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SEPARATION AND CONCENTRATION OF CATIONIC SURFACTANT SOLUTIONS WITH THE USE OF CERAMIC MODULES

This paper presents the findings of experimental research on employing ultrafiltration and microfiltration ceramic modules (150 kDa, 0.14 μm , 0.45 μm) for removal and concentration of the cationic surfactant Tequat LC90i (TEAQ) from water solutions. The filtration tests were performed at a semi-pilot installation in a crossflow regime. The feed solution parameters (surfactant concentration, pH of the treated solution, the presence of inorganic salt), and process conditions (transmembrane pressure and linear velocity) on the membrane filtration efficiency were evaluated. In all tests, very satisfactory TEAQ retention coefficients (in the range of 70–95) have been achieved. However, surfactant fouling occurred resulting in deterioration of the permeability of the modules. Modules characterized by the pore sizes greater than the size of surfactant particles (i.e., 0.45 μm modules) proved to be the most fouling resistant ones. It was also proven that process performance at high linear flow velocity can efficiently reduce the intensity of membrane pore blocking.

1. INTRODUCTION

Cationic surfactants have found applications in many areas of the industry due to numerous features of their chemical structure. A cationic surfactant molecule consists of a hydrophobic tail and a positively charged hydrophilic head. As a consequence, these substances exhibit antiseptic, antifungal, antiviral, and disinfection (quaternary ammonium salts such as benzalkonium chloride or cetrimonium bromide [1]) or lubricating/antistatic action (e.g., esterquats). Triethanolamine-based esterquats (TEAQ) have been the primary ingredient in European fabric softeners [2]. Due to the strong effect of cationic surfactants on water/soil properties and their toxicity versus many species, it is necessary to remove them from industrial wastewater.

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Biodegradation [3], coagulation [4], foaming [5] or photocatalytic methods [6] may be effective in surfactant removal from water solutions. However, membrane-based techniques are very promising technologies for the removal of surfactants. Their great advantage is the ability to recover valuable ingredients from wastewater. Amin et al. [7] listed numerous advantages of ceramic membranes; the main ones are as follows: high chemical, thermal, mechanical, and physical stability, long working life, and good environmental performance. Fernández et al. [8] reported anionic (SDS) and nonionic (Tergitol NP-9) surfactant removal in the range of 60–70% using the ultrafiltration ceramic membrane Membralox[®]. Polak et al. [9] examined tubular ceramic membranes (Mantec Technical Ceramics Ltd) for laundry wastewater treatment. The experiments showed COD reduction from an initial concentration of 1024 mg/dm³ to 200 mg/dm³ after 90 min of membrane filtration. The literature reports that discuss the removal of cationic surfactants in membrane processes are limited and mainly concern polymeric membranes. Boussu et al. [10] investigated cetrимide separation with the use of nano-filtration membranes. The initial surfactant concentration was 40 mg/dm³. The retention coefficients reported were very variable – 17, 21, 89, and 97% of cetrимide was removed, depending on the type of membrane applied.

Our preliminary research [11] proved that membrane filtration can be an effective method for cationic surfactant removal. Application of polymeric flat-sheet ultrafiltration membranes (in dead-end regime) allowed the retention of up to 100% of TEAQ. However, significant simultaneous membrane permeability deterioration was observed. To reduce membrane blocking by surfactants, the following actions can be implemented: filtration in a crossflow regime and the use of larger pores, i.e., microfiltration membranes which may be less susceptible to pore blocking. In this paper, a crossflow set-up equipped with ultrafiltration and microfiltration ceramic modules was tested for TEAQ removal from water solutions.

2. EXPERIMENTAL

A crossflow semi-pilot filtration set up (J.A.M. Inox, Poland) was employed for the experimental research (Fig. 1). In all experiments, the initial volume of the feed solution was 8 dm³ and its temperature was 20 °C. During the filtration experiments, the linear flow velocity was maintained in the range from 5 to 6 m/s, from 4 to 5 m/s and from 2 to 2.5 m/s for 0.45 µm, 0.14 µm, and 150 kDa modules, respectively. The first part of the tests involved 120-minute membrane filtration tests, which were performed under the transmembrane pressure (*TMP*) of 3 bar. 20-cm³ permeate samples were collected at 15 min intervals for measurement of surfactant concentration, and the concentration of TEAQ in the feed solution was maintained at a constant level. In the next part of the tests (i.e., in concentration batch mode), the transmembrane pressure was increased to 3.5 bar, and the processes were performed until the resistance of the modules precluded

further filtration. During this stage of the tests, both surfactant concentration in the concentrate and permeate stream were monitored every 30 min. Cationic surfactant Tequat LC90i, TEAQ (dihydrogenated tallowethyl hydroxyethylmonium methosulfate and di-tallowethyl hydroxyethylmonium methosulfate, PCC Rokita, Poland) solutions at concentrations of 50, 100, 250, 500 and 1000 mg/dm³ were prepared for the research. Critical micelle concentration (*CMC*) of the surfactant amounted to 0.026±0.0067 mg/dm³. The micelle size distribution was 115.9±6.9 nm, and the monomer length, which is approximately the half of the micelle diameter, was 58 nm (DLS method, Malvern Zetasizer Nano ZS, United Kingdom, wavelength 532 nm). TEAQ concentration in the samples was monitored by TOC measurements (IL550 TOC-TN, HACH, United States). Based on the calibration curve, TEAQ concentration can be calculated with high accuracy ($R^2 = 99.2\%$) from TOC measurements using the following formula

$$C = 1.384TOC \quad (1)$$

where C is TEAQ concentration, mg/dm³, and TOC is total organic carbon concentration, mg/dm³.

