Environment Protection Engineering

Vol. 49 2023 No. 4

DOI: 10.37190/epe230407

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SURFACTANT FOULING IN PRESSURE-DRIVEN MEMBRANE PROCESSES

The fouling phenomenon of porous polymeric ultrafiltration and nanofiltration membranes was investigated during the purification of solutions containing surfactants. The effects of surfactant type, concentration, and membrane pore size on process performance were evaluated. The highest intensity of membrane fouling was caused by micellar solutions, resulting from the coexistence of monomeric and aggregated surfactant forms. A significant role of hydrophobic/hydrophilic interactions between surfactants and the polymer surface in membrane fouling was proved. Interpretation of the theoretical fouling model showed that cake formation is the dominant fouling mechanism of membranes.

1. INTRODUCTION

Pressure-driven membrane processes (PDMP) have been widely investigated as effective technologies for treating solutions containing organic compounds [1–4]. The applications of PDMPs in industrial and environmental engineering are determined by their separation and transport properties. During membrane filtration, a decrease in permeate flux is observed, the level of which varies for different membrane techniques. The phenomenon of membrane fouling is a serious problem in PDMPs. It refers to the blockage of membrane pores during filtration by combining the sieving and adsorption of compounds on the membrane surface and within its pores [5].

A specific group of organic compounds that significantly influence the transport properties of porous membranes are surfactants. Their classification is based on their dissociation in aqueous solutions, leading to four types: anionic, cationic, nonionic, and amphoteric surfactants. The surfactant molecule contains both hydrophilic and hydro-

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phobic components. At lower concentrations, surfactant molecules predominantly exist as monomers. At concentrations exceeding the critical micelle concentration (CMC), they self-assemble to form micellar structures usually consisting of several hundred monomers. The radius of the spherical micelle is assumed to be equal to the length of the monomer.

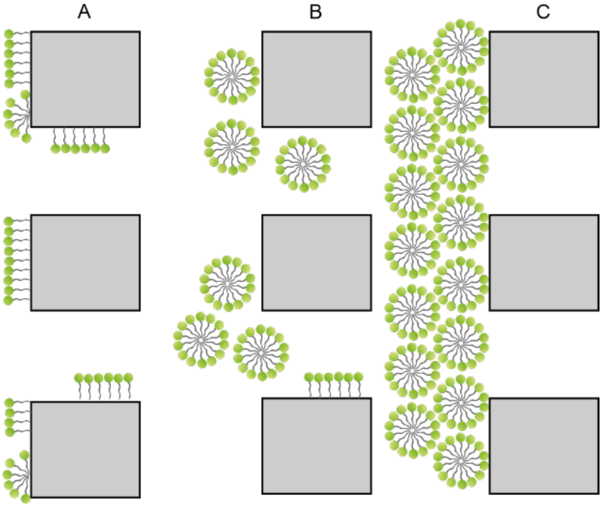

Fig. 1. Fouling of porous membranes caused by: A – adsorption of surfactant particles, B – pore blocking, C – formation of a gel layer (according to [11])

The presence of the surfactants in a treated solution significantly affects the transport properties of the membranes. On the one hand, surfactants can enhance the hydrophilicity of the active layer of hydrophobic membranes, which can produce positive effects concerning hydraulic performance [6, 7]. On the other hand, surfactants are recognized as compounds that strongly pollute membranes [8–10]. The fouling mechanism of porous membranes is associated with the adsorption of surfactant molecules on the surface of the active layer and inside the pores, resulting in pore blocking and the formation of a gel layer by concentrated micelles near the surface of the membrane (Fig. 1). Adsorption of ionic surfactants occurs mainly as a result of electrostatic and hydrophobic interactions between the particles present in the solution and the membrane surface.

2. MATERIALS AND METHODS

The tests used model solutions of three surfactants (Table 1) dissolved in distilled water in the concentration range of 0.1–8.0 CMC.

Table 1

Characteristics of the surfactants

Parameter	Surfactant		
	Triton QS-44	CTAB	Triton X-100
Supplier	Sigma	Sigma	Fluka
Purity, %	80	>98	>99
Type	anionic	cationic	nonionic
CMC at 22 °C, mg/dm^3	250	370	165
Aggregation number	–	170	100–155
Diameter of the micelle, nm	–	2–3 [12]	7.5 [13]

A dead-end filtration cell equipped with polyetherosulfone flat-sheet nanofiltration (N series) and ultrafiltration (U series) membranes were used for the experiments (Table 2). The effective membrane surface area was 45.4 cm^2, and the volume of the filtration cell was 350 cm^3.

