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Investigation of parameters affecting the ultrafiltration of oil-in-water emulsion wastewater

Zsolt László Kiss, Szabolcs Kertész, Sándor Beszédes, Cecilia Hodúr, Zsuzsanna László*

Faculty of Engineering, University of Szeged, H-6725, Szeged, Moszkvai krt. 9, Hungary
Tel. +36 62 546561; email: zsizsu@mk.u-szeged.hu

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ABSTRACT

The ultrafiltration (UF) of model oily wastewater containing an emulsifier was investigated in order to determine the main parameters affecting the flux, retention and membrane fouling. The experiments were carried out with a laboratory UF device, using regenerated cellulose UF membranes. The finding that the fall in flux with time correlated best with the cake formation model is in accordance with the result that increasing resistance during filtration is caused predominantly by the concentration polarization, while the participation of membrane fouling in the total resistance is negligible. Analysis of the parameters affecting the UF of oily wastewater demonstrated that the flux is mainly influenced by temperature and concentration (besides the membrane pore size), while the concentration and the stirring speed are the parameters affecting the resistance. The retention increased slightly with concentration, but this was mainly determined by the membrane pore size.

Keywords: Ultrafiltration; Oily wastewater; Membrane fouling; Modelling

1. Introduction

Oily wastewaters and oil-in-water emulsions are among the main pollutants discharged into the water environment [1,2]. The amounts of oily wastewater generated from metal-working facilities are increasing every year [3]. Oily emulsion wastes contain considerable amounts of mineral oil, which is highly resistant to biochemical decomposition. These emulsions consist of a complex mixture of water, oil and additives such as emulsifiers, corrosion inhibitors, antifoamants and extreme pressure agents. Oils lose their functional properties in time, because of the severe operating conditions and the presence of contaminants and must therefore, be replaced. The disposal of a large volume of oily wastewater would impose places a significant burden on the environment, and hence removal of the oil (2–10 vol.% of the total waste [1]) and other pollutants is required before disposal [4–7].

Free or suspended oils can readily be separated from the aqueous phase of these wastes by simple physical processes. However, chemically stabilized oil-in-water solutions must be managed in an

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*Corresponding author.

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appropriate manner. The process most commonly used for the treatment of oily wastewater, comprising of a series of physical and chemical steps, is not effective in removing smaller oil droplets and emulsions. Such disadvantages have promoted the development of new processes for oily wastewater treatment [8].

Many publications have reported the application of membrane filtration for the treatment of oily wastewater. Membrane processes such as ultrafiltration (UF), are techniques used successfully for the treatment of oily emulsion wastewaters [9,10]. Earlier studies revealed that the main parameters affecting the UF of oily wastewaters are the membrane type (a hydrophilic membrane exhibits a higher flux), pressure, oil concentration and flow velocity [1].

Oily wastewaters may contain numerous other substances and contaminants, including detergents, emulsifiers, greases, solvents, rusts, paints, insulation materials, etc. The presence of chemical emulsifiers and detergents in oily wastewaters poses greater difficulty in separation than the treatment of conventional oil-in-water emulsions, because of the changed surface interactions between the emulsion droplets and the membrane materials.

Few studies have been performed on the UF of high emulsifier-containing oil-in-water emulsions. Vatai et al. found that a stable oil-in-water emulsion (the water-soluble cutting oil concentration in the emulsion was 5 wt.%) could be separated by cross-flow UF and the use of a static mixer led to a considerable increase in the permeate flux [11]. Hu et al. studied the UF separation behaviour of an oil-in-water emulsion with a high surfactant content used for metalworking fluids, and showed that the polarization layer contained mainly oil [12].

The aim of our present study was to investigate the nature of the fouling during the UF of a high emulsifier-containing oil-in-water emulsion, and to determine the main parameters affecting the UF.

Table 1
Composition of MOL Makromil 200 oil

Content	Concentration (wt.%)
Petroleum motor oil (C_{24}–C_{50})	Max. 62
Tetrapropylene succinic acid monobutyl ester	Max. 6.3
2-Hydroxyethyl oleate	Max. 12.3
Sodium sulfonate	Max. 4.4
Alcohols, C_{12}–$C_{16} > 98\%$	Max. 6.8
2,2′,2″-(Hexahydro-1,3,5-triazine-1,3,5-triyl) triethanol	Max. 2.0

2. Methods and materials

2.1. Ultrafiltration of oily solutions

2.1.1. Materials

Model solutions with oil concentration of 3, 5 and 7 wt.% were prepared from environmentally friendly oil (MOL Makromil 200 environmentally compatible metalworking fluid), the composition of which in presented in Table 1, [13].

