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XIANGUO HU*, ERIKA BEKASSY-MOLNAR**,
GYULA VATAI*, ANDRAS KORIS*

ULTRAFILTRATION OF OILY EMULSION FOR METAL CUTTING FLUID: ROLE OF FEED TEMPERATURE

The oil-in-water emulsions as industrial wastewaters are produced in a large amount in the metal working, food producing and other industrial branches. Separation of oil from water, both being the phases of emulsion, is economically realizable by membrane techniques. There are so many membrane operation factors which influence the permeate flux, such as transmembrane pressure, feed concentration, feed temperature, design of flow route and so on, besides membrane material compositions. This article describes the results of water removal from oil-in-water emulsion by different ultrafiltration membranes at variable temperatures. The experimental results show that the effect of feed temperature on the permeate flux depends on the variations of membrane property (including membrane material and MWCO), concentration of feed emulsion and transmembrane pressure. Based on the relationship between the gel resistance and the feed temperature it was found that the gel resistance decreased with temperature. The concentration polarization of PES (polyethersulfone) membrane is higher than that of PVDF (polyvinylidene fluoride) membrane. At higher emulsion concentration the concentration polarization becomes very serious. In our experimental conditions, the enhancement effect of the temperature on the permeate flux at higher emulsion concentration is better than that of lower emulsion concentration. Some models of the effects of feed temperature on permeate flux variation were presented and analyzed based on the experimental data. In addition, the COD values and oil concentrations in the permeate were analyzed at different temperatures.

Keywords: *oily emulsion, feed temperature, ultrafiltration*

1. INTRODUCTION

In recent years, considerable attention has been focused on the discharge of oily wastewater and its impact on the environment. Pollution of water by oily hydrocarbons is especially harmful to the aquatic life, as it attenuates the light and perturbs the normal

* Faculty of Mechanical Engineering, Hefei University of Technology, 230009 Hefei, PR China.
** Faculty of Food Science, Corvinus University of Budapest, H-1118 Budapest, Hungary.

mechanism of oxygen transfer. Consequently, removing oil from wastewater is an important aspect of pollution control in many fields of industry [1]–[4]. For unstable emulsions or primary emulsions which contain oil droplets of diameter greater than 100 μm, chemical separation techniques such as flocculation and coagulation are applied. The oil-in-water emulsions as industrial wastewaters are produced in a large amount in the mechanical engineering and in the food industry [5]. The neutralization or treatment of these wastewaters is an important environmental task. Separation of the oil from water that are the phases of emulsion is economically realizable by membrane technique. The main advantage of the method is that the clean water is reusable in the technology or can be discharged into sewage or into surface water, while the oil can be burned or reused.

The water removal from wastewater by ultrafiltration is influenced by the membrane material, the physical performance and the operation conditions. For a selected membrane it is necessary to choose the best operation parameters in order to assure that the membrane works under optimal conditions. In our former researches, we studied the effects of several kinds of ultrafiltration membranes of different nominal molecular-weight cut-off (MWCO), pore size and transmembrane pressure on the treatment efficiency of the oil-in-water emulsions of different oil concentrations [6]–[9]. However, the effect of temperature on the permeate flux of oil-in-water emulsions is one of operating parameters. Usually, changes in temperature result in a wide range of effects that go beyond the viscosity of the permeate alone [10]. The effect of temperature on permeate flux is often described by the expression of the form of the Arrhenius equation:

$$J_T = J_{20} \exp\left(\frac{s}{T}\right), \tag{1}$$

where J_T is the permeate flux at an arbitrary temperature T, J_{20} is the permeate flux measured at a reference temperature of 20 °C, and s is an empirical constant that must be evaluated for each membrane. Thus the temperature correction factor by which permeate flux at some reference temperature (in this case, 20 °C) is multiplied is the ratio of J_T to J_{20}.

Using a reference temperature of 25 °C, POHLAND [11] reported that the following expression for the temperature correction factor was correct within approximated 3 per cent:

$$\frac{J_T}{J_{25}} = 1.03^{(T-25)}. \tag{2}$$

MARCH and ERIKSSON [12] give the following formulas for the temperature correction factor to be applied to a FilmTec FT30 membrane:

$$\frac{J_T}{J_{25}} = \exp\left[2640\left(\frac{1}{298}\right) - \frac{1}{273+T}\right] \quad \text{for } T \geq 25\ ^\circ\text{C}, \tag{3}$$

$$\frac{J_T}{J_{25}} = \exp\left[3480\left(\frac{1}{298}\right) - \frac{1}{273+T}\right] \quad \text{for } T \le 25\ ^\circ\text{C}. \tag{4}$$

Recently, AGASHICHEV et al. [13] developed a model for temperature polarisation which is caused by convective and conductive heat transport between bulk and membrane surface in ultrafiltration process of non-Newtonian fluid. The model is applicable to plate and frame channels. Transport expressions for viscous, temperature and diffusion boundary layers are the core of the model.

