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Treatment of oily wastewater using membrane with 2-hydroxyethyl methacrylate-modified surface

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Abstract−To enhance the hydrophilicity, the surface of polysulfone membrane was modified by UV-irradiation induced coating of HEMA in the presence of AIBN as free radical source. The permeation characteristics of oily water through the surface-modified membrane were investigated. The fluxes of wastewater with oil concentrations of 100 ppm, 200 ppm and 400 ppm through an un-coated membrane were 0.123, 0.081, and 0.076 $g/cm^2\cdot min$, respectively. However, the fluxes through the surface-modified membrane were 0.253, 0.242, and 0.173 $g/cm^2\cdot min$, respectively. The fluxes through the surface-modified membrane were much higher than those through an un-coated membrane: 2.1, 3.0 and 2.3 times higher fluxes. The rejection of oil emulsions by the membrane was higher than 99%. The membrane with HEMA-modified surface, which has a higher flux and less fouling than an original polysulfone membrane, may be a promising candidate for wastewater treatments as well as oily wastewater treatments.

Key words: Hydrophilicity, Polysulfone Membrane, HEMA, UV Coating

INTRODUCTION

Water pollution has been seriously progressing with oily water becoming one of the most serious issues of water pollution. Oily wastewater is discharged from several industries, such as the steel, machine, petroleum refining, metal cutting and metal forming, and textile industries. Discharged into the environment, oily wastewater creates a major ecological problem. The commonly used techniques for oily wastewater cleaning are flotation [Gu and Chiang, 1999; Jung and Kang, 2003], gravitational methods, chemical treatment, and biological treatment [Chaudhary et al., 2003]. These traditional methods of oily waste water treatment are not efficient enough, especially when the oil droplets are finely dispersed and oil concentration is very dilute. In addition, the treatment process is complicated due to different composition of the wastewater. As discharge regulations on oily water pollution are expected to become more stringent and conventional treatment methods have inherent limitations mentioned above, the study of other treatment techniques is indispensable. Membrane separation seems to be a promising alternative for the treatment of oily wastewater, since it is highly efficient especially in a low concentration of oil.

Membrane processes have many advantages such as simple equipment, economic, highly efficient, and easy scale-up. The major drawback in the extensive use of membranes is membrane fouling, which results in flux decline during operation. There are many reports for oily water cleanup with membranes [Gryta et al., 2001; Arnot et al., 2000; Kong and Li, 1999; Daiminger et al., 1995; Bae et al., 2005]. The investigation for reducing the fouling tendency of the membrane surface by oil-drops is important for oily wastewater treatment. In order to increase hydrophilicity, the membrane surface may need to be modified to obtain less fouling and higher fluxes [Yamagishi et al., 1995; Yang et al., 1996; Thiruvenkatachari et al., 2004].

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In this study, since the HEMA (2-hydroxyethyl methacrylate, Aldrich Co.) has a hydroxyl group (-OH) and shows hydrophilicity, the base membrane (polysulfone; PSf) surface was coated by treatment with HEMA monomers and AIBN(2,2'-azobisisobutylonitrile, Junse Chemical Co.) as free radical source in the presence of UV irradiation. The primary objective of this work was to investigate the effects of various surface-modification parameters on the performance of the membrane. Investigation of the permeation behavior of simulated oily wastewater was carried out by using a flat sheet of PSf ultrafiltration (UF) membrane modified by UV-irradiation induced coating of HEMA.

MATERIAL AND METHOD

1. Materials

Commercially available porous polysulfone (PSf) UF flat sheet membranes (Pure Envitech. Co.; MWCO 300,000), HEMA and AIBN were used for UV-irradiation modification. The model solution of oily waters of 100 ppm, 200 ppm and 400 ppm was prepared by emulsifying Cutting oil (LG Caltex, Korea) with homogenizer

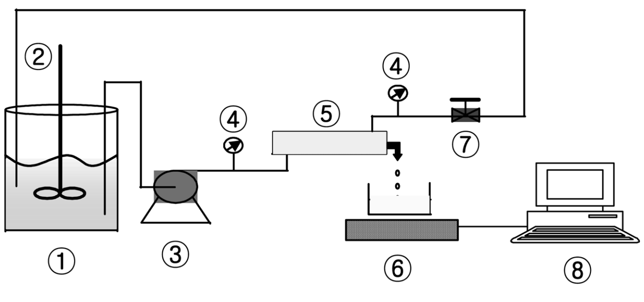


Fig. 1. Schematic diagram for the flux measurement.

