Korean Membrane Journal
Vol. 1, No. 1, December, 1999, 43-49

Ultrafiltration of Oily Wastewater with Surface Pretreated Membranes

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(Received November 15, 1999, Accepted November 29, 1999)

Abstract: Separation of soluble oil was investigated during filtration of cutting oil emulsion using various commercial ultrafiltration membranes. The surface properties of membranes used were hydrophilic, hydrophobic and modified surfaces by various surfactant pretreatments. Conditions varied include stirring speed, transmembrane pressure, membrane type and surfactant type for pretreatment. The results give some indication of mechanisms occurring at the membrane surface. Surfactant pretreatments significantly improved water flux and UF flux of hydrophilic regenerated cellulose (up to 2.4x for YM100) and hydrophobic polysulfone (up to 2.2x for PTHK) membranes depending on surfactant type and operating conditions. The UF flux enhancement was attributed to membrane swelling and reduction of interfacial surface tension between oil droplets and membrane surface. Unexpectedly, the hydrophilic membranes revealed greater flux enhancement than the hydrophobic membranes. The results also showed a greater improvement in UF flux at lower operating pressure.

1. Introduction

Metal transformation industries such as rolling mills, forges and mechanical workshops produce large quantities of oily wastes, which need to be treated before discharging into the environment. Although different methods [1] have been used for the treatment of soluble oil wastes, membrane process [2-9] may be an attractive alternative. Compared to the generally used systems of chemical flocculation and coagulation, followed by dissolved air flotation, the major advantages of membrane systems are high oil removal efficiency, lower capital cost and operating cost, and no use of chemicals. However, the membrane suffers from flux loss with time due to concentration polarization and fouling.

Temporary surface modification [10-14] of membranes by adsorption of surfactants and soluble polymers [12] has been used to reduce interactions between membranes and solutes, and so control fouling. In this study, the membrane surfaces were pretreated with various surfactants in order to protect the surface and/or pores from the components in the emulsion, which include oil, emulsifier and antifoam agent. Conditions varied include stirring speed, transmembrane pressure, membrane type and surfactant type for pretreatment. The results give some indication of mechanisms occurring at the membrane surface.

2. Experimental

2.1. Preparation of Oil-water Emulsion

The oil-water emulsion (0.01% v/v) were prepared by diluting Caltex Trusol DD (viscosity 30.6 cP at 40℃) in distilled water. The dilute emulsion was a stable milky white dispersion with zeta potential -38 mV at pH 5.9. Trusol DD is high quality general purpose emulsifiable cutting oil

giving good performance over a wide range of operations on more readily machineable steels. In general, soluble oil is a blend of mineral oil, petroleum sulfonates, rosin and/or fatty acid soaps, a coupling agent (ethylene, propylene, or hexylene glycol) and an antifoam agent.

2.2. Characterisation of Water-Oil Emulsions

The concentration of the emulsion was determined by turbidimetry (HACH Model 2100A) using a calibration curve which was linear up to 0.04 v/v% as Trusol DD.

The size distributions and mean particle size of the emulsions were measured by laser-light scattering using a Malvern Submicron Particle Analyser (Type 4600SM), fitted with a photon correlation spectrometer and the Malvern LOGLIN dual function digital correlator (Type 7027).

2.3. Filtration of Water Oil-Emulsion

The membranes used were PTTK (30 kDa) and PTHK (100 kDa) from Millipore, and YM30 (30 kDa) and YM100 (100 kDa) from Amicon. Whilst the Millipore membranes are made from polysulfone (relatively hydrophobic), the Amicon membranes are made from regenerated cellulose (hydrophilic). All membranes showed >99% rejection of Trusol DD.

Surfactant pretreatment of membranes was achieved by ultrafiltering 50 ml of 0.01% surfactant solution at 100 kPa without stirring. The anionic surfactant Aerosol OT-100 (AOT; sodium di-2-ethylhexyl sulfosuccinate; MW 444) was obtained from Cyanamid Australia. The nonionic surfactant obtained from I.C.I. Australia was N15 (MW 880), a polyoxyethylene nonyl phenol with 15 polyethylene oxide units. The cationic surfactant, cetyltrimethyl-ammonium bromide (CTAB, MW 364) was obtained from BDH Chemicals, U.K.

