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Purification and concentration of surfactant solutions using tubular nanofiltration modules

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ABSTRACT

The effectiveness of tubular nanofiltration modules used for the purification and concentration of a cationic surfactant solution was investigated. Commercially available modules (AFC 80 and AFC 30) were employed for the experiments. Cationic surfactant hexadecyltrimethylammonium bromide (CTAB) solutions were treated. During the first stage of the tests, the usefulness of the modules for the treatment of solutions in a wide range of concentrations (50–1,000 mg/L) was assessed. The next part concerned the surfactant concentration process. The feed solution of 500 mg/L was examined. During both stages, the separation efficiency of membranes, as well as the surfactant effect on their hydraulic properties were assessed. The conducted experiments proved that properties of membranes and the initial surfactant concentration were important factors for both, the contaminant rejection, as well as the membrane hydraulic capacity. The AFC 80 module enabled the highest CTAB removal (up to 98%) for a 1,000 mg/L solution, while AFC 30 proved to be more suitable for a low-contaminated solution treatment and achieved up to 100% removal from the feed of 50 mg CTAB/L. It was found that during concentration experiments, AFC 30 was more fouling-resistant. On the other hand, AFC 80 showed a better selectivity of the surfactant. The CTAB concentration in the permeate ranged from 35 to 236 mg/L and from 119 to 200 mg/L for AFC 80 and AFC 30, respectively. During the experiments, the maximum surfactant concentration in the concentrate solutions amounted to 770 (AFC 80) and 1,170 mg/L (AFC 30).

Keywords: Surface-active agent; Biocide; Pressure-driven membrane process; Recovery

1. Introduction

Industrial wastewater containing surface active agents (surfactants) is problematic, due to the characteristics of the surfactants. Surfactants are chemical compounds containing hydrophilic and hydrophobic parts, which make them soluble in both polar and nonpolar liquids [1]. Depending on their concentration, surfactants may exist in solutions in a monomeric and/or an aggregated form. The level of concentration, above which monomers form aggregates (micelles) is named the critical micelle concentration (CMC). Micelles consist of dozens of monomers, thus both their size and molecular weight are greater than that of the monomers. The ideal scheme of a hexadecyltrimethylammonium bromide (CTAB) monomer and its micelle is plotted in Fig. 1.

Surfactants may strongly influence on the properties of a solution (lower the surface tension, induce foaming, limit the oxygen penetration to water), thus discharging surfactant-contaminated wastewater to the environment is hazardous. Surface active agents are frequently applied in many industrial and household uses as cosmetics; detergents; antistatic, wetting, and softening agents; biocides; germicides; deodorizers; and emulsifiers [3,4].

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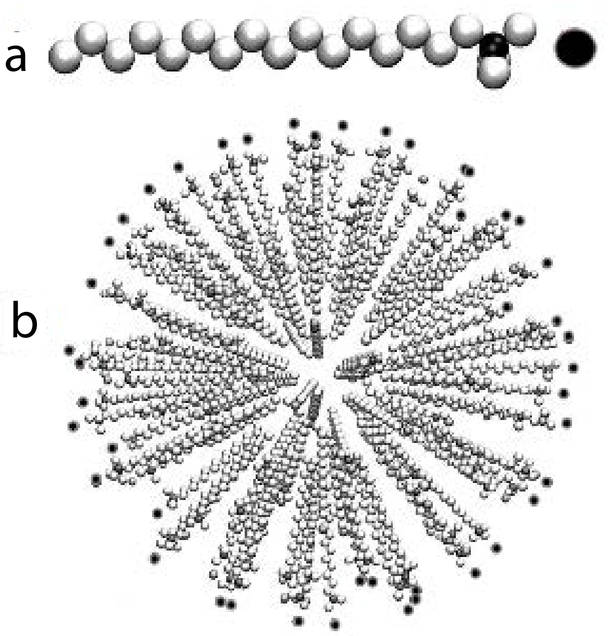

Fig. 1. CTAB molecule: (a) monomer and (b) micelle. Carbon atoms – light gray, nitrogen atoms – dark gray, bromide atoms – black [2].

There are four groups of surfactants, differing in polar part charge: anionic, cationic, nonionic, and amphoteric. According to CESIO statistics [5], surfactants production (excluding ethoxylates) in the UE in 2013 amounted to 1,663 kT.