① Feed tank	⑤ Membrane module
② Homogenizer	⑥ Balance
③ Metering pump	⑦ Needle valve
④ Pressure gauge	⑧ Computer

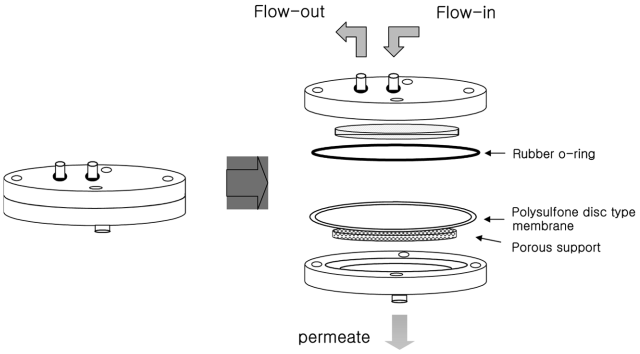


Fig. 2. Flat type membrane module.

Table 1. Coating conditions of polysulfone UF membrane

AIBN/HEMA (g/g)	AIBN (g/*l*)	HEMA (g/*l*)	UV irradiation (min)	Solvent
1/200	0.15	30	120	
1/150	0.20	30	120	Methanol
1/120	0.25	30	120	(75 vol%)
1/100	0.30	30	120	

in deionized water (Milli-Q UF plus). The average oil-drop size was 200 nm (Particle Size Analyzer 90plus, BIC, USA). The concentration of oil in the permeate stream was analyzed with TCD equipped Gas Chromatograph (Shimadzu GC-14B).

The permeation flux was measured for 180 min at room temperature by a microbalance and was acquired by PC as shown in Fig. 1. The feed volume (2,000 ml) largely exceeds the permeation volume (10 ml/min) to avoid variation of feed concentration. The flow in feed compartment of the membrane module may be cross-flow type as shown in Fig. 2. The effective membrane area was 13.4 cm^2.

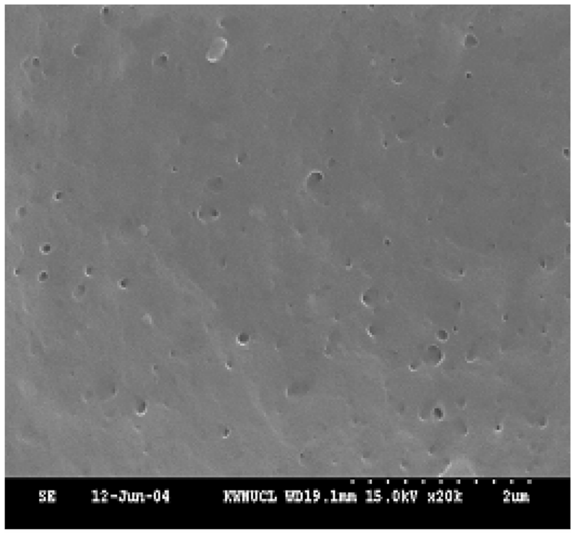
2. Membrane Surface Coating

The PSf membrane was immersed in aqueous methanol solution (75 vol% methanol) containing HEMA monomer as a coating material and AIBN as an initiator. UV(300 W, emission wavelength 253.7 nm) was irradiated at room temperature. After UV irradiation for a given time, the residual HEMA monomer on the surface was removed by several washings with deionized water and the membrane was dried. The coating conditions were summarized in Table 1.

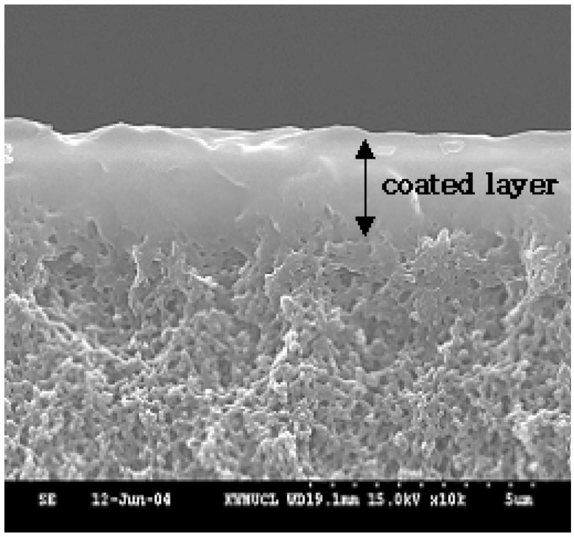
For surface analysis, the typical SEM (Scanning electromicroscope) pictures of the surface and cross section of the HEMA-coated membrane are shown in Fig. 3, and Fig. 4 shows FT-IR spectra of the unmodified PSf and the HEMA-coated membrane. The presence of HEMA on the membrane surface was confirmed by the C=O vibration peak at 1,600-1,700 cm^{-1} and the characteristic bands at 3,200-3,600 cm^{-1} corresponding to hydroxyl group (-OH) in HEMA monomer.