The diluted cutting oil (0.01% Trusol DD in water) was filtered through a membrane (15 cm^2) placed in a 110 ml capacity stirred cell with continuous introduction of the emulsions from a feed reservoir under nitrogen pressure (25-300 kPa) at room temperature (about 22℃). Stirring was provided by a magnetic bar located above the membrane surface at speeds from 200 to 400 rpm, with most experiments at 300 rpm. Flux was measured gravimetrically by an electronic balance. At the end of each filtration, the water permeability of the fouled membrane (J_{wf}) was measured at 100 kPa. The membrane was then washed with 100 ml of distilled water at 300 rpm for 5 minutes and the water flux (Jww) was measured again at 100 kPa.

3. Results

3.1. Characterisation of Water-Oil Emulsions

When the Trusol DD was diluted in distilled water, the emulsion showed similar droplet size distributions at dilutions of 0.002, 0.010 and 0.080% v/v (Fig. 1). The mean droplet size for 0.01% v/v emulsion was 196±7 nm. At 0.10% v/v the drop size was smaller at about 100 μm.

The effect of stirring speed on the droplet size of oil emulsion (Table 1) was evaluated after stirring for 30 minutes at each speed, progressing from 200 to 400 rpm. The droplet size remained the same up to the stirring speed of 370 rpm and decreased at the higher stirring speed of 400 rpm. At 400 rpm, while the number of small (<150 nm) and large droplets (dia.>300 nm) decreased, that of medium size (150-300 nm) droplets increased.

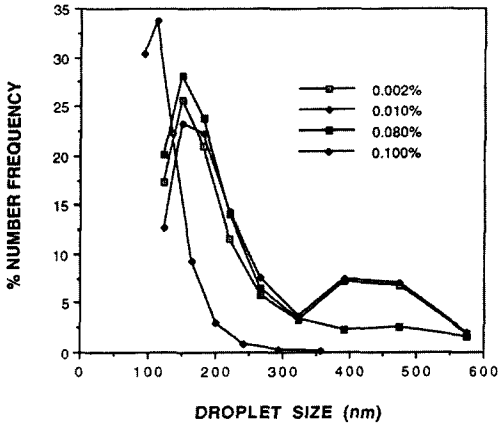


Fig. 1. Size distribution of oil emulsions.

Table 1. Effect of Stirring Speed on Oil Emulsion Size (0.01 v/v % Emulsion)

Emulsion Diameter (nm)	Mean	Minimum	Maximum
Hand Shaking	203.1	111.4	517.1
200 rpm, 30 min	200.1	111.4	517.1
300 rpm, 30 min	203.4	111.4	517.1
400 rpm, 30 min	194.7	111.4	426.8

3.2. Surfactant Pretreatment and Water Flux of the Membranes

Relative water flux measured at 100 kPa after the pretreatment is shown in Table 2 for PTHK and YM100 membranes. Surfactant pretreatment increased the water flux of regenerated cellulose (YM30 and YM100) membranes, but decreased polysulfone membranes (PTTK and PTHK), except for use of CTAB. The adsorption of surfactant in general causes a drop in the water flux due to reduction in effective pore radius [11-13,15,16]. However, Swaminnathan et al. [17] reported a considerable increase in pure water flux when PM30, XM100A and XM300 membranes were treated with non-ionic detergent Teepol (5% v/v), which was attributed to swelling of the membranes. This may have occurred for the YM membranes in this study.

3.3. Filtration Performance of Oil Emulsion

Operating conditions were varied to establish their interaction with surfactant pretreatment, and to provide insight into the mechanisms involved. Conditions varied include stirring speed, transmembrane pressure, membrane type and surfactant type for pretreatment.

3.3.1. Performance of Untreated Membranes

The profiles of permeate volume versus time for the filtration of 200 ml oil emulsion (0.01% v/v) with various untreated membranes at 300 rpm and 100 kPa are shown in Fig. 2. The curves of relatively hydrophobic polysulfone membranes (PTTK & PTHK) deviate more rapidly from linearity than those of hydrophilic regenerated cellulose membranes (YM30 & YM100), indicating greater loss of filtration performance with polysulfone membranes.

Table 2. Relative Water Flux Measured at 100 kPa after Surfactant Treatment

	AOT	CTAB	N15
PTHK	88-98	99-102	79-86
YM100	107-115	96-106	110-123

Relative water flux (%)=(J_{wt} /J_{wi})×100, where J_{wi} and J_{wt} represent water fluxes of the initial and after the surfactant treatment, respectively.