The feed temperature affects not only oil viscosity, but also water viscosity, hence in oil-in-water emulsion, the mass and heat transfers become complex. It is necessary to study the role of temperature, especially the combined multifactor influence, including tramsmembrane pressure and other factors.

2. EXPERIMENTAL

The experimental UF membranes were produced by the Hoechst Company, Germany (TS 6V 205), and by the Zoltek Viscosa Corporation, Hungary (Mavibran FS-202-09 and FP 055A). The physical properties of the membranes are shown in table 1.

Table 1

Properties of UF membranes

Membrane	Material[(a)]	MWCO kD	Water fux[(b)] dm^3/m^2 h	Max. temp. °C
TS 6V 205	PES	100	800	60
FP 055 A	PVDF	60–80	1000	60
FS 202-09	PES	20	700	60

[(a)] PES: polyethersulfone; PVDF: polyvinylidene fluoride.
[(b)] At feed pressure of 3 bar and temperature of 20 °C.

The stable oil-in-water emulsion which contains engine oil, surfactants and deionized water was used. Two different oil concentrations of oil-in-water emulsion were prepared in batches of 10 dm^3. The oil concentrations in the emulsion were 0.5 vol. % and 5 vol. %, respectively. The emulsions produced were quite resistant to coalescence. Viscosity of feed oil-in-water emulsion at 20 °C was: $\eta = 1.381 \times 10^{-3}$ N s/m^2 at 5% oil concentration; $\eta = 1.139 \times 10^{-3}$ N s/m^2 at 0.5% oil concentration.

The experiments were carried out in an UF membrane apparatus [14]. The effective membrane area is 35 cm^2. The oil concentrations in the feed and permeate solutions were determined using UV spectrophotometer. The COD (mg/dm^3) was measured using the potassium dichromate method.

3. RESULTS AND DISCUSSION

3.1. INFLUENCE OF THE OPERATING TEMPERATURE

The influence of the feed emulsion temperature on the permeate flux is obvious. In general, the flux increases with an increase in the temperature. A higher temperature may lead to the enhancement of the activity of water molecules and the decline of the emulsion viscosity, therefore the permeate flux increases. The rise in the temperature from 20 °C to 60 °C caused 20–100% increase in the permeate flux under the present experimental conditions, as shown in figures 1 and 2. The temperature coefficients are 0.0047/1 °C and 0.008/1 °C at the feed emulsion concentrations of 0.5% and 5%, respectively. This means that the permeate flux increased subsequently by about 0.47% and 0.80%, respectively, as the temperature increased by 1 °C. Too high temperature, however, may lead to the damage of the membrane, to an increase in the resistance of the permeation and to a decrease in the flux.

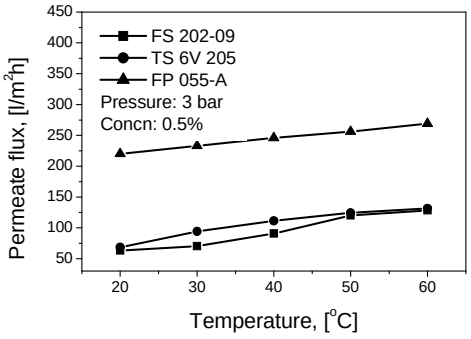

Fig. 1. Effect of temperature on permeate flux at emulsion concentration of 0.5%

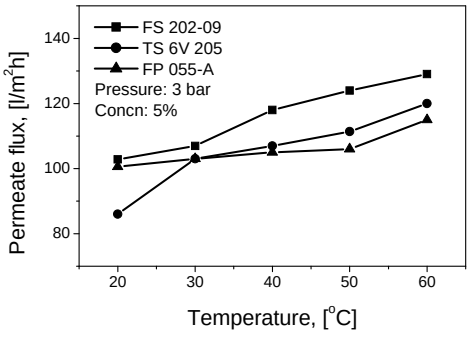

Fig. 2. Effect of temperature on permeate flux at emulsion concentration of 5%

The selection of the operation temperature is based on the physicochemical properties and biostability of the fluid [14]. The operation temperature should be below the permissible temperature of the membrane apparatus and the treated fluid. The higher the temperature, the lower the viscosity of the fluid and the better the efficiency of mass transfer. Thus, an increase in the fluid temperature can improve the permeate flux. The relation of temperature to diffusion coefficient can be described as follows [15]:

$$\eta D/T = \text{constant}. \tag{5}$$

The higher the temperature T and the lower the viscosity η, the greater the diffusion coefficient D. On the other hand, however, too high temperature may be responsible for the membrane deformation and compactness and it also decreases the

flux, as mentioned before. From the experimental results it can be found that the effect of temperature is more obvious at higher feed concentration than at lower one.