Table 2

Characteristics of the Microdyn-Nadir® membranes

Membrane	Cut-off [kDa]	Pore size [nm]	Distilled water flux[a] [dm^3/(m^2·h)]	Contact angle[b] [deg]
NP030	0.5–0.7 [14]	0.59–0.93 [14]	6.0	58.4±2.8
NP010	1–1.4 [14]	0.80–1.29 [14]	26.6	63.7±2.4
UP005	5	0.62 [15]	37.0	52,8±1,8
UP010	10	2.04 [15]	150	55.4±2.4

[a] TMP = 0.2 MPa, $T = 22$ °C.
[b] For brand-new membranes.

Membrane filtration was carried out under a transmembrane pressure (TMP) of 0.20 MPa with constant stirring at 300 rpm. During the experiments, to characterize the fouling tendency, the relative flux (J/J_0) was determined, which is the ratio of the permeate flux (J, dm^3/(m^2·h)) to the distilled water flux (J_0, dm^3/(m^2·h)).

3. RESULTS AND DISCUSSION

3.1. EFFECT OF SURFACTANT CONCENTRATION

The membrane resistance changes during filtration due to specific interactions between the surfactant and the membrane structure. As surfactants exist in aqueous solutions in monomeric and aggregated forms, their concentration (and consequently their form of occurrence) affects the intensity and mechanism of the fouling. The changes in the relative flux of the membranes for the CTAB solutions in the concentration range of 0.1–8 CMC are shown in Fig. 2. The least pronounced membrane fouling was observed during monomeric solution filtration (0.1 and 0.3 CMC). In contrast, the most fouling tendency ($J/J_0 < 0.6$) was observed for solutions with concentrations greater than CMC (1.4, 3, and 8 CMC).

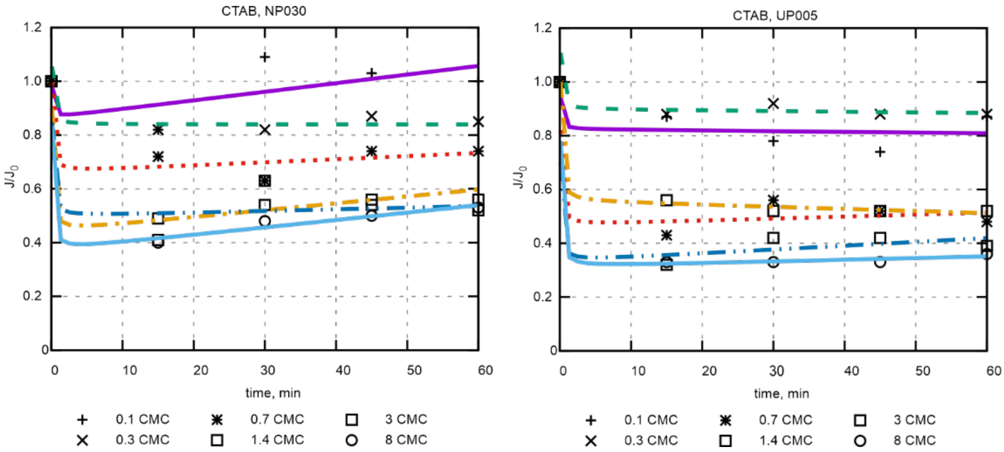

Fig. 2. Relative flux (J/J_0) of the NP030 and UP005 membranes during the 60 min membrane filtration of the CTAB solution

An increase in the surfactant concentration is associated with a higher amount of free monomers in the solution. After penetrating the porous structure of the membrane, these monomers reduce the pores' size. The coexistence of monomeric and aggregated surfactant forms in highly concentrated solutions may lead to the simultaneous blocking of pores and the occurrence of a gel layer on the membrane surface. Furthermore, an increase in surfactant concentration results in higher values of the electrokinetic potential of the solutions (11 mV for 0.1 CMC and 45 mV for 3 CMC), thus intensifying the electrostatic interactions which contribute to the chemisorption of CTAB particles on negatively charged membrane surfaces.

In tests with NP030 membranes at the lowest surfactant concentration (0.1 CMC), the relative flux reached a higher value than that obtained for distilled water. This phenomenon may be attributed to the reduction in the free energy of the system and, consequently, an increase in the hydrophilicity of the membrane surface. Boussu et al. [16] reported an increase in the hydrophilicity of polymer membranes due to interaction with surfactant particles. The contact angle of the new Desal 51HL membrane was 47°. After membrane filtration of the surfactant solution, it was reduced to 40°.