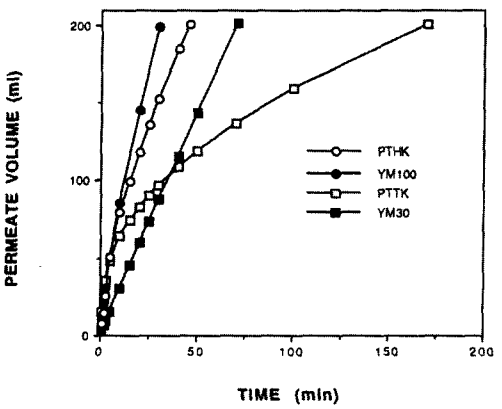


Fig. 2. Profiles of permeate volume versus time for oil emulsion using various membranes (0.01% v/v, 100 kPa, 300 rpm).

3.3.2. Performance of Surfactant treated Membranes

When the membranes were pretreated with surfactants (0.1 wt.%) the performance varied with surfactant type and operating conditions (Table 3). For all surfactants, the advantage of treatment diminished with increasing filtration pressure for both PTHK and YM100 membranes. Flux improvement decreased in order of N15, AOT then CTAB. Surprisingly the treatment was more advantageous for flux improvement on the hydrophilic YM100 membranes, especially with CTAB, than the hydrophobic PTHK membrane in all cases. A similar trend was observed with the treatment of tighter PTTK and YM30 membranes.

Table 3. UF Flux Improvement and Flux Decline due to Surfactant Treatment

⊿P (kPa)		PTHK				YM100			
		Untr.	AOT	CTAB	N15	Untr.	AOT	CTAB	N15
25	FI (%)		56.3	-76.5	116.3		67.6	61.1	143.6
	FL (%)	18.7	18.8	18.8	23.9	5.1	6.6	10.4	19.8
50	FI (%)		38.9	-67.9	54.7		47.6	44.3	54.5
	FL (%)	28.8	34.6	29.0	42.8	17.1	27.4	33.1	37.3
100	FI (%)		-36.5	-45.8	-31.1		14.4	14.4	7.9
	FL (%)	56.6	76.9	57.0	78.5	31.9	41.3	36.5	35.1
200	FI (%)		-68.1	-23.2	-21.4		12.3	14.8	4.4
	FL (%)	79.5	82.9	73.5	84.4	56.9	57.3	57.4	57.9

FI (Flux improvement) (%)=[(Jtreated/Juntreated)-1]×100.
FL (Flux loss) (%)=[1-(J200 ml/J50 ml)]×100.

3.3.3. Effect of Pressure

The effects of transmembrane pressure on the flux upon passage of 200 ml of permeate, when filtering 0.01% emulsion through PTTK, PTHK, YM30 and YM100 membranes at 300 rpm are shown in Fig. 3. The fluxes of regenerated cellulose (YM30 & YM100) membranes increased with increasing pressure, but approached limits of pressure independent flux. That is, the experiments were carried out in the pre-gel-polarization region. However, for the polysulfone (PTTK & PTHK) membranes, the flux becomes dramatically lower with increasing pressure (above 50 kPa). That is, the flux was controlled by the boundary layer conditions and fouling, since flux fell away sharply from the polarization limiting flux. It is possible that for the more hydrophobic membranes pressures >50 kPa exceed the oil intrusion pressure and pore penetration occurs. For PTHK (Fig. 4a), deviation from linearity increases with increasing pressure and becomes significant after 5 minutes at 200 kPa. For YM100 membrane (Fig. 4b), the deviation is much less than for PTHK, and there is no indication of loss of production rate up to 300 kPa. However, production efficiency on PTHK was worse at 300 kPa than at 100 kPa, with data in Fig.3 and Fig. 4a indicating a critical flux of 175 l/m^{2}h at 50 kPa. Similarly, PTTK showed a critical flux of 160 l/m^{2}h at 50 kPa.

Fig. 5. demonstrates how the starting pressure has an effect on the flux. For both PTHK and YM100 membranes, one set of membranes started filtering oil emulsion at low pressure (from 25 kPa) and the pressure was progressively increased after flux had reached a steady state at each pressure. The other set of membranes was used to filter the emulsion from high pressure to low pressure, starting at 200 kPa. The results show that when the filtration was started at high pressure, the performance as pressure was decreased was controlled by the boundary layer conditions set at the initial high pressure.