Comparing the experimental results in figures 1 and 2 it is found that the membranes tested have similar permeate flux of water at a higher feed concentration. At a lower emulsion concentration PVDF membrane has a superstability in the permeate flux of water. So, FP 055A membrane is especially suitable to treat oil-in-water of lower concentration. In addition, FES membranes (FS 202-09 and TS 6V-205) may have a stronger ability to resist concentration polarization than PVDF (FP 055A), because there is an obvious difference in the flux permeating the FP 055A membrane as the emulsion concentration is different [16].

3.2. COMBINED INFLUENCE OF THE TRANSMEMBRANE PRESSURE AND TEMPERATURE

The influence of feed temperature on the permeate flux is not independent; and there is a combined effect exerted by other factors, including transmembrane pressure, oil concentration, etc. [17]. In this study, the experiments were run at an emulsion concentration of 0.5 and 5 vol. % and the influent feed rate of 0.9 m/s. Experiments were performed at initial transmembrane pressures of 1, 2, 3, 4, 5 and 6 bar to evaluate the effect of transmembrane pressure. The feed emulsion temperatures of 20, 30, 40, 50, 60 °C were selected to evaluate the effect of temperature. The variations in permeate flux of different temperature and transmembrane pressure for the selected membranes at two feed concentrations are shown in figures 3–8.

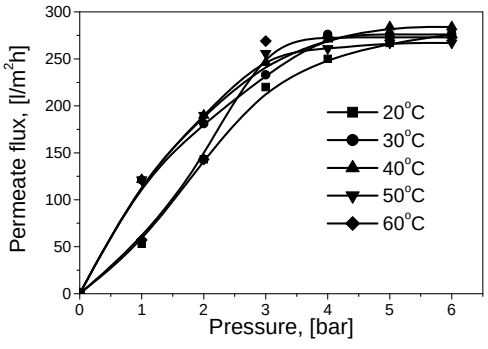

Fig. 3. Permeate flux as a function of pressure for FP 055A at emulsion concentration of 0.5%

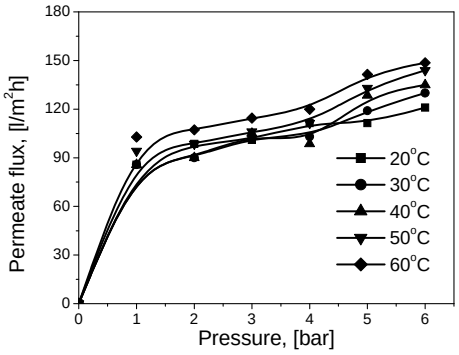

Fig. 4. Permeate flux as a function of pressure for FP 055A at emulsion concentration of 5%

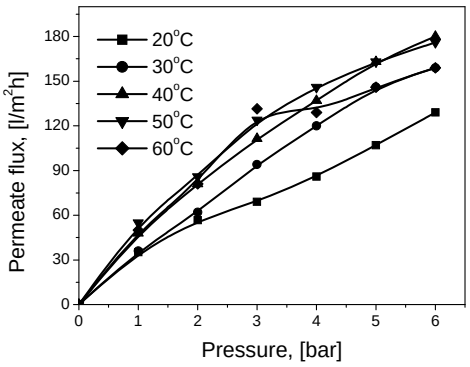

Fig. 5. Influence of pressure on flux of TS 6V 205 (PES) at emulsion concentration of 0.5%

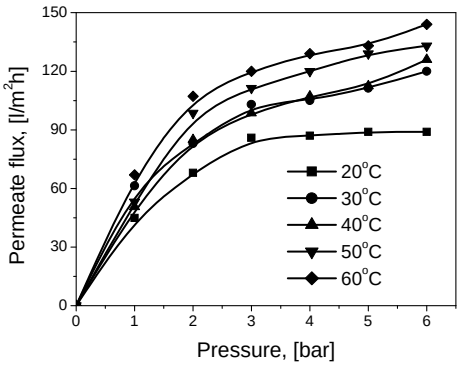

Fig. 6. Influence of pressure on flux of TS 6V 205 (PES) at emulsion concentration of 5%