2.1.2. Experimental design

The membrane filtration experiments were carried out in a batch stirred cell (Millipore, Serial No. 96) with a capacity of 400 cm^3; and the stirring radius was 0.066 m. Flat-sheet RC membranes of Amicon (PL series, Millipore) with different molecular weight cutoffs (MWCO: 1, 5, 10 or 30 kDa) and a membrane effective area of 0.00418 m^2 were used. Before UF experiments, the membrane was left immersed in distilled water for overnight. The initial feed volume was 200 cm^3, and experiments were carried out at 200 kPa until 100 cm^3 of the total sample had been filtered. Membranes were cleaned after every experiment by rinsing with deionized water for 45 min, followed by a cleaning procedure with an alkaline solution (0.5 wt.% for 30 min at 50˚C) and a final rinse with deionized water. The cleaning procedures were repeated until at least 95% of the initial water flux had been recovered.

Determination of the chemical oxygen demand (COD) was based on the standard method involving potassium dichromate oxidation; for the analysis, standard test tubes (Lovibond) were used. The digestions were carried out in a COD digester (Lovibond, ET 108); the COD values were measured with a COD photometer (Lovibond PC-CheckIt). The particle size distribution (range 0.1–1,000 μm) was measured with a Mastersizer 2000 (Malvern Instruments); the injection temperature was 20 or 50˚C.

Viscosity measurements were made with an AND SV-10 vibro-viscometer (A&D Company, Japan), in a temperature-controlled water bath (Cole Palmer, USA) maintained at 20.0 ± 0.1 or 50.0 ± 0.1˚C. The density of each solution was measured at 20 and 50˚C with a Densiti 30PX digital density meters (Mettler Toledo, Japan).

The critical micelle concentration (CMC) was determined conductometrically [14] with a multi-parameter analyser (Consort C535). The conductivities of solutions were measured at 20 and 50˚C.

Diffusion coefficients were determined at 20 and 50˚C with an Armfield CERb apparatus (Armfield, Great Britain), according to the manufacturer's instructions. Measurements were carried out with 5%

Table 2
Filtration laws

Fouling mechanism	Filtration law	Constant pressure filtration J_0 $A = \text{const.}$
Complete pore blocking	$J = J_0 e^{-k_b t}$ (1)	$\ln J = \ln J_0 - k_b \cdot t$ (5)
Gradual pore blocking (standard pore blocking)	$J = J_0\left(1 + \frac{1}{2}K_S(A \cdot J_0)^{0.5} \cdot t\right)^{-2}$ (2)	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s \cdot t$ $k_s = 0.5K_s A^{0.5}$ (6)
Intermediate filtration	$J = J_0 \cdot (1 + K_i \cdot A \cdot J_0 \cdot t)^{-1}$ (3)	$\frac{1}{J} = \frac{1}{J_0} + k_i \cdot t$ $k_i = K_i A$ (7)
Cake filtration	$J = J_0(1 + 2K_c(A \cdot J_0)^2 \cdot t)^{-0.5}$ (4)	$\frac{1}{J^2} = \frac{1}{J_0^2} + k_c \cdot t$ $k_c = 2K_c A^2$ (8)

oil solution, by measuring the change in conductivity in distilled water. The diffusion coefficients at 20 and 50°C were 3.12 and 4.46 10^{-11} $m^2 s^{-1}$, respectively.

2.2. Fouling models

2.2.1. Filtration laws

The fouling mechanisms that have been widely used are cake filtration, intermediate filtration, standard pore blocking and complete pore blocking [15,16], the filtration laws for which, formulated in terms of flux per unit time, are given in Table 2.

In Eqs. (1)–(8), J is the flux, J_0 is the initial flux, the various k are the fouling coefficients, and A is a constant. In Eq. (8), A can be expressed as

$$A = \sqrt{\frac{k_c}{2K_c}} \tag{9}$$

The various K terms are the mass transfer coefficients for the associated filtration laws. The solute mass transfer coefficient was calculated from the following correlations [17,18]:

$$K_c = 0.285\frac{D}{b} \cdot \mathrm{Re}^{0.55} \cdot Sc^{0.33} \quad \text{if Re} < 3,200 \tag{10}$$

$$K_c = 0.0443\frac{D}{b} \cdot \mathrm{Re}^{0.75} \cdot Sc^{0.33} \quad \text{if Re} > 3,200 \tag{11}$$

where $\mathrm{Re} = \frac{\omega \cdot b^2 \cdot \rho}{\eta}$, $Sc = \frac{\eta}{\rho \cdot D}$, b is the stirring radius, ω is the stirring velocity (in rad s^{-1}) and D is the diffusion coefficient (in $m^2 s^{-1}$).