RESULTS AND DISCUSSION

The effects of various parameters such as ratios of AIBN/HEMA (wt/wt), feed flow rates, and concentration of oil emulsion on the permeation flux were investigated. The performance of the modified membrane was evaluated with respect to their permeation flux and oil rejection and was compared to those of the un-modified PSf membrane.



(a)



(b)

Fig. 3. FT-IR spectrum of UF disc-type membrane coated with HEMA.

1. The Flux of Oily Water through the Un-coated PSf Membrane

In order to find the effect of feed flow rate on the permeation flux at a transmembrane pressure difference (Δp) of 3 psi and an oil concentration of 100 ppm, the flux of un-coated membrane was measured at the flow rate of 0.87 *l*/min, 1.18 *l*/min and 1.41 *l*/min. The flux declined drastically in the early stage of operation, which means that there was severe fouling of membrane surface with oil. The flux reached a steady value of flux with each feed flow rate. In the range of the feed flow rate of this experiment, the flux increased with increasing feed flow rate; the flux was 0.082, 0.085 and 0.123 g/cm^2·min, respectively, as shown in Fig. 5. The increase in flux might be due to the boundary layer thickness. The thinner the bound-

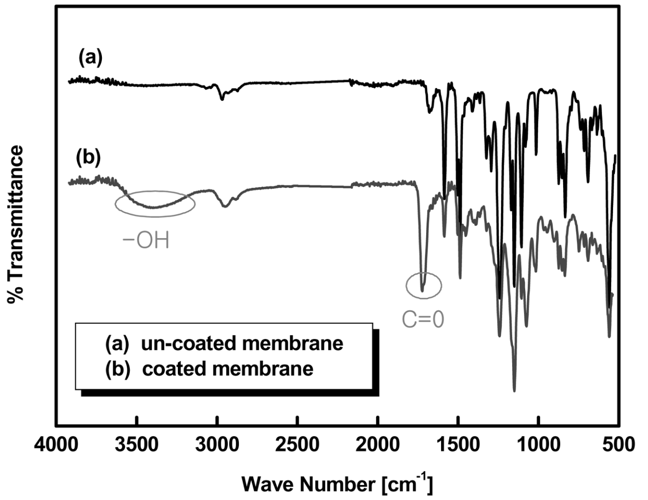


Fig. 4. SEM photographs of the coated PSf disc-type membrane with HEMA. (a) surface (b) cross section.

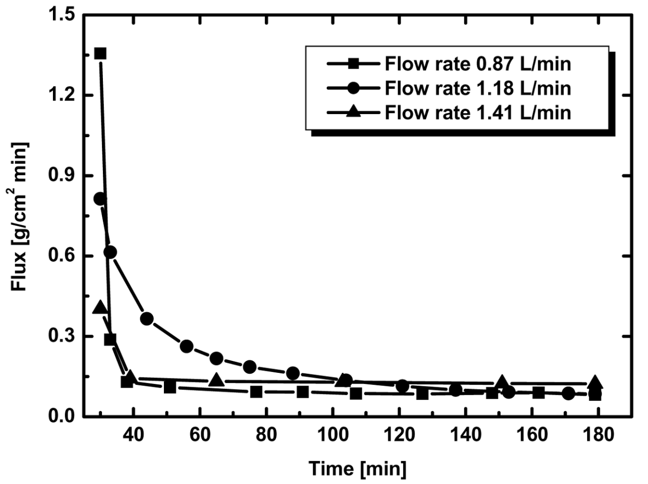


Fig. 5. Effect of feed flow rate on the permeate flux for un-coated PSf membrane at Δp=3 psi and oil=100 ppm.

ary layer is, the higher is the flux. The thinner boundary layer thickness and the higher flux are due to the self-cleaning effect of cross-flow pattern in the feed compartment of the membrane module.

At a higher oil concentration of 200 ppm, the flux increased to 0.047, 0.050 and 0.081 g/cm^2·min at the feed flow rate of 0.87 *l*/min, 1.18 *l*/min and 1.41 *l*/min, respectively.

