Analysis and Characterization of Membrane Fouling of Ultrafiltration Separation for Oil-in-Water Emulsion*

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Ultrafiltration membrane fouling and cleaning in the process of oil-in-water emulsion treatment was investigated. The effects of flow velocity and feed emulsion temperature on the membrane surface fouling and the permeate flux are discussed. The results show that the effects of the feed temperature and cross-flow velocity on the reduction of membrane fouling are significant at higher emulsion concentration, while at lower emulsion concentration the influence of feed temperature on membrane fouling is not obvious. The fouled membrane surface was observed by scanning electron microscopy and the chemical composition of foulants was analyzed by Fourier transform infrared spectroscopy. The experimental results show that the permeability of ultrafiltration membrane can be recovered with the help of a micellar solution of sodium dodecyl sulfate—pentan-1-ol—water.

The direct discharge of oily emulsions, used widely in metal working, food, petroleum, and other industries, may cause serious environmental pollution [1, 2]. It is testified that the ultrafiltration (UF) is a feasible way to control the oil concentration in the permeate [3—8]. Flux decline, however, due to the concentration polarization and fouling, is an important problem in membrane filtration. Filtration efficiency improvement and the membrane fouling suppression is the goal of many studies in the field of membrane technology.

There are several methods to limit the membrane fouling, such as backwash, vibration filtration, ultrasound wave, chemical cleaning, *etc.* [9—12]. These techniques include a periodic reversal in flow direction to prevent particulates from clogging the module inlet. Periodic back-flushing of the membrane by reverse flow of permeate removes the surface foulants from the membrane, periodic reductions in feed pressure, while maintaining a high cross-flow decreases the gel layer growth. Large-diameter tubular membranes can be cleaned mechanically using sponge balls [13]. *Belkacem et al.* introduced the application of specific micellar cleaning solutions (microemulsions) for fouled membranes to restore their initial water permeability and hydrophilic properties [13]. The microemulsions are used to effectively clean the membranes fouled with oily macroemulsions. As these solutions contain antifoam and anticorrosion products as well as bactericides, they are well suited for the industrial use. In addition, at low macroemulsion concentration they can even prevent the membrane fouling.

The present study concerns the analysis of membrane fouling of an ultrafiltration membrane used for separation of oil-in-water emulsion. Moreover, various cleaning solutions were evaluated, which could restore the permeability of membranes.

EXPERIMENTAL

Three UF membranes, TS 6V-205 (Hoechst, Frankfurt, Germany), FP 055A and FS 202-09 (Zoltek Co., Hungary) were examined; their basic properties are summarized in Table 1. A fresh stable oil-in-water emulsion, HW-1, was provided by Anhui Petrochemical Company (Hefei, China). The batches of emulsion of 10 dm^3 each were prepared by dispersing the engine oil in deionized water using anion and nonion emulsifiers. The oil content in such emulsion was 5 vol. %. The emulsion used was quite stable with respect to coalescence. Its dynamic viscosity at 20 °C was $\eta = 1.381 \times 10^{-3}$ Pa s.

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Table 1. Properties of UF Membranes

Membrane	Material	MWCO × 10^{-3}	Water flux* / $dm^3\ m^{-2}\ h^{-1}$	Maximum operation temperature/°C
TS 6V-205	PES	100	800	60
FP 055A	PVDF	60	1000	60
FS 202-09	PES	20	700	60

PES: polyethersulfone; PVDF: poly(vinylidene fluoride); MWCO – relative molecular weight cut-off.
* At feed pressure 0.3 MPa and temperature 20 °C.

The oil-in-water emulsion was stored in a tank placed in a thermostated bath and pumped to the ultrafiltration cell using a variable-speed screw pump. This volumetric pump ensured a constant flow rate and thus a constant velocity at the inlet of the ultrafiltration cell. The flow rate was monitored by an electromagnetic flow meter, the concentrate was recycled into the tank. The pressure at the outlet of the module could be adjusted with a discharge valve. Two pressure transducers measured the pressure at the inlet and outlet of the module in the concentrate compartment. The permeate mass was measured by a balance the voltage output of which was converted into a signal which was converted in a personal computer to the flow rate [14].

The membrane fouling by oil-in-water emulsion was measured in the following way: after the permeate flux decreased to a plateau, filtration was continued for another 30 min. Then a clean water flux test (CWFT) was performed on the fouled membrane to evaluate the degree of membrane fouling. The membrane was then chemically cleaned and another CWFT was performed subsequently to determine the degree of restored permeate flux.