3.2. EFFECT OF MEMBRANE CUT-OFF

The analysis of hydraulic performance confirmed that membranes with large pore diameters of the separation layer were more susceptible to fouling (Fig. 3). For example, after 60 min of the process run, the J/J_0 ratio for the UP010 membrane amounted to 0.28 (8 CMC) and 0.40 (0.3 CMC), while values of 0.74 (8 CMC) and 0.85 (0.3 CMC) for the NP030 membrane were observed. Furthermore, the relative flux of the UP010 membrane decreased throughout the process. In contrast, for the NP030 and UP005 membranes, this parameter reached its minimum in the first stage of filtration and then stayed constant or improved. The lack of further deterioration in the hydraulic performance of the NF membrane may be attributed to its lower adsorption capacity compared to that of the UF membrane.

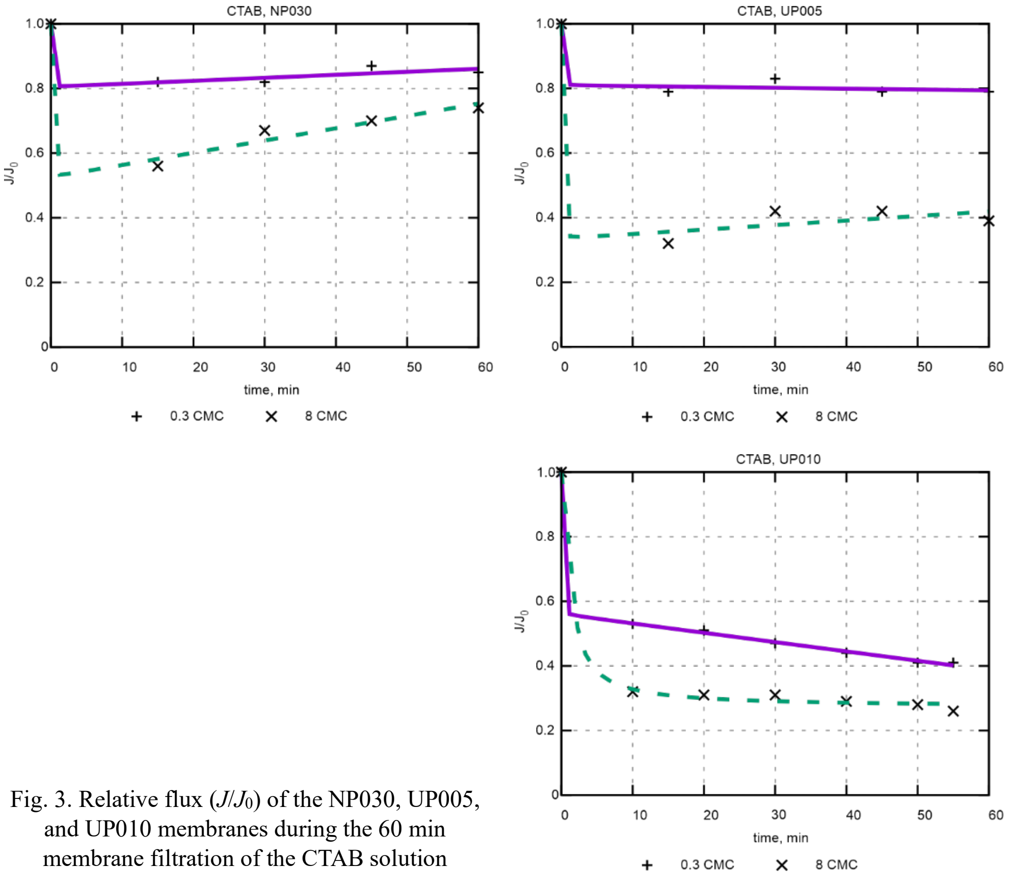

Fig. 3. Relative flux (J/J_0) of the NP030, UP005, and UP010 membranes during the 60 min membrane filtration of the CTAB solution

In the context of the surfactant adsorption mechanism in the porous structure of membranes, the relationship between the length of the hydrophobic chain and the size of the membrane pores is crucial [17]. When the size of the monomer is significantly smaller than the pore radius, the thickness of the adsorption layer is equal to the length of the monomers. In the opposite situation, i.e., when the pore radius is smaller or comparable to the length of the monomers, the filling of pore space occurs as a result of the folding of the alkyl chains of the monomers (Fig. 4).