2. The Effect of Coating Conditions on the Flux through the HEMA-Coated Membrane

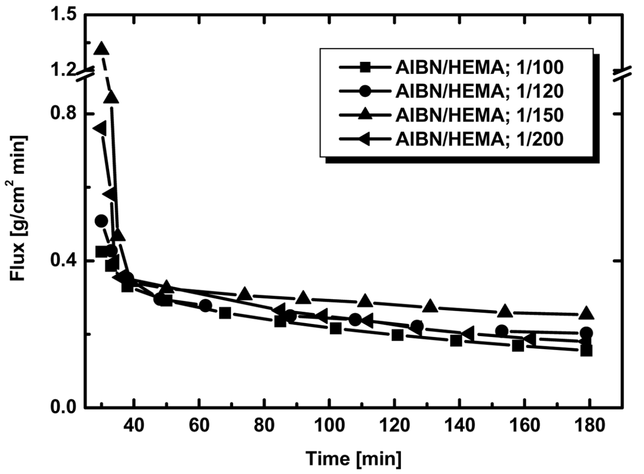


Fig. 6. The flux of oil emulsion with operating time at oil 100 ppm (UV irradiation: 120 min; Δp=3 psi).

To find the effect of coating condition on the flux, the substrate PSf membrane was modified at various AIBN/HEMA ratios of 1/100, 1/120, 1/150 and 1/200 with 120 min of UV irradiation; the flux at a transmembrane pressure difference (Δp) of 3 psi and an oil concentration of 100 ppm was 0.156, 0.203, 0.253, 0.180 g/cm^2·min, respectively, as shown in Fig. 6. At higher oil concentrations, the flux decreased with increasing oil concentration, as shown in Table 2.

The highest permeation flux was obtained at 1/150 of AIBN/HEMA (wt/wt) at various oil concentrations. This means that there is an optimum ratio of AIBN/HEMA (wt/wt) to obtain higher flux at a given UV irradiation.

3. The Effect of Oily Wastewater Concentration on the Flux through the HEMA-Coated Membrane

The flux of oil emulsion through the membrane with HEMA-modified at 1/150 of AIBN/HEMA (wt/wt) was compared with that of un-coated membrane at various oil concentrations. The flux through the HEMA-coated membrane decreased rapidly and showed a similar pattern with the flux through the un-coated membrane. However, the flux reached 0.253 g/cm^2·min at given conditions of an oil concentration of 100 ppm in the feed and a transmembrane pressure difference (Δp) of 3 psi. The flux was about 2.1 times higher than that of un-coated membrane (0.123 g/cm^2·min), as shown in Fig. 7.

At 200 ppm of oil concentration in the feed, the flux of the surface-modified membrane was 0.242 g/cm^2·min and that of the un-coated membrane was 0.081 g/cm^2·min. The flux was about 3.0 times higher than that of un-coated membrane, as shown in Fig. 8.

Table 2. Permeation fluxes of oily water through the surface-modified membrane

Oil concentration	Permeation flux (g/cm^2·min)					Flux ratio (a/b) (coated/un-coated)
	AIBN/HEMA				Un-coated membrane[b]	
	(1/100)	(1/120)	(1/150)[a]	(1/200)		
100 ppm	0.156	0.203	0.253	0.180	0.123	2.1
200 ppm	0.106	0.180	0.242	0.127	0.081	3.0
400 ppm	0.092	0.109	0.173	0.100	0.076	2.3

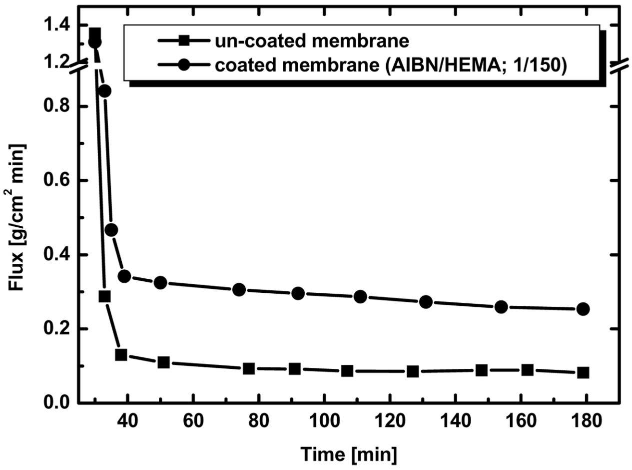


Fig. 7. The flux of oil emulsion with operating time at 100 ppm (Δp =3 psi).