Two membrane cleaning procedures were applied. In the case of the first one the fouled membrane was washed for 30 min with the micellar cleaning solution containing 1.9 mass % sodium dodecyl sulfate, 3.7 mass % pentan-1-ol, and 94.4 mass % H_2O. Then the membrane was rinsed with distilled water and the permeate flux of regenerated membrane was measured. The second procedure consisted in subsequent immersion of the fouled membrane for 10 min into 2 % HCl aqueous solution, gasoline, and 2 % NaOH aqueous solution. After each step the membrane was rinsed with deionized water. Finally, the permeate flux at 0.3 MPa transmembrane pressure and 20 °C was measured.

The influence of the cross-flow velocity on the permeate flux was measured in the range of 0.5—1.5 m s^{-1} (Re = 3500—10500) at 0.3 MPa transmembrane pressure and 5 % oil content in the emulsion.

The topography of the membrane surface and the fouling substances compositions were analyzed with the help of Hitachi scanning electron microscope S-570 (Tokyo, Japan) and MAGNA-750 FT-IR (Nicolet, Madison, WI, USA) equipment, respectively.

RESULTS AND DISCUSSION

Feed temperature and cross-flow velocity are two important operation parameters influencing the membrane fouling [15]. By changing the cross-flow velocity the hydrodynamic conditions within the membrane module changed too, while a variation of feed temperature influenced the mass transfer coefficient. The convection to and diffusion away from the membrane surface determines the rate of build-up of fouling. The rate of convection to the membrane is a function of the permeate flux, and the diffusion away is linked to the degree of turbulence. An increase of the cross-flow velocity will increase the degree of physical scouring at the membrane surface and improve the back-transport into the bulk solution.

Cross-flow velocities of 0.5 m s^{-1}, 0.9 m s^{-1}, and 1.5 m s^{-1} were investigated at constant operating conditions of 0.3 MPa transmembrane pressure and 5 % oil in emulsion. The velocities correspond to the Reynolds numbers of 3500, 6300, and 10500, respectively, which are in the turbulent region. The effect of the velocity on the permeate flux is shown in Table 2. As it was observed, the higher the cross-flow velocity was applied, the higher the transmembrane flux was achieved. However, the increment of flux became lower by a further increase in the flow velocity. The increase of the cross-flow velocity does not always lead to an improvement in the permeate flux, because the state of dispersion of the oil droplets and the size distribution also affects the flux. Too high cross-flow velocity may not only cause too high pressure drop, but also speeds up the reduction of the membrane's separation efficiency. On the other hand, a lower flow velocity may lead to the concentration polarization, causing a decrease in the permeate permeability and the permeate water quality. Selection of the flow velocity depends on the membrane module and the feed composition used [12].

The influence of the operation temperature on the permeate flux is known [9]

$$\eta D/T = \text{const} \qquad (1)$$

The decrease of emulsion viscosity, η, with temperature, T, is compensated by the increase of the diffusion

Table 2. Influence of the Cross-Flow Velocities on Permeate Flux of FP 055A Membrane at the Transmembrane Pressure of 0.3 MPa, Temperature 40 °C, and Feed Containing 5 vol. % of Oil

Cross-flow velocity/(m s^{-1})	Reynolds number	Permeate flux/(dm^3 m^{-2} h^{-1})
0.5	3500	85
0.9	6300	105
1.5	10500	110

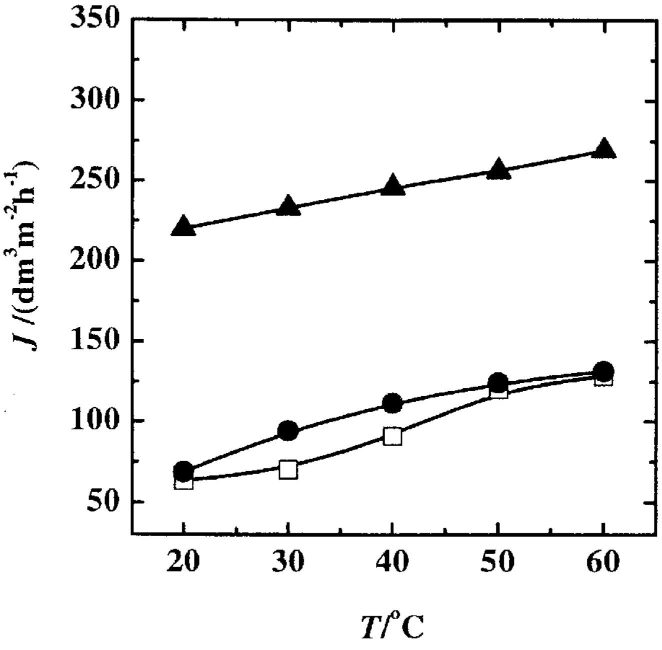


Fig. 1. Effect of temperature on permeate flux at emulsion content of 0.5 vol.% and transmembrane pressure of 0.3 MPa for FP 055A (□), FS 202-09 (▲), and TS 6V-205 (●) membranes.