With the assumption of a convection–diffusion mechanism during filtration, the flux is generally expressed by a simplified equation [19]:

$$J = K_c \cdot \ln\left(\frac{c_M - c_P}{c_F - c_P}\right) \tag{12}$$

where c_M is the concentration on the membrane surface, c_P is the permeate concentration, c_F is the feed concentration, and J is the flux. The polarization layer concentration was calculated according to the following equation:

$$c_M = (c_F - c_P)e^{\frac{J_c}{K_c}} + c_P \tag{13}$$

where J_c is the constant flux at the end of the concentration test.

2.2.2. Resistances-in-series model

The membrane resistance was calculated as [20]

$$R_M = \frac{\Delta p}{J_w \eta_w} \quad [m^{-1}] \tag{14}$$

where R_M is the membrane resistance, Δp is the pressure difference between the two sides of the membrane (Pa), J_W is the water flux of the clean membrane and η_W is the viscosity of the water (Pas).

The fouling resistance was determined by measuring the water flux through the membrane after the UF and rinsing it with deionized water to remove any particles of residue layer from the surface, by subtracting the resistance of the clean membrane:

$$R_F = \frac{\Delta p}{J_{WA}\eta_W} - R_M \tag{15}$$

where J_{WA} is the water flux after the concentration test. The resistance of the polarization layer can be calculated as

$$R_G = \frac{\Delta p}{J_C \eta_{WW}} - R_F - R_M \quad (16)$$

where R_G is the polarization layer resistance [m^{-1}], R_F is the fouling resistance (mainly resulting from the fouled pores) [m^{-1}], J_c is the constant flux at the end of the concentration and η_{ww} is the wastewater viscosity.

RT, the total resistance [m^{-1}], can be evaluated from the steady-state flux by using the resistance-in-series model:

$$R_T = R_M + R_F + R_P \quad (17)$$

3. Results and discussion

3.1. Emulsion characteristics

In the first series of experiments, the effects of temperature and concentration on the particle size in emulsion were examined. It was found that a higher concentration resulted in a larger particle size, while the change of temperature did not cause a change in the average size of the droplets, but led to a slightly increased bandwidth in the size distribution diagram. The median particle diameter was found to be 0.29 µm in the 3 wt.% solution, 0.31 µm in the 5 wt.% solution and 0.335 µm in the 7 wt.% solution (Fig. 1).

The effects of temperature (20 and 50˚C and stirring speed (200–500 rpm) on the c.m.c. were also determined. It was found that neither parameter affected the c.m.c. significantly its value was 11.875 ± 0.095 wt.%.

3.2. Effects of membrane pore size on filtration parameters

In the next series of experiments 3 wt.% oil emulsions were filtered through membranes with different pore sizes. Fig. 2, depicts typical variations in flux as a function of the volume reduction ratio (VRR). As expected, the permeate flux increased with membrane pore size. Analysis of the results obtained by fitting the filtration models (Table 3) to the experimental data showed that the cake filtration model gave the best correlation. From the fit of Eq. (8) to the experimental data, the initial flux J_0 and fouling coefficient k_c were determined. With the assumption of a convection–diffusion mechanism during filtration, the mass transfer coefficients and the concentration on the membrane surface were calculated by means of Eqs. (10)–(13). The results of calculations and the retention values are to be seen in Table 3. The retention calculated from the COD decreased with increasing MWCO, but it remained above 90% in all cases.

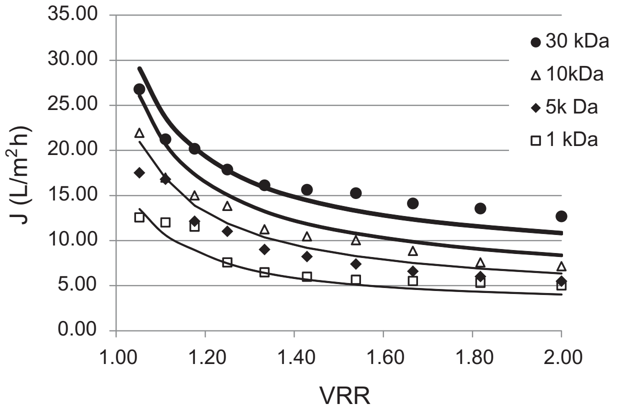

Fig. 2. Variation of permeate flux with time for different pore size membranes (the 3 wt.% oil emulsion at 50˚C and a stirring speed of 200 rpm). The continuous lines illustrate the fitted data calculated with Eq. (4).