A reduction of surfactant production, as well as solving the problem of surfactant wastewater disposal may be achieved by the implementation of effective recovery/recycling methods. Pressure-driven membrane processes are widely applied in water and wastewater treatment due to their advantages, that is, low energy consumption and the reduction of both raw materials and waste production [6].

Literature data concerning surfactants solutions purification via pressure-driven membrane processes is limited and mainly focused on the anionic surfactants separation. Fernández et al. [7] tested ceramic ultrafiltration membrane Membralox in sodium dodecyl sulfate and Tergitol NP-9 removal. High surfactants retention (in the range from 60% to 70%) was achieved for solutions characterized by the low contaminant concentration (below the CMC value). Forstmeier et al. [8] applied nanofiltration membranes (Desal 5K, spiral wound module) in a surfactant removal from effluents received from detergent production plant – the experiments performed achieved 96% COD reduction. Korzenowski et al. [9] reported 92% COD removal from wastewater from detergent industry with the use of the nanofiltration membranes NF-90, NF-200, and NF-270 (FilmTec Corp., USA). Goers et al. [10] proved that a crucial parameter, which played a significant role in surfactants rejection by means of the pressure-driven membrane processes was the CMC of surfactants.

Kertész et al. [11] examined the recovery of anionic surfactant (CL80) with the use of nanofiltration DL composite membrane ($MgSO_4$ retention of 96%). The surfactant rejection exceeded 94% (feed solutions of 500–5,000 mg/L).

2. Materials and methodology

2.1. Chemicals

The cationic surfactant solution was prepared from distilled water (conductivity 2.6 μS/cm) and CTAB (≥96.0% pure, purchased from Fluka Analytical, Poland). In the purification tests, a wide range of CTAB concentration was applied (50, 100, 250, 500, and 1,000 mg/L). In the concentration tests, the CTAB content in the feed amounted to 500 mg/L. The molecular weight of the surfactant monomer was 364.5 Da and of the micelle – 22,235 Da [12]. The CMC, measured by means of the measurement of electrical potential in the function of the concentration, amounted to 380 mg/L.

2.2. Modules and experimental system

The experiments were performed in a cross-flow regime with the use of a semi-pilot installation made of stainless steel. The scheme of the installation is plotted in Fig. 2.

In the experiments, commercially available modules purchased from the PCI Membranes Filtration Group (Poland) were applied. Characteristics of the modules are presented in Table 1.

Membrane filtration was performed in a continuous batch concentration mode, with the retentate recirculation from the membrane back to the feed tank; the permeate stream was collected separately. In the first stage of experiments, that is, during 2 h of purification tests under a transmembrane pressure (TMP) of 0.3 MPa, the concentration of CTAB in the feed solution was maintained at a constant level. The total volume of the feed amounted to 8 L.

In the second part of the tests, due to the reduction in feed volume, an increase in the surfactant concentration in

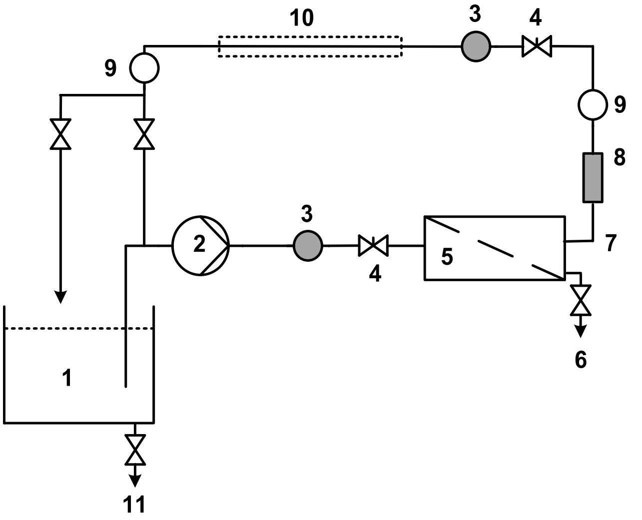

Fig. 2. Schematic diagram of the membrane installation: (1) feed tank, (2) circulation pump (Grundfos, Poland), (3) manometer, (4) pressure regulation valve, (5) membrane module, (6) permeate, (7) retentate, (8) rotameter, (9) thermometer, (10) cooler, and (11) drain valve.