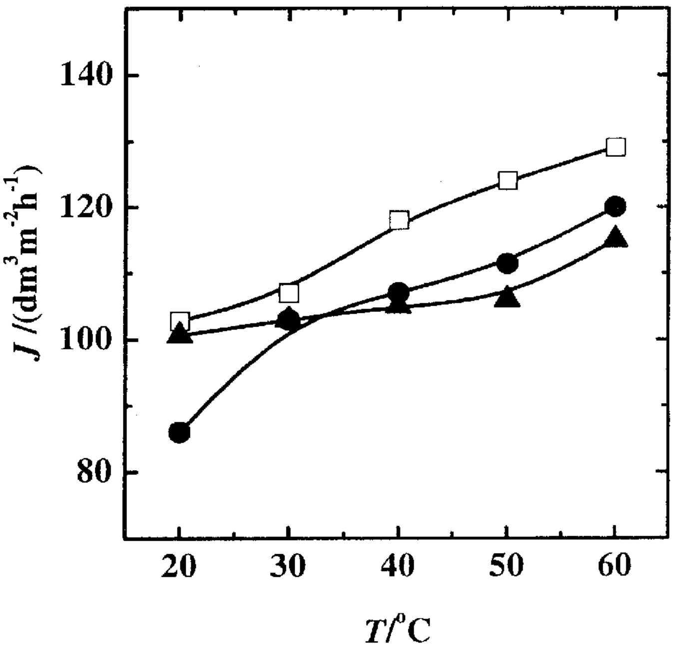


Fig. 2. Effect of temperature on permeate flux at emulsion content of 5 vol.% and transmembrane pressure of 0.3 MPa for FP 055A (□), FS 202-09 (▲), and TS 6V-205 (●) membranes.

coefficient, D. As a result, with increasing the temperature also the water permeate flux increases.

On the other hand, high temperature may lead to the damage of the membrane and to the emulsion decomposition. Thus, it may increase the resistance against the water permeation, resulting in the decrease of the permeate flux.

The temperature increase from 20 °C to 60 °C caused 20—100 % increase in the permeate flux (Figs. 1 and 2). For the feed emulsion contents of 0.5 % and 5 %, the temperature coefficients of about 0.0047 $°C^{-1}$ and 0.008 $°C^{-1}$, respectively, were obtained. That means that *e.g.* for the emulsion containing 5 vol. % of oil a 1 °C increase in the temperature caused a permeate flux increase of about 0.8 %. Fig. 2 shows that the tested membranes exhibited similar permeate fluxes of water at this oil content. At a lower oil content in the emulsion, the performance of the PVDF (FP 055A) membrane was clearly superior to the other membranes (Fig. 1). On the other hand, at higher oil concentration PES membranes (FS 202-09 and TS 6V-205) seem to resist the concentration polarization better than PVDF. Finally, the effect of temperature on the permeate flux is more important at a higher oil feed content.

The pretreatment and cleaning of the membrane depends on the membrane form and the characteristics of the membrane fouling. Usually the membrane fouling is identified by analysis of the pollution substance and by dissecting the fouled membrane units [16]. The fouling substance could be inorganic, organic, and biosubstance. The oil-in-water emulsion used generally may contain inorganic substances, particles from the metal surface machined and sands from the grinding wheel. The organic fouling matters are the surfactants and engine oil, which might suffer an attack by microbes leading to the emulsion rupture and propagation of microorganisms into the fluid.