Membrane resistances were calculated through the use of Eqs. (14)–(17). The membrane resistances (R_M), fouling resistances (R_F), polarization layer resistances

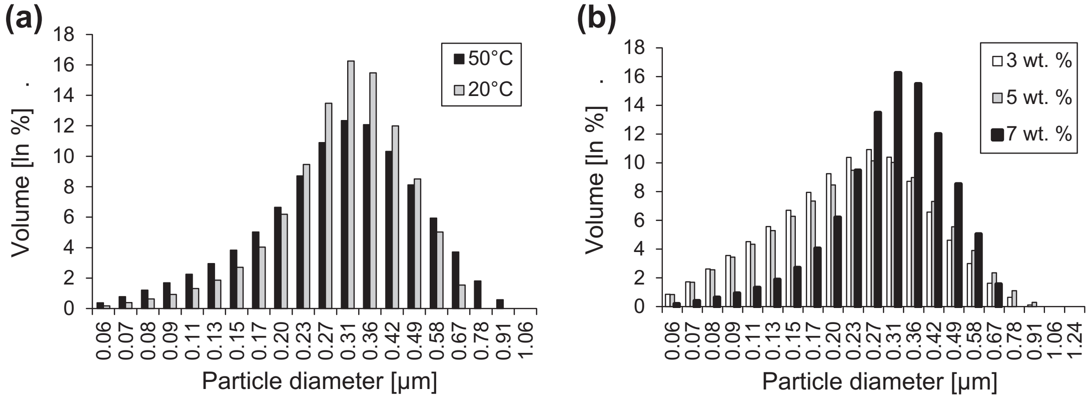

Fig. 1. (a) Particle size distribution diagrams in 7 wt.% emulsion at different temperatures and (b) The effect of emulsion concentration on particle size distribution at 20˚C.

Table 3
Results of calculations

Membrane pore size (kDa)	k_c ($m^4 L^{-6} h^{-1}$)	J_0 ($L m^{-2} h^{-1}$)	$J_0 A$ ($m^3 m^{-2} s^{-1}$)	K_c ($m s^{-1}$)	c_M (wt.%)	R (COD)%
1	0.02683	22.20	18.30 ± 3.32	$2.25 \cdot 10^{-6}$	5.11	99.22
5	0.0213	30.01			7.32	95.36
10	0.0160	35.35			9.67	92.08
30	0.0063	37.79			12.98	90.2

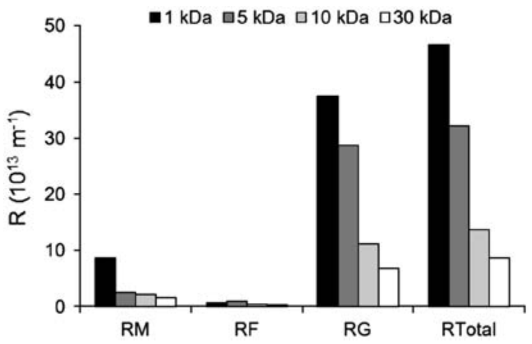

Fig. 3. Membrane resistances during UF of 3 wt.% oil emulsion at 200 rpm and 50°C.

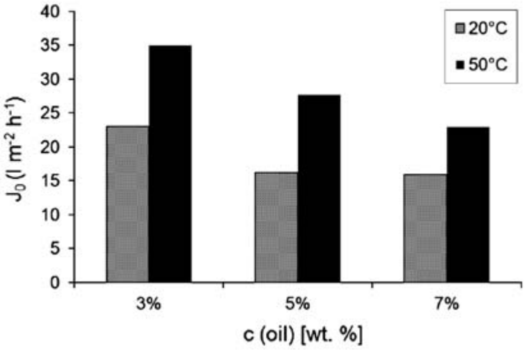

Fig. 5. Changes in initial flux as a function of oil concentration at 20 and 50°C, with a stirring speed of 500 rpm.

(R_G) and total resistances (R_T) presented in Fig. 3 reveal that the resistance is mainly due to building-up of a polarization layer, and the polarization layer resistance increases with decreasing MWCO.