Table 1
Characteristics of the modules

Module name	AFC 80	AFC 30
Salt retention	80% NaCl	75% $CaCl_2$
Pure water flux ($L/m^2/h$)[a]	8.0	22.3
Molecular weight cut-off (Da)	<200 [13]	200 [14]
Membrane material	Polyamide film	
Hydrophilicity	Hydrophilic	
Surface charge [15]	Strongly negative	
Membrane surface area (m^2)	0.024	
Module diameter (m)	0.0125	
Module length (m)	0.3	
Configuration	Tubular	

[a] Determined by the authors, TMP = 0.4 MPa, 25°C.

the feed during the experiment occurred. The concentration process was realized at TMP = 0.4 MPa until the resistance of the modules precluded further filtration.

2.3. Analytics

During the purification tests, the permeate samples were taken each 15 min. About 0.01 L of the permeate was collected every 15 min in order to surfactant concentration measurements; in the concentration part of the tests, the time interval was equal to 30 min. Permeate and concentrate samples were collected for surfactant concentration analysis. A potentiometric titrator 785 DMP Titrino (Metrohm, Poland) was employed for the measurement of the CTAB concentration. The separation efficiency was assessed based on Eq. (1) as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100(\%) \tag{1}$$

where R is the retention coefficient (%), C_f and C_p are the CTAB concentration in the feed and permeate (mg/L).

In order to evaluate the membrane's hydraulic properties, volume flux was determined according to Eq. (2) as follows:

$$J = \frac{V}{A \times t}\left(\mathrm{L/\,m^2\,h}\right) \tag{2}$$

where J is the volumetric permeate flux (L/m^2h); V is the volume of the permeate sample collected (L); A denotes the membrane's surface area (m^2); t is the filtration time (h).

To assess susceptibility to fouling, the normalized flux was calculated on the basis of Eq. (3) as follows:

$$\mathrm{RF} = \frac{J}{J_0}(-) \tag{3}$$

where RF is the relative flux; J is the volumetric permeate flux after time t; and J_0 is the distilled water permeate flux (L/m^2h).

The permeate recovery was calculated according to Eq. (4) as follows:

$$\mathrm{PR} = \frac{V_p}{V_0} \times 100(\%) \tag{4}$$

where PR is the permeate recovery ratio (%) and V_p and V_0 denote the volume of the permeate after the time t and the volume of the feed, respectively.

3. Results and discussion

3.1. Purification

Fig. 3 presents CTAB retention coefficients, as well as relative fluxes of the AFC 30 and AFC 80 modules obtained during purification processes. As it can be observed, for both modules the initial surfactant concentration plays an important role in the process performance. Modules exhibited permeability deterioration in the presence of CTAB. However, the biggest drop in relative flux (44%–50%) was seen for the AFC 80 module when the CTAB concentration in the feed was equal to 500 mg/L. AFC 30 achieved the lowest values of the relative flux at the level of 65%–73% and 67%–75% for 500 and 1,000 mg CTAB/L, respectively. Generally, the AFC 30 module proved to be more fouling resistant than another module. Moreover, in the AFC 30 experiments, relative flux values were in the pseudosteady state, while a slight decrease tendency was noted for the AFC 80 module.

During the membrane processes, surfactant molecules created a polarization-concentration layer near the membrane surface. As a result, the surfactant concentration near the membrane was significantly higher than its concentration in the volume of the feed, which led to a membrane permeability decrease. For the feed solutions of 500 mg CTAB/L, this phenomenon was particularly pronounced due to the creation of micelles and premicelles, which gathered near the membrane surface and caused a reduction in flux. For the AFC 80 module, increasing the CTAB concentration to 1,000 mg/L gave an improvement in the permeability, which could be explained by the phenomenon of the electrostatic repulsion – strongly charged micelles departed from each other and a greater volume flux may have been achieved.

As it can be observed in Fig. 3, the modules exhibited various separation efficiencies. AFC 30 rejected 80%–100% of CTAB from the 50 mg/L solution, while for the same concentration, AFC 80 showed a much lower retention, that is, from 50% to 60%. The better selectivity of the AFC 30 module for the lowest contaminated solution may be explained by the surfactant adsorption within the membrane pores. According to Jönsson and Jönsson [16], the monomer competition to the hydrophobic spots on the membrane is low and probably the monomers "lie" horizontally along the surface. Due to the larger pore size (comparing to AFC 80), monomers were able to bind to the membrane structure.