In order to characterize the composition and topography of the foulants present at the membrane surface, measurements were carried out with fresh stable HW-1 emulsion, and infrared (IR) spectrum analyses were done by MAGNA-750 FT-IR spectrometer. Fig. 3 shows the FTIR subtraction spectra of the substances on the three membrane surfaces before and after ultrafiltration. In the spectra, the peaks at $\tilde{\nu}$

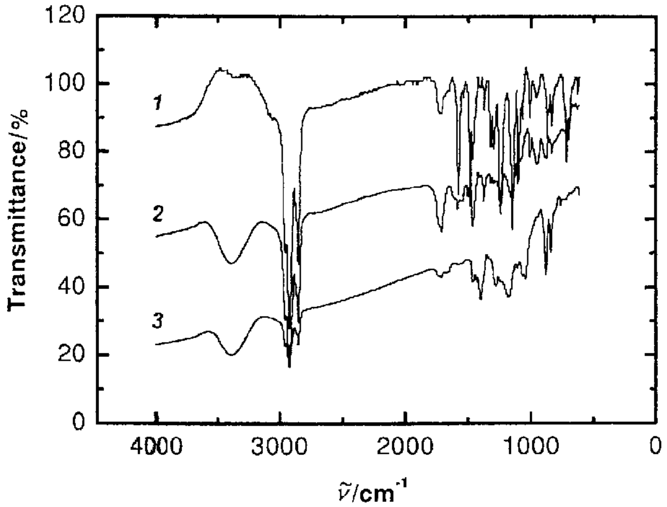


Fig. 3. Infrared subtraction spectra of the foulants on FS 202-09 (*1*), TS 6V-205 (*2*), and FP 055A (*3*) membrane surfaces.

= 2954 cm^{-1}, 2854 cm^{-1}, and 1464 cm^{-1} were attributed to adsorption by alkyl group, typical for hydrocarbons. As expected the amount of oily foulants was high, only a small amount of other impurities was found in the IR spectra.

The foulants found in IR spectra were identified by scanning electron microscopy (SEM). The SEM image of fouled and subsequently cleaned membrane surfaces is shown in Figs. 4 and 5, respectively. Combined with the results from FTIR above, the white spots in the SEM image represent the stain and residue from oil droplets adsorbed on the membrane surface, the main source of membrane fouling at given experimental conditions.

Accumulation of emulsified droplets at the membrane surface is related to the concentration polarization. In the boundary layer, the water depletion causes the increase of oil drops concentration [6]. Moreover, the collisions between oily particles become more frequent. At certain frequency of collisions, the interactions between the droplets may become strong enough to form aggregates. With increasing concentration the aggregates become more numerous and larger. After a certain time, a dynamic equilibrium can be reached with a certain number of aggregates per unit volume, the so-called gel.

In ultrafiltration of oil-in-water emulsion the principal foulant is the oil. If the oil adsorbed on the membrane surface is removed thoroughly, it is expected that the wettability of the membrane attains its original value and complete recovery of permeate flux could be obtained. Recently the micellar solution, consisting of a surfactant and an alcohol in water, was found efficient for removing the oil adsorbed on the membrane surface [6]. The adsorbed oil combined with the micellar solution forms a microemulsion, which could be removed, thus restoring the membrane's permeability.

Regeneration of the fouled FP 055A membrane was performed using either the micellar solution or acid-gasoline-alkali step cleaning process. After the cleaning, the water permeation through the membrane was measured. Table 3 presents the efficiencies of cleaning solutions, φ, and the recovery of the membrane permeability, ϕ, defined by the following expressions

$$\varphi = \frac{J_\mathrm{a} - J_\mathrm{b}}{J_\mathrm{o} - J_\mathrm{b}} \times 100\ \% \tag{2}$$