A comparison of the calculated R_T and the k_c (Fig. 4 (a)) indicated that these parameters changed in parallel with increasing MWCO, while the changes in polarization layer resistance and concentration on the surface of the membrane in reverse proportion (Fig. 4(b): somewhat surprisingly, the gel concentration increased as the total resistance decreased. This phenomenon can be explained by the convection–diffusion mechanism of the process. The concentration in the polarization layer is proportional to J/K_c (Eq. (13)); since the stabilized fluxes at lower MWCO are very low, the diffusion from the polarization layer to the feed solution is more expressed, while at higher fluxes convection is the major mechanism.

3.3. Parameters affecting ultrafiltration of oily wastewater

In the next series of experiments, the effects of stirring speed, temperature and concentration on the flux,

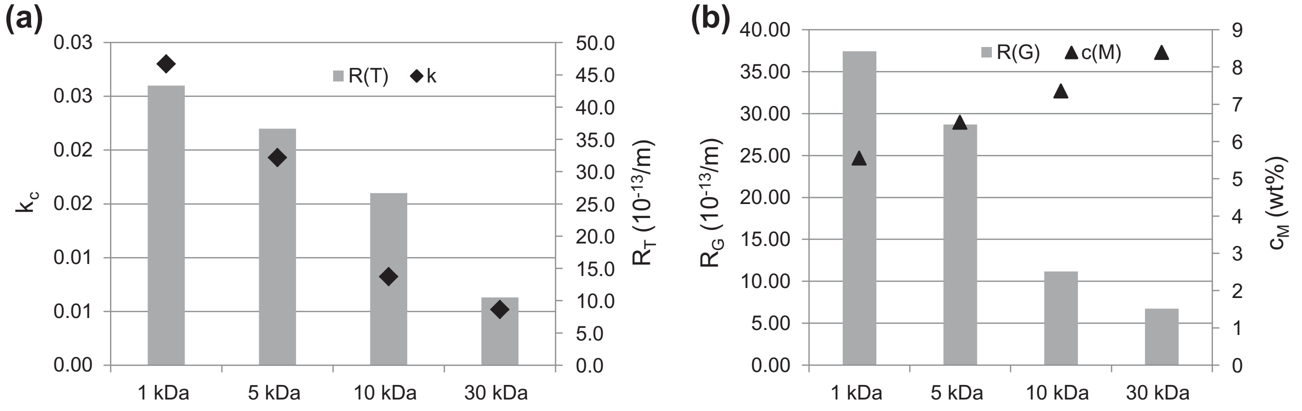

Fig. 4. (a) Comparison of k_c and R_T and (b) Concentrations on the surface of the membrane and the resistance of the polarization layer.

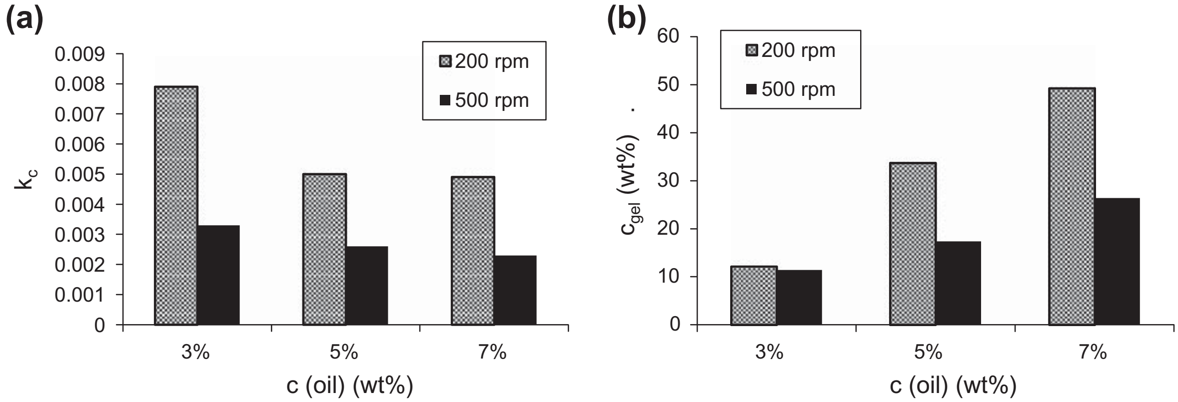

Fig. 6. Fouling coefficient and concentration on the membrane surface as functions of the feed concentration at 20˚C.