It should be stressed, that in most of the experiments, a decrease tendency in the separation was observed over the filtration time. The changes in CTAB concentration in the permeate over the filtration time might be a consequence of the membrane adsorption capacity exhaustion. It can therefore be summarized that surfactant adsorption is the mechanism that has a significant role in surfactant separation on nanofiltration membranes.

A distinct correlation between the surfactant concentration in the feed and the retention coefficient was noted for the AFC 80 module – the higher the concentration of surfactant, the better separation was achieved. For micellar solutions,

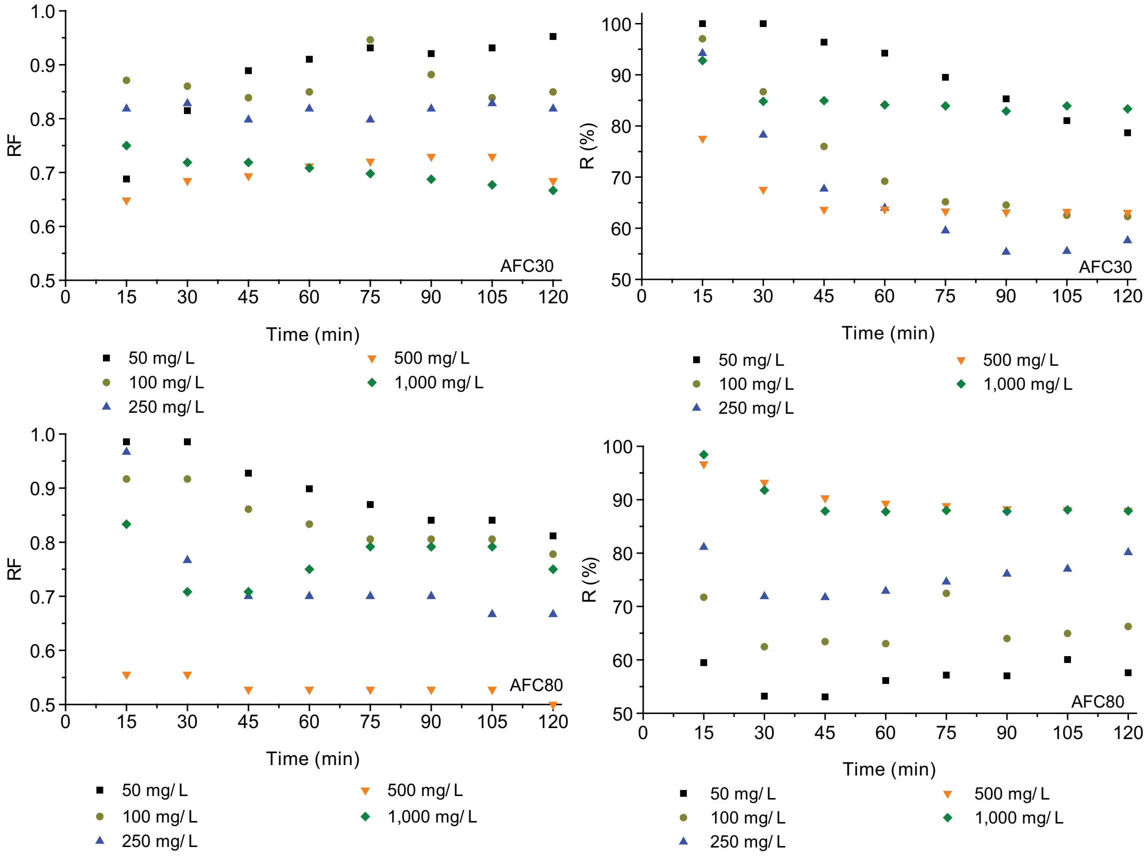

Fig. 3. Relative flux and retention coefficient versus filtration time for AFC 30 and AFC 80 modules (TMP = 0.3 MPa).

that is, for 500 and 1,000 mg CTAB/L, retention rose up to 97%–98%, respectively. Presumably, in AFC 30 experiments, due to the greater accessibility for monomers penetration within the pores, the mechanism of separation may be described by the adsorption phenomenon, while in AFC 80 tests – more likely by the sieving mechanism and the electrostatic interaction between the negatively charged membrane surface and positively charged CTAB particles.