$$\phi = \frac{J_\mathrm{a}}{J_\mathrm{o}} \times 100\ \% \tag{3}$$

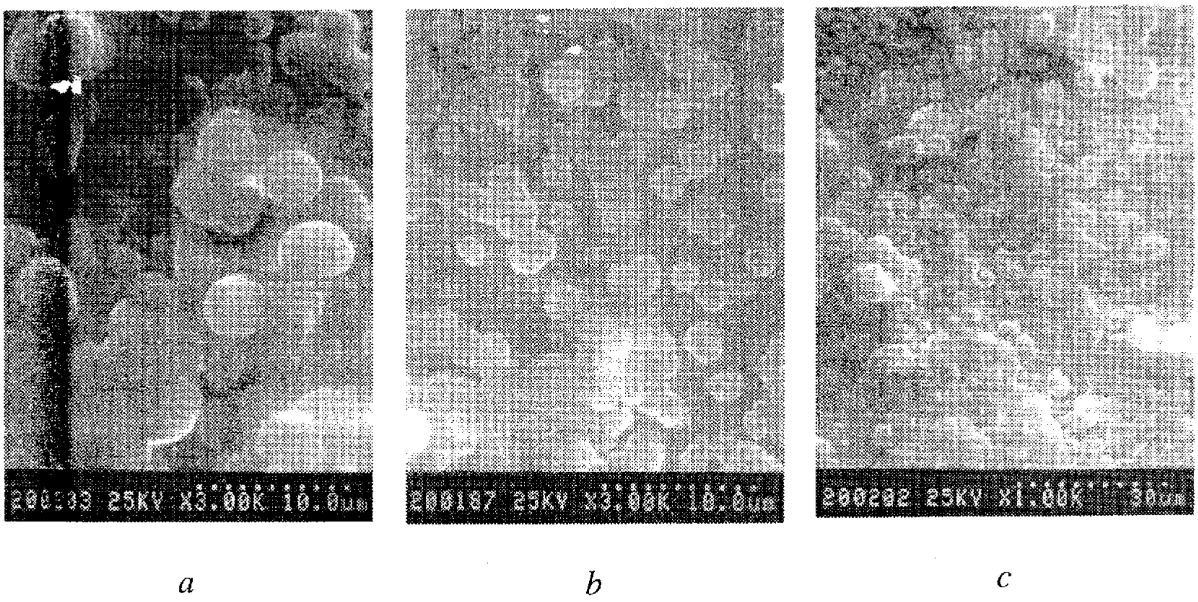
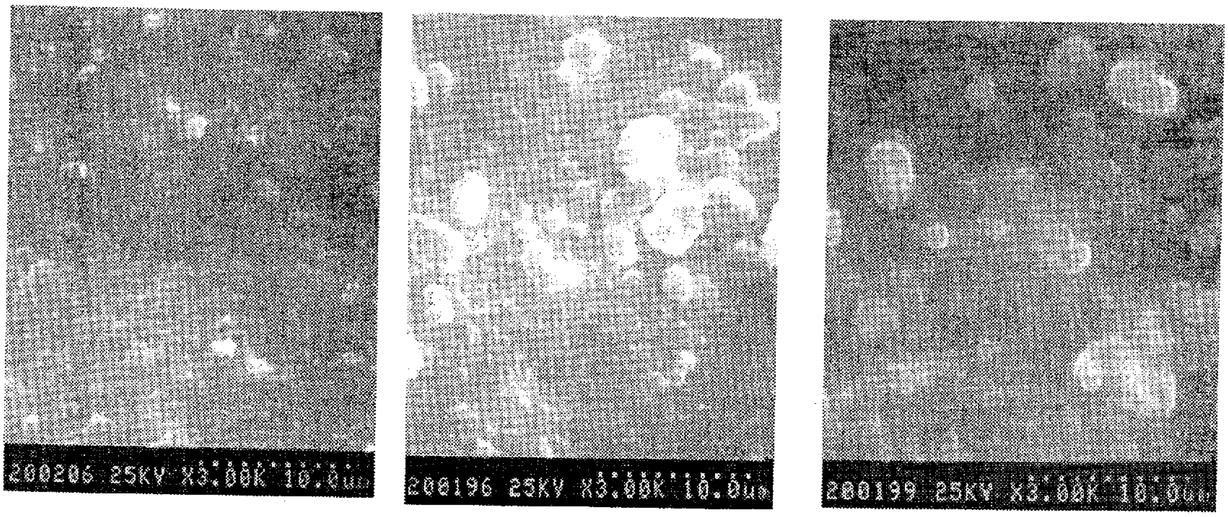


Fig. 4. SEM images of fouled membrane surfaces: *a*) FP 055A; *b*) FS 202-09; *c*) TS 6V-205.

Table 3. Influence of Washing Liquid on Recovery of FP 055A Permeate Flux (Original Permeate Flux 324 dm^3 m^{-2} h^{-1})

Washing liquid	Permeate flux/(dm^3 m^{-2} h^{-1}) before cleaning	Permeate flux/(dm^3 m^{-2} h^{-1}) after cleaning	Efficiency φ/%	Recovery ϕ/%
Micellar solution	284	312	70.0	96.3
Acid-gasoline-alkali	286	315	76.3	97.2



a *b* *c*

Fig. 5. SEM images of cleaned membrane surfaces: *a*) FP 055A; *b*) FS 202-09; *c*) TS 6V-205.

J_a being the membrane permeability after cleaning, J_b permeability before cleaning, and J_o the original permeability of unused membrane.

The removal of oil drops from the membrane surface was evidenced by SEM (Fig. 5). The results show that both micellar solution and acid-gasoline-alkali cleaning process could be used to restore the original properties of a membrane. However, the use of micellar solution is favourable since the acid-gasoline-alkali step cleaning procedure is more complicated.

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