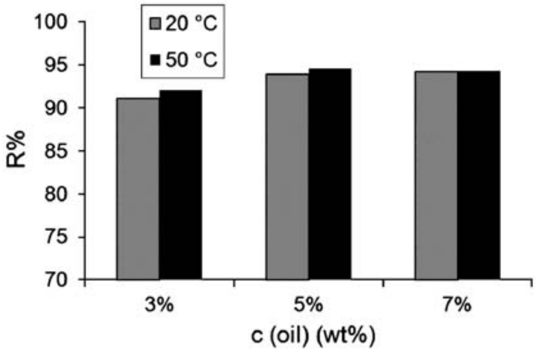

Fig. 7. Retention values at 20˚C, at a stirring speed of 200 rpm.

fouling coefficient k_c and retention were investigated with the 10 kDa MWCO RC membrane. It was found that the flux decreased with increasing concentration (Fig. 5), in accordance with the results of Rezvanpour et al. [1].

The elevation of temperature led to an increased initial permeate flux, which can be explained by the change in the viscosity of the oil at higher temperature. The stirring speed did not have a significant effect on the flux, but the higher stirring speed decreased the fouling coefficient and in parallel resulted in a lower oil concentration on the surface of the membrane, due to the reduced gel layer-building ability. The temperature did not exert a significant effect on either the fouling coefficient or the gel concentration.

As can be seen in Fig. 6, the gel concentration increased with increasing feed concentration, but surprisingly the fouling index decrease with increasing feed concentration tended to taper off. This can probably be explained the concentration of the gel layer being near to the c.m.c. by in the case of the 3% solution, while at higher concentrations, above the c.m.c., the particle size in gel layer is increased due to micelle formation; thus, the oil droplets cannot infiltrate and foul the membrane pores. This is in accordance with the observation that the oil retention slightly (not significantly) increased with increasing feed concentration (Fig. 7). Neither the temperature nor the stirring speed had a significant effect on the retention values.

4. Conclusions

Following the use of micellar enhanced UF with a regenerated cellulose membrane to determine the main filtration parameters of a model oily wastewater with high surfactant content, analysis of the fall in flux with time and VRR indicated that the cake formation model gave the best correlation to the experimental data. The resistances-in-series model revealed that the increase in resistance during UF is caused mainly by the concentration polarization, and the part played by membrane fouling in the total resistance is negligible. With the assumption of the convection–diffusion mechanism during UF, calculation of the concentration in the polarization layer on the surface of the membrane in comparison with the resistances demonstrated that for smaller membrane pore sizes the resistances during UF are influenced significantly by diffusion, while for larger membrane pore sizes the decisive mechanism, involves convection.

As concerns the parameters affecting the UF of oily wastewater, the flux is mainly influenced by the temperature and the stirring speed, while the factors affecting the resistance are the concentration and the stirring speed. The retention increases slightly with increasing concentration, but it is mainly determined by the membrane pore size.

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List of symbols

J — flux [$\mathrm{L\,m^{-2}\,h^{-1}}$]
J_0 — initial flux
J_c — constant flux at the end of the concentration test [$\mathrm{L\,m^{-2}\,h^{-1}}$]
J_{WA} — water flux after concentration tests [$\mathrm{L\,m^{-2}\,h^{-1}}$]
J_w — water flux [$\mathrm{L\,m^{-2}\,h^{-1}}$]
k_c — fouling coefficient
A — experimental constant
K_c — mass transfer coefficient [$\mathrm{m\,s^{-1}}$]
b — stirring radius [m]
ω — stirring velocity [$\mathrm{rad\,s^{-1}}$]
D — diffusion coefficient ($\mathrm{m^2\,s^{-1}}$)
Re — Reynolds number
Sc — Schmidt number
η — dynamic viscosity [Pas]
ρ — density [$\mathrm{kg\,m^{-3}}$]
c_M — concentration on membrane surface [wt.%]
c_P — permeate concentration [wt.%]
c_F — feed concentration [wt.%]
R_M — membrane resistance [$\mathrm{m^{-1}}$]
R_F — fouling resistance [$\mathrm{m^{-1}}$]
R_G — polarization layer resistance [$\mathrm{m^{-1}}$]
R_T — total resistance [$\mathrm{m^{-1}}$]
Δp — transmembrane pressure [Pa]
η_w — viscosity of the water [Pas]
η_{ww} — viscosity of the wastewater [Pas]

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