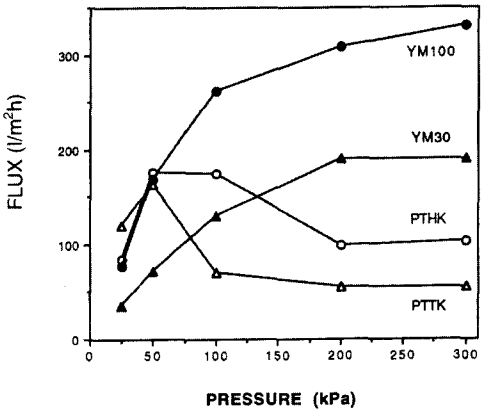
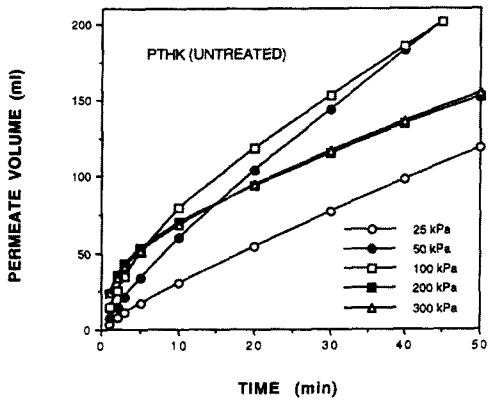
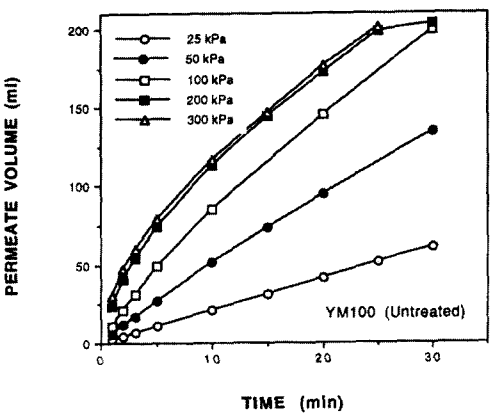


Fig. 3. Flux (200 ml permeate) profiles of oil emulsion (0.01% v/v) as a function of pressure for PTTK, PTHK, YM30 and YM100 membranes at 300 rpm.



(a) PTHK



(b) YM100

Fig. 4. Profiles of permeate volume versus time for oil emulsion (0.01% v/v, 300 rpm) at various transmembrane pressure.

Changes in the size distribution of the oil emulsion due to pressure was investigated. Using the PTHK or YM100 membrane, the stirred cell (300 rpm) containing 100 ml of feed emulsion was pressurised to 25 or 200 kPa until 50 ml of permeate was passed, then the retentate was analyzed for droplet size distribution (Fig. 6). The relative droplet size distribution was calculated by dividing by the filtration concentration factor (2) and dividing by the droplet size distribution of the original feed (n_{io}).

$$n\hat{i} = n_i / 2n_{io}$$

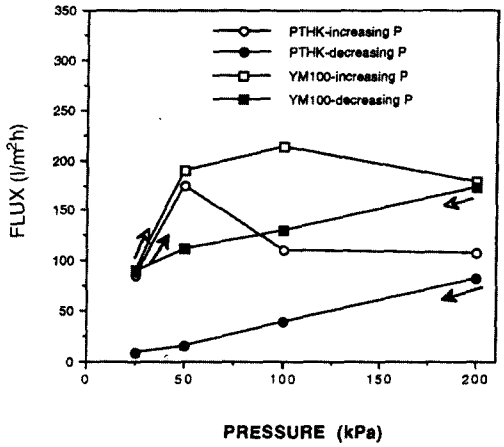


Fig. 5. Steady state flux versus pressure under different operating conditions (0.01% v/v oil emulsion, 300 rpm).

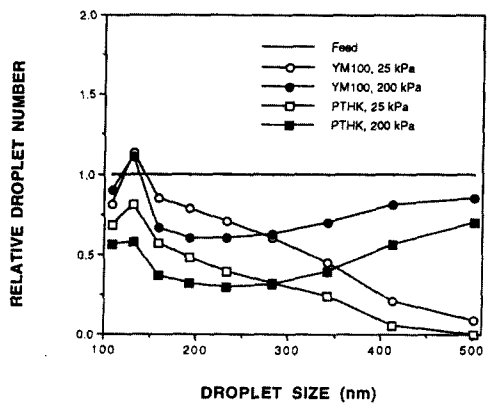


Fig. 6. Changes in size distribution of oil emulsion due to operating pressure using PTHK and YM100 membranes at 300 rpm.

where n_i = retentate droplet size distribution, n_{io} = feed and $n\hat{i}$ = relative droplet distribution of retentate.