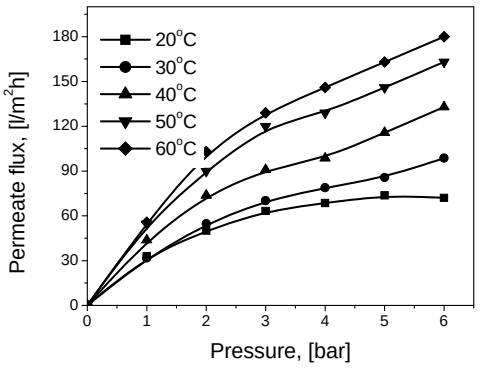

Fig. 7. Effect of pressure on permeate flux of FS 202-09 (PES) at emulsion concentration of 0.5%

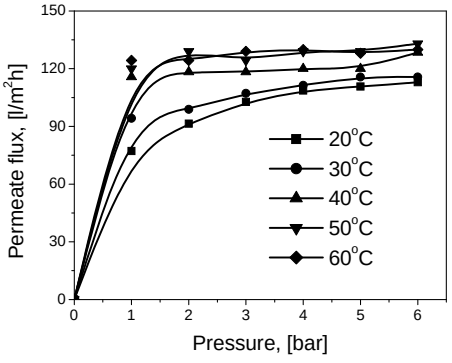

Fig. 8. Effect of pressure on permeate flux of FS 202-09 (PES) at emulsion concentration of 5%

Taking figures 3–8 into account, some phenomena being common for the membranes tested can be observed. At a lower emulsion concentration the UF membranes have higher permeate flux. At each experimental temperature the flux increased approximately with pressure in the case of the PES membrane. The permeate flux of PVDF membrane reaches a plateau after attaining a critical pressure. The extent of concentration polarization of FVDF (FP 055A) membrane is lower than that of PES membranes (FS 202-09 and TS 6V-205) at lower feed concentration (see figures 3, 5 and 7), in which the permeate flux of FVDF (FP 055A) membrane increased approximately linearly with transmembrane pressure till a critical pressure was reached. In the case of PES membranes (FS and TS 6V), the effect of pressure on the flux is controlled by temperature. At different temperatures the pressure influence is different. MANTTARI [18] reported the effect of temperature on the retention of glucose during nanofiltration in the temperature interval

from 25 °C to 65 °C. An increase in temperature decreased the retention until a critical temperature of the membrane was exceeded. Most nanofiltration membranes seemed to be almost completely wetted at a pressure of 25 bar. This is the difference between ultrafiltration and nanofiltration.

The flux increases with temperature rise at either lower or higher feed concentration because of the enhancement of diffusion coefficient. This kind of synergistic effect of pressure and temperature on the permeate flux (dm^3/m^2h) can be identified by the results of FP 055A at feed concentration of 5 vol. % as shown in table 2.

Table 2

The synergistic effect of pressure and temperature on the permeate flux
(membrane: FP 055A, feed concentration of 5 vol. %)

Temp., °C	Transmembrane pressure, bar					
	1	2	3	4	5	6
	Flux, dm^3/m^2h					
30	85.8	90	103	103	119	130
50	94.2	98.6	106.1	111.4	133	144
60	102.8	107.2	114.5	120	141.5	148.6

The effect of transmembrane pressure was based on the variation of membrane resistance which was related to the concentration polarization and gel polarization. At lower emulsion concentration (0.5 vol. %), the permeate flux increased almost linearly with an increase in transmembrane pressure. At higher emulsion concentration (5.0 vol. %) the effect of pressure on the permeate flux depended on the pressure. When the transmembrane pressure is over a critical value, the flux is controlled by gel layer. The critical transmembrane pressure approached 2 bar in the case of FS 202-09 or FP 055A and 3 bar for TS 6V under the present experimental conditions.

3.3. VARIATIONS OF COD AND OIL CONCENTRATION

The values of critical pressure for different membranes are different and dependent on the capillary pressure. When transmembrane pressure is over the capillary pressure, oil can easily pass and deposit in the membrane pores, thus decreasing membrane pore size and increasing membrane fouling [19]. At higher operating pressure the effect of membrane fouling is more important than the effect of pressure. The critical pressures for FS 202-09 and FP 055A membranes approach 2 bar, whereas it is about 3 bar for TS 6V membrane at 5% feed emulsion.