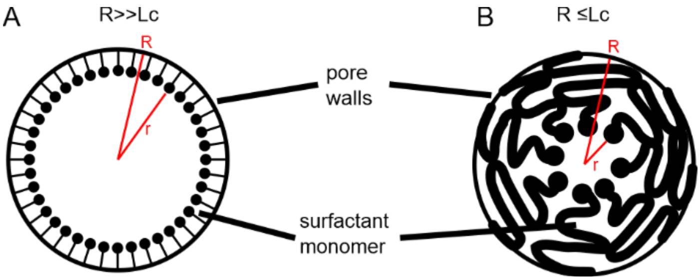

Fig. 4. Adsorption of surfactant monomers in membrane pores:
A – with a radius larger than the length of the monomer,
B – with a radius comparable to the length of the monomer;
R – membrane pore radius, *r* – radius of the free channel,
Lc – length of the hydrophobic chain (according to [17])

The pores of the UP010 membrane were characterized by a size of approximately 2 nm (Table 2), allowing the penetration of CTAB monomers (approximately 1.5 nm long) into their structure. Consequently, there was a significant reduction in pore size, leading to a decrease in the hydraulic performance of the membrane. The pores of the NP030 membrane (0.6–0.9 nm) were smaller and less accessible to monomers compared to the pores of the UP010 membrane.

3.3. EFFECT OF SURFACTANT TYPE

The interactions between the surfactant particles and the membrane surface may be electrostatic and/or hydrophilic/hydrophobic. For nonionic surfactants, the hydrophilic /hydrophobic interactions between surfactant molecules and the active layer of the membrane are of greatest significance.

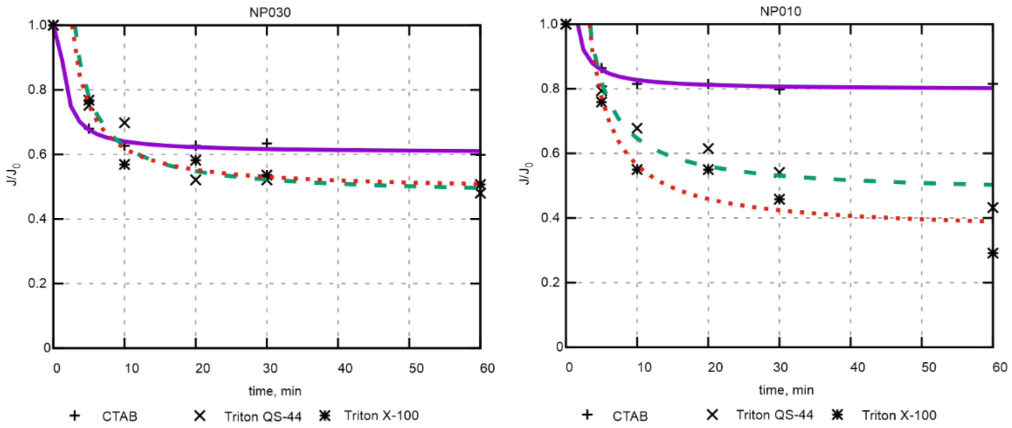

Fig. 5. Relative flux (J/J_0) of the NP030 and NP010 membranes
during the 60 min membrane filtration of surfactant solutions (0.5 CMC)

Consequently, membranes with an active layer composed of hydrophobic materials are more susceptible to blockage by nonionic surfactant molecules [16]. On the contrary, electrostatic interactions are of particular importance when filtering solutions of ionic surfactants. Figure 5 shows the relative flux of the NP030 and NP010 nanofiltration membranes obtained during the filtration of solutions containing various types of surfactants (concentration 0.5 CMC).

Comparing the curves obtained for the dense NP030 membrane, it can be stated that the type of surfactant had a negligible impact on blocking this membrane. This indicates that the most significant factor in the blocking mechanism of the semi-hydrophilic compact membrane was the hydrophilic/hydrophobic interactions. However, when membrane NP010, characterized by larger pores, was applied, the difference in hydraulic performance for various types of surfactants was more pronounced. Despite the electrical attraction between CTAB and the active membrane layer (resulting from opposing electrical charges), this surfactant induced the least fouling for both membranes tested. It also proves that the size of the surfactant particle appears to be significant for pore blocking. The CTAB monomer has nearly twice the shorter length than the nonionic surfactant Triton X-100 monomer. As a result, the reduction in pore diameter by CTAB monomers could be much smaller.

3.4. FOULING THEORETICAL MODEL

One of the mathematical models used to describe fouling phenomena is the Hermia model [18–20]. This filtration blockage model offers a valuable methodology to evaluate flux data in porous membranes, covering four distinct mechanisms. According to Hermia, during the membrane filtration of colloidal dispersions, particles may deposit on the membrane surface (cake formation) or in the membrane pores, resulting in their blocking. The pore-blocking mechanism can be further categorized into three models: complete, intermediate (partial), and standard (internal) blocking (Fig. 6).