There are significant losses of large droplets for both PTHK and YM100 membranes, although the loss is greater for the PTHK. At 200 kPa, the medium size (150-300 nm) droplets diminished more rapidly than the smaller or larger ones. The large droplets at higher pressure decreased more slowly than those at lower pressure. Loss of droplet numbers in any size range were due to adsorption on the membrane, as there was no

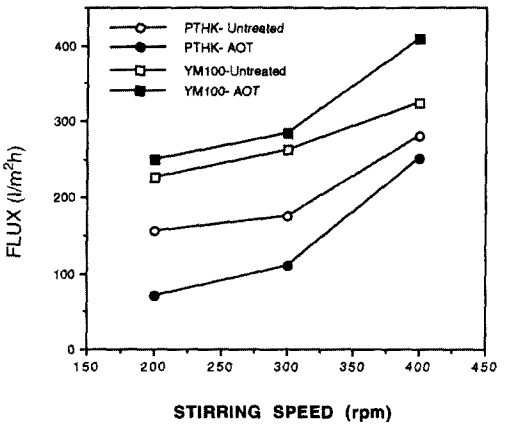


Fig. 7. Effect of stirring speed on the fluxes of oil emulsion through untreated and surfactant (AOT) treated PTHK and YM100 membranes (0.01% v/v oil emulsion, 100 kPa).

significant increase in any droplet size above that of the original feed, and there was no loss of oil to permeate (rejection 0.999).

3.3.4. Stirring Speed

Increasing the stirring speed from 200 to 400 rpm increased flux in all cases (untreated, surfactant treated). However, it was shown that the average droplet size decreased with time at higher stirring speed of 400 rpm (Table 1), but was more stable at 300 rpm.

For AOT treatment (Fig. 7), fluxes of the treated YM100 membranes were greater than those of the untreated at all stirring speeds. In the case of PTHK membranes, the treatment produced reduced fluxes at all stirring speeds.

4. Discussion

Emulsified oil droplets accumulate near the membrane surface due to concentration polarization. Large droplets will adsorb onto the surface more easily. The greater decrease of larger size droplets for both PTHK and YM100 membranes at 25 kPa (Fig. 6) provides evidence of this. At high operating pressure, in addition to the surface adsorption, droplets smaller than membrane pore size can enter pores and adsorb internally causing dramatic flux decline. The hydrophilic and hydrophobic surfaces will provide different level of access to the oil droplets. The oil droplets can adsorb more easily onto the hydrophobic surface than to the hydrophic surface. This is shown as greater flux loss of the hydrophobic PTHK (22% loss from pure water flux) than that of hydrophilic YM100 (3% loss) when the surface was initially exposed to the emulsion. It is also evident in Fig. 3 where the hydrophobic membranes suffer a dramatic drop in flux as pressure is increased.

The unexpected greater advantage of surfactant treatment in UF flux enhancement for the hydrophilic membranes than the hydrophobic membranes could be attributed to two factors. One is the greater swelling of the hydrophilic membranes as evidenced by increase in water flux of the treated membranes. The other is reduction of interfacial tension between the membrane surface and the oil droplets resulting in easier separation. Greater UF flux loss (Table 4) of the treated membranes reveals that the improvement in UF flux for the treated membranes involves other mechanism than reduced fouling (reduced flux decline). If the role of surfactant adsorbed onto the membrane surface was to reduce interfacial tension between membrane surface and emulsion, so increasing flux, then low pressure will provide more favorable conditions due to lower emulsion concentration in the boundary layer. As shown in Table 2, the improvement by treatment was indeed greater at lower pressure than that at higher pressure.

5. Conclusions

Surfactant pretreatments increased the water flux of regenerated cellulose (YM30 and YM100) membranes, but decreased that of polysulfone membranes (PTTK and PTHK), except for some cases of CTAB.

Surfactant pretreatment can enhance UF flux of oil emulsion. Flux improvement varied with surfactant type and operating conditions. For all surfactants studied, the advantage of treatment diminished with increasing pressure for both PTHK

and YM100 membranes. Flux improvement by surfactant pretreatments was in order of N15>AOT> CTAB. The treatment was more advantageous for flux improvement on the hydrophilic YM100 membrane than the hydrophobic PTHK membrane in all cases.

All untreated and surfactant treated membranes showed a greater response to greater stirring speed.

Acknowledgments

Dr P. V. Stevens and Mrs H. Wu are thanked for his stimulating discussion and her assistance with UF experiments, respectively. The authors gratefully acknowledge funding from the Australian Government for the UNESCO Centre for Membrane Science and Technology at the University of New South Wales.

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