The measurements of COD and oil concentration in the permeate at the critical pressure and at 40 °C are presented in table 3. It is shown that three membranes operate satisfactorily at low feed concentration (0.5%). This means that the permeate from

both membranes, i.e. TS 6V-205 and FS 202-09, achieved the suitable level to be discharged (the oil concentration in permeate should be <10 mg/dm^3, and COD <100 mg/dm^3). At high feed concentration (5%), however, the COD values are high, whereas the oil concentration is acceptable. When the pressure was increased to 4 bar, the COD values and oil concentrations in the permeate increased rapidly as shown in table 4. Therefore these membranes are not suitable to treat the investigated emulsion of a high feed concentration at high transmembrane pressure. This can be explained by the fact that the membrane fouling (loss of permeability) becomes more important as the pressure is over the critical value. A probable reason for this phenomenon is as follows: the concentration polarization gives a higher probability that the drops will come into contact with the membrane pores, and at some pores the operating pressure will exceed the capillary pressure so that the oil drops can be deformed and enter the membrane structure [9], [14].

Table 3

Oil concentration and COD in permeated water at 2–3 bar

Membrane	COD mg/dm$^{3(a)}$	COD mg/dm$^{3(b)}$	Oil concen. mg/dm$^{3(a)}$	Oil concen. mg/dm$^{3(b)}$
TS 6V-205 (3 bar)	62	124	2.0	5.0
FP 055 A (2 bar)	158	140	19	8.0
FS 202-09 (2 bar)	80	160	7.0	9.0

[(a)] Feed oil concentration of 0.5%.
[(b)] Feed oil concentration of 5%.

Table 4

Oil concentration and COD in permeated water at 4 bar

Membrane	COD mg/dm$^{3(a)}$	COD mg/dm$^{3(b)}$	Oil concen. mg/dm$^{3(a)}$	Oil concen. mg/dm$^{3(b)}$
TS 6V-205	290	1870	26	54
FP 055 A	435	2560	65	78
FS 202-09	376	2950	42	126

[(a)] Feed oil concentration of 0.5%.
[(b)] Feed oil concentration of 5%.

Based on the mass-transfer theory and resistance-in-series equation of ultrafiltration, a calculation model for oil concentration in boundary layer was expressed by equation (6). The validity of this equation is confirmed by the feed temperature from 20 to 60 °C and the transmembrane pressure from 1 to 6 bar. The average per cent deviation is less than 0.5% [20]:

$$C_m = C_b \exp\frac{1}{K}\left(\frac{\Delta P}{\eta(R_m + \alpha \Delta P)}\right), \tag{6}$$

where K is the coefficient of mass transfer (m h^{-1}); C_m (vol. %) and C_b (vol. %) are the oil concentrations at the membrane surface and in the bulk emulsion of feed, respectively; η is the permeate viscosity (N s m^{-2}); ΔP is the transmembrane pressure (bar); R_m is the intrinsic membrane resistance (m^{-1}) and R_g (m^{-1}) is the gel-layer resistance; α is the constant (m^{-1} bar^{-1}).

On the basis of the above equation the oil concentration can be calculated approximately within the concentration polarization region at different pressures and the gel concentration C_g on the membrane surface. As the operating pressure increases, C_m approaches C_g. The C_g (vol. %) was about 30 vol. % under the present experimental conditions as shown in table 5.

Table 5

Oil concentrations at the membrane surface

C_b, vol.%	Transmembrane pressure, bar					
	1	2	3	4	5	6
	C_m, vol.%					
0.5	2.84	7.14	12.67	18.71	24.82	30.75
5.0	13.94	19.99	24.04	26.88	28.98	30.58

4. CONCLUSIONS

1. An increase in the temperature can enhance the flux at 0.5 vol.% and 5.0 vol.% emulsion concentrations. The effect of pressure on the flux is controlled by the temperature of PES membranes (FS and TS 6V). At different temperatures the pressure influence is different.

2. An increase in the transmembrane pressure and temperature can improve the permeate flux. At lower emulsion concentration (0.5%), the concentration polarization is not obvious. At higher emulsion concentration (5%) when the pressure is above 2–3 bar the permeate flux is controlled by the gel layer. As the operating pressure increases, the oil concentration at the membrane surface approaches 30 vol. %.

3. The gel resistance decreases with the rise in temperature, which decreases the viscosity of feed emulsion and improves the mass-transfer effect.

4. Ultrafiltration membranes TS 6V 205, FS-202-09 or FP 055A used for treating oily wastewater allowed very efficient reduction of the COD and oil concentrations in the permeate. However, at the higher temperature the oil concentrations and COD values increase obviously as the transmembrane pressure exceeds the critical value.

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