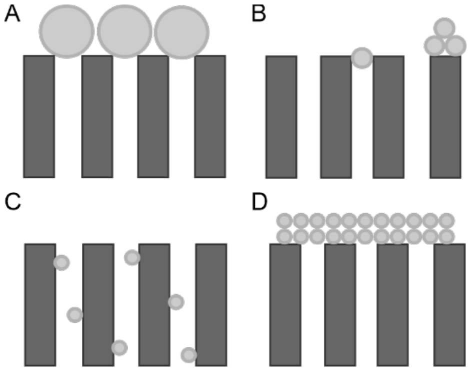

Fig. 6. Blocking mechanisms by Hermia [20]: A – complete blocking, B – intermediate blocking, C – standard blocking, and D – cake formation

The original ordinary differential equation was solved for four different discrete values of n, each value with its blocking mechanisms [20]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{1}$$

- complete blocking ($n = 2$)

$$\ln J = \ln J_0 - kt \tag{2}$$

- intermediate blocking ($n = 1$)

$$\frac{1}{J} = \frac{1}{J_0} - kt \tag{3}$$

- standard blocking ($n = 1.5$)

$$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} - kt \tag{4}$$

- cake formation ($n = 0$)

$$\frac{1}{J^2} = \frac{1}{J_0^2} - kt \tag{5}$$

where t is the time measured from the beginning of the filtration experiment, J is the permeate flux at time t, J_0 is the permeate flux at time $t = 0$, and k is a real constant determined experimentally.

Table 3

The correlation coefficients (R^2) for fitting the experimental curve to the model curves as a function of the parameter n at the end of membrane filtration ($t = 60$ min) of CTAB solutions on NP030 and UP005 membranes

n	0.1 CMC	0.7 CMC	1.4 CMC	3 CMC
NP030				
0	0.7585	0.8255	0.81414	0.8040
1	0.7822	0.8217	0.80805	0.8040
1.5	0.7906	0.8194	0.80519	0.8035
2	0.7969	0.8170	0.80262	0.8028
UP005				
0	0.3408	0.7323	0.7364	0.6652
1	0.3283	0.6743	0.6582	0.5810
1.5	0.3223	0.6451	0.6211	0.5435
2	0.3174	0.6189	0.5758	0.5101

The results of the Hermia model analysis are presented in Table 3. Calculations were performed for representative CTAB solutions (monomeric and micellar) and the two types of membranes applied. The correlation coefficient R^2 was calculated to assess the quality of fit of the equations representing the Hermia model to the experimental data. The analysis carried out demonstrated that for solutions at concentrations around 0.7 CMC and above CMC, the correlation coefficients were closest to unity for the parameter $n = 0$ (cake formation). Cake formation caused by micelles is indicated as the main fouling mechanism of membranes during the purification of micellar surfactant solutions [11]. However, for the NP030 test, the coefficient R^2 exhibited similar values for all concentration ranges of surfactant; thus, determining the dominant fouling mechanism becomes a challenge because it is likely that all of the phenomena discussed occurred simultaneously during membrane filtration.

4. CONCLUSIONS

The intensity of fouling during the filtration of surfactant solutions is the result of specific interactions between the surfactant and the membrane structure. The most important factors influencing the transport and separation properties of membranes are the porosity of the active layer (together with their surface charge and hydrophilic /hydrophobic character), the structure (monomer and micelle size) and ionic nature of the surfactant, and its concentration, which determine the form of aggregation in aqueous solution (monomers, hemi-micelles, and micelles).

Within the entire range of concentrations tested, the NP030 membrane, with the smallest pore diameter, was the least susceptible to blocking. This is due to the effective limitation of monomer penetration into the membrane structure. During the filtration of the solution with the lowest CTAB concentration, the relative flux reached an even higher value compared to that obtained for distilled water ($J/J_0 \approx 1.1$) as a result of hydrophilisation of the polymer material coated with surfactant monomers.

Using Hermia's blocking models, the membrane fouling mechanisms in the early stage of filtration were found to change from standard, via intermediate blocking, to cake formation, depending on the surfactant concentration. The dominant mechanism of the flux decrease for solutions at concentrations around and above CMC at the end of the filtration cycle was cake formation caused by the concentrated micelles at the membrane surface.

ACKNOWLEDGEMENTS

This work was supported by the Department of Environmental Protection Engineering, Wrocław University Science of Technology.

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