3.2. Concentration

Fig. 4 presents the permeate recovery ratios of model CTAB solutions in the function of filtration time for both tested modules. The obtained data is consistent with the hydraulic performance of the modules – a higher volumetric flux corresponded with a higher PR in a shorter period of time. During the concentration process of solutions with initial surfactant concentration of 500 mg/L, the maximum recorded concentration of CTAB in the retentate was equal to 770 and 1,170 mg/L for AFC 80 and AFC 30 modules, respectively.

As it can be seen in Fig. 5, the CTAB concentration in the permeate during the process was in a pseudosteady state for AFC 30 module. In average, the surfactant concentration in the permeate amounted to 150 mg/L. In the case of AFC 80, the retention coefficient during the concentration process

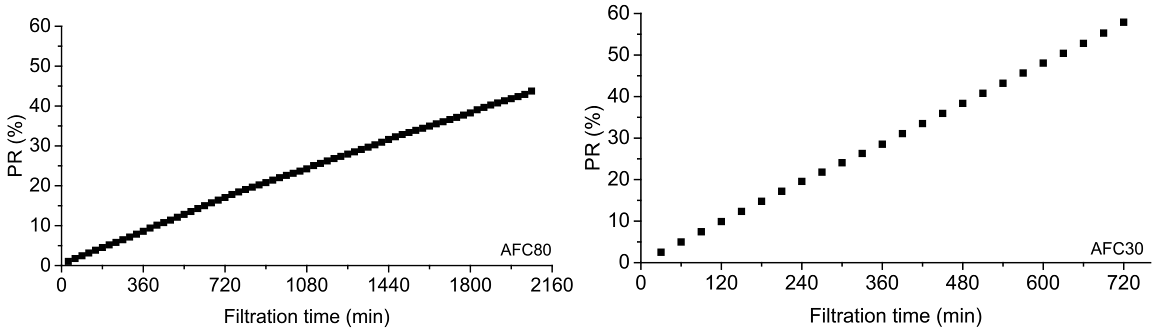

Fig. 4. Permeate recovery ratio versus filtration time for AFC 80 and AFC 30 modules (TMP = 0.4 MPa).

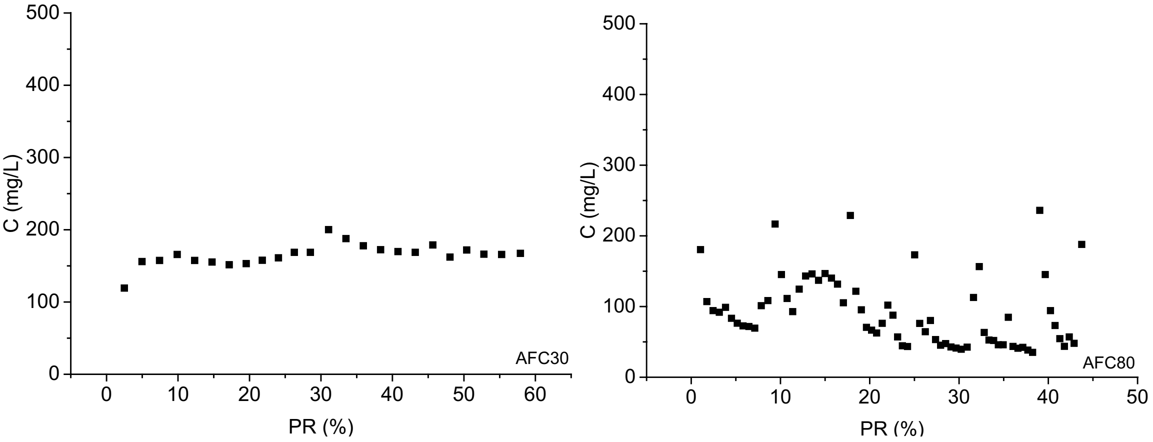

Fig. 5. CTAB concentration in the permeate versus permeate recovery for AFC 30 and AFC 80 modules (TMP = 0.4 MPa).

was in the range from 52% to 94% (Fig. 5), which resulted in a permeate concentration in the range from 35 to 256 mg CTAB/L. The lowest retention values were obtained at the beginning of the filtration cycles, which were performed for 6 h. During the installation start-up, surfactant molecules deposited onto the membrane detached and passed to the permeate side. An enhancement in AFC 80 membrane selectivity during the process was noted. Due to the lower molecular weight cut-off (MWCO), the AFC 80 module generally provided a better separation ratio. In turn, the process with AFC 30 was more stable.

