt %Al_2O_3	72±5	236.02	71±2
1 wt %Al_2O_3	65±2	1289.12	77±5
5 wt %Al_2O_3	56±3	1336.6	79±6

Porosity

In general, membrane porosity is dependent on the mass transfer of the dope solution during the phase inversion (Hong and He, 2014). Al_2O_3 membranes porosities were given in Table 1. Consequently, the pore formation process would be enhanced with addition nanoparticle to the membrane matrix. As shown in Table 1, the porosity of membranes increased from 63% for the pure PSF membrane to 79% for membranes with 5 wt% 20 nm Al_2O_3 nanoparticles.

Pure water flux

The pure PSF membrane showed the lowest water flux of 20.51 L/m^{2}h at 4 bar, and the highest water flux was obtained for the membranes with 5 wt% 20 nm Al_2O_3 nanoparticles as

1336.6 L/m^{2}h at 4 bar. This result could be explained by the enhancing potential of Al_2O_3 nanoparticle in terms of the hydrophilicity (Table 1) and porosity compared to the pure PSF membranes.

BSA rejection

BSA filtration experiments were carried out using 2.5 g/L BSA solution was used because of its hydrophobic nature and appropriate molecular size to evaluate the separation performance. The BSA rejection values of the pure PSF and PSF/PEI membranes were 83% and 72%, respectively. All of the prepared PSF/PEI/Al_2O_3 nanocomposite membranes rejected more than 90% of the BSA.

Oil rejection performance

Fig. 2 illustrated oil rejection ratio of Al_2O_3 nanocomposite membranes. All Al_2O_3 nanocomposite membranes reached similar oil rejection over 90%. Oil rejections demonstrated that, PSF/PEI/Al2O3 nanocomposite membranes have a potential for acceptable separation performance was determined for O/W emulsion treatment.

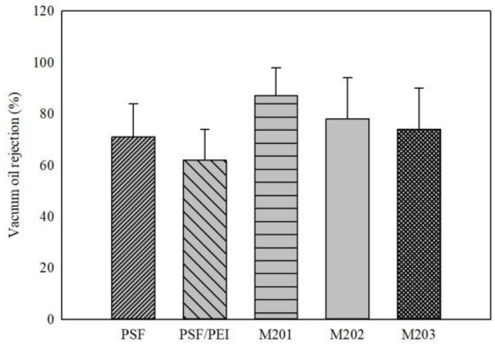

Figure 2: Oil rejection of membranes.

CONCLUSIONS

The hydrophilicity, porosity, water flux of the PSF/PEI/Al_2O_3 nanocomposite membranes enhanced as the increase of Al_2O_3 content in membrane matrix. PSF/PEI/Al_2O_3 membranes with 20 nm 5 wt% Al_2O_3 nanoparticles showed excellent water flux of 1336.6 L/m^{2}h at 4 bar with a contact angle of 56°, porosity of 79%. PSF/PEI/Al_2O_3 nanocomposite membranes showed also higher BSA rejections of over 95%. All Al_2O_3 nanocomposite membranes reached similar oil rejections over 90%.

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