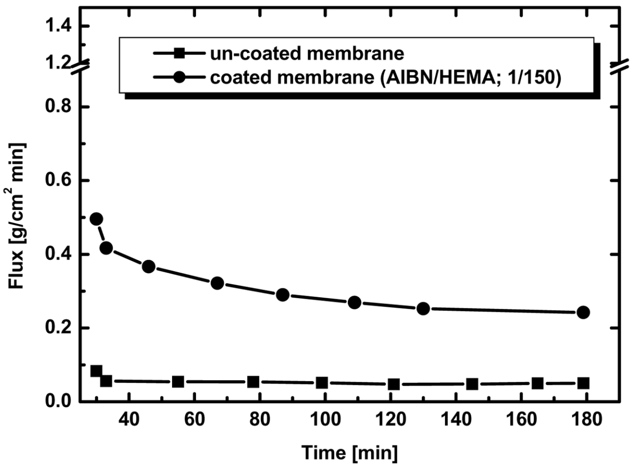


Fig. 8. The flux of oil emulsion with operating time at 200 ppm (Δp =3 psi).

At 400 ppm of oil concentration in the feed, the flux of the surface-modified membrane was 0.173 $g/cm^2 \cdot min$ and that of the un-coated membrane was 0.076 $g/cm^2 \cdot min$. The flux was about 2.3 times higher than that of un-coated membrane, as shown in Fig. 9.

As mentioned above, the fluxes of oily water through the surface-modified membrane at oil concentrations of 100 ppm, 200 ppm and 400 ppm were more than 2 times higher than that of un-coated membrane.

When the membrane used for oil emulsion experiment was washed out, in addition, the surface-modified membrane recovered the initial flux, which means that fouling due to the plugging of pores with oil emulsion did not occur. However, the flux of un-coated membrane was not recovered after washing-out. These experimental results mean that the surface-modified membrane was highly resistant to the fouling by oil emulsion.

4. The Rejection of Oil Emulsion by the Surface-modified Membrane

The feed of oily water was cloudy like dilute milk. However, the permeate was very clear. Even the naked eye could tell that all the oil emulsion was almost rejected by the membrane. The concentration of oil in the permeate stream was analyzed with gas chromatograph (Shimadzu GC-14B). The concentration of oil was undetectable by GC (TCD equipped), which means that the rejection of oil emulsion was higher than 99%.

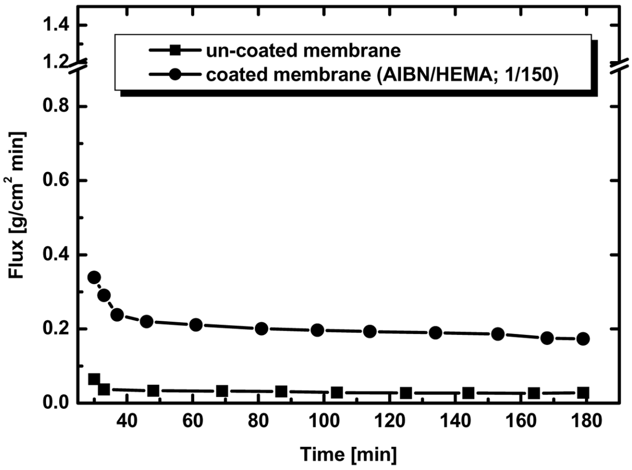


Fig. 9. The flux of oil emulsion with operating time at 400 ppm (Δp =3 psi).

CONCLUSIONS

The major drawback in the extensive use of membranes is membrane fouling, which results in flux decline during operation. The HEMA-coated and uncoated membranes showed a similar pattern of drastic flux-decline in the early stage of operation. However, the coated membrane maintained 2 times more flux than did the uncoated one.

The surface-modified membrane recovered the initial flux after washing-out, which means that the fouling due to the plugging of pores with oil emulsion did not occur.

This study shows that there is an optimum coating condition of AIBN/HEMA (wt/wt) ratio for a higher flux. The highest permeation flux was obtained at 1/150 of AIBN/HEMA (wt/wt) at various oil concentrations.

The increase in flux with increasing the feed flow rate might be due to the self-cleaning effect of cross-flow pattern in the feed compartment of the membrane module.

A high flux membrane with HEMA-modified surface may eliminate the major drawback (fouling) of membrane processes, and may be applicable for wastewater treatments as well as oily wastewater treatments.

ACKNOWLEGEMENT

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