Considering the membrane MWCO and the CTAB monomer molecular weight, the obtained results were not satisfactory; especially as the feed solution concentration exceeded the CMC value. Iqbal et al. [17] reported much better CTAB rejection with the use of ultrafiltration membranes, that is, 95%–96%, however, the treated solutions were characterized by a concentration exceeding 5 CMC.

In the course of the concentration experiments, relative flux deterioration due to surfactant fouling was observed (Fig. 6). Generally, the obtained data were consistent with the first part of tests (separation experiment results, Fig. 3). The fouling phenomenon occurred in the first stage of the process – after 60 min of the filtration – relative flux amounted to 0.58 and 0.75 for modules AFC 80 and AFC 30, respectively. The decrease in permeate volume flux was more pronounced for the AFC 80 module. Moreover, in the AFC 80 tests, a slight decrease tendency over the test was observed. At the end of the concentration process, the RF value was equal to 0.46. As in the case of the separation scheme (Fig. 5), changes in the general RF trend could be observed. The peaks of relative flux values were noted for the process start-up. In the experiments with AFC 30, the reduction in hydraulic capacity membranes did not exceed 33%.

As it was already stated, the decrease in the permeate flux over the process was primarily attributed to the concentration polarization layer created by the micelles near the membrane surface. According to Mizoguchi et al. [18], for a surfactant concentration below the CMC, the membrane pore blocking can also be caused by the premicelles formed in the concentration polarization layer.

The rising concentration of the feed during the concentration process resulted in the formation of more saturated micelles, which in turn created even more packed concentration polarization layer. As a result, "an additional membrane" came into existence and the resistance of modules increased. The phenomenon of electrostatic attraction between positively charged surfactant molecules and a

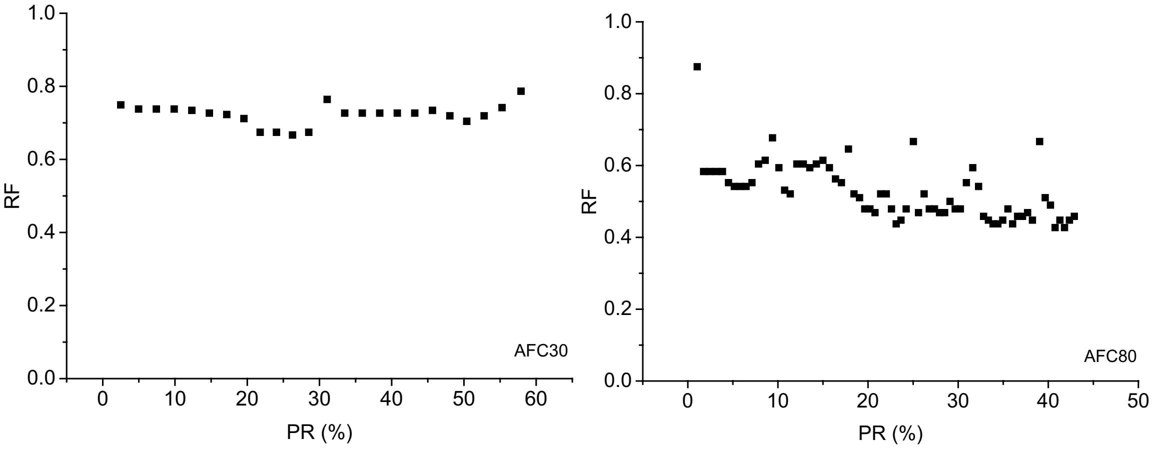

Fig. 6. Relative flux versus permeate recovery ratio for AFC 30 and AFC 80 modules (TMP = 0.4 MPa).

negative membrane surface also contributed to the intensification of fouling. Due to the lower membrane pore size, the drop in the permeate flux for AFC 80 module could be attributed to the gel layer near the membrane.

4. Summary

The experimental research showed that surfactant concentration and the membrane MWCO were crucial parameters that affected both the rejection efficiency and the hydraulic performance. An increase in surfactant concentration resulted in rejection enhancement for membranes with a lower pore size. For both modules, surfactant fouling was particularly pronounced for the solution around and above the CMC. In the course of the concentration process, the concentration factor was strongly depended on membrane pore size – module AFC 30 was characterized by the higher permeate volume flux, which enabled to obtain a higher concentration factor value. For both modules, surfactant caused fouling to occur. However, AFC 30 module was more resistant to the phenomenon. Taking into account separation properties, module AFC 80 enabled a better surfactant retention.

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