To verify the separation properties, the retention coefficient R was calculated

$$R = \frac{C_f - C_p}{C_f} \times 100 \quad (2)$$

where C_f and C_p are surfactant concentrations, mg/dm³, in the feed and permeate, respectively.

Permeate volumetric flux is an important factor for evaluating membrane processes efficiency. It seems that membrane pore blocking occurs in the presence of surfactants causing a decrease in membrane permeability [12]. To evaluate the modules' hydraulic properties, volume flux was determined according to the following equation

$$J = \frac{V}{At} \quad (3)$$

where J is the permeate volume flux, dm³/(m²·h), V is the volume of the permeate sample collected, dm³, A denotes the membrane surface area, m², and t is the filtration time, h.

To assess susceptibility to fouling, the normalized flux was calculated:

$$RF = \frac{J}{J_0} \quad (4)$$

where RF is the relative flux, J is the permeate volume flux after time t , and J_0 is the distilled water permeate flux.

The permeate recovery was calculated according to the following equation:

$$PR = \frac{V_p}{V_0} \times 100 \quad (5)$$

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.

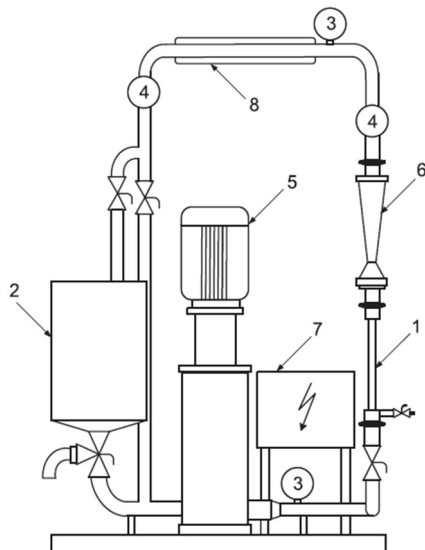


Fig. 1. Laboratory set-up: 1 – membrane module, 2 – feeding tank (10 dm³), 3 – manometer, 4 – thermometer, 5 – pump (Grundfos), 7 – control panel, 8 – cooler

Commercially available UF and MF CÉRAME INSIDE[®] modules purchased from Tami Industries (France) were chosen for the tests. The parameters of the membranes are given in Table 1.

Table 1

Characteristic of CÉRAME INSIDE[®] (Tami Industries) modules

Parameter	Value		
Pore diameter, μm /cut-off, kDa	0.45 μm	0.14 μm	150 kDa
Number of channels	7	7	1
Inner channel diameter, mm	2	2	7
Filtration area, m ²	0.0130	0.013	0.005
Distilled water flux, dm ³ /(m ² ·h) ^a	293.5	260.6	19.2
Max. operating pressure, bar	10		
Mechanical resistance, bar	>90		
Chemical resistance	pH=0÷14		
Max. operating temperature, °C	<350		

^aDetermined by the authors at $TMP = 3$ bar and temperature 22 °C.

The last part of the experiments included the effect of the treated solution parameters (pH and presence of the electrolyte) and the change in process parameters (linear flow velocity and transmembrane pressure) on the membrane process performance. Sodium chloride (NaCl, Poch, Poland) was used for the tests. In order to correct the pH values to 3.5, 4.5 and 9, 0.1 M HCl and 0.1 M NaOH solutions were added to the surfactant solutions.

3. RESULTS AND DISCUSSION

3.1. PURIFICATION

Table 2 presents the TEAQ retention coefficients obtained during the 120-minute purification processes with the use of three modules. High separation ratios (above 70%) were noted for all tested modules. However, a slight trend can be observed where a smaller pore size gives a bigger retention coefficient. The 150 kDa module gave an average retention coefficient in the range from 82 to 95%. It should also be noted that changes in the initial TEAQ concentration did not significantly affect the separation efficiency. Due to the very low value of *CMC* (0.026 mg/dm³), all of the tested solutions were the micellar ones. Taking into account the micelle size distribution (0.115 µm), relatively high separation ratios were noted for microfiltration modules, especially for the 0.45 µm module. Even though the pore size was fourfold greater than the TEAQ micelle size, surfactant retention coefficients exceeded 70%.

Table 2

Average TEAQ retention coefficients *R* in the feed solution [%]

Initial TEAQ concentration [mg/dm ³]	Module type		
	150 kDa	0.14 µm	0.45 µm
50	84	82	80
100	91	88	80
250	82	83	72
500	91	93	75
1000	95	95	85

Figure 2 shows relative flux values versus filtration time depending on module type and initial TEAQ concentration. As can be seen, the presence of the cationic surfactant in treated solutions negatively affects the transport properties of the modules. Depending on the feed solution concentration, it was observed that the microfiltration modules achieved various relative permeabilities. A particularly interesting case was observed when the 0.45 µm module was applied. Treatment of solutions in the concentration range of 100–500 mg/dm³ brought the relative flux into the range from 0.55 to 0.60; while for the highly concentrated solution, i.e., 1000 mg/dm³, the module was almost

completely fouled; relative flux at the end of the filtration cycle amounted to 0.007. However, for the 150 kDa module, the initial surfactant concentration did not have as much effect on the relative permeability as for the other modules. After 30 min of membrane filtration on the 150 kDa module, the relative flux was in the range of 0.14–0.23 for initial TEAQ concentrations of 100–1000 mg/dm³ and 0.53 for 50 mg/dm³. It must be stressed that the surfactant fouling phenomenon was more pronounced for the modules with the pore sizes close to the separated particle's size (micelle 0.115 μm , monomer 0.058 μm), i.e., for the 0.14 μm module and the 150 kDa module for which, according to Calvo et al. [13], the pore size distribution is 0.055–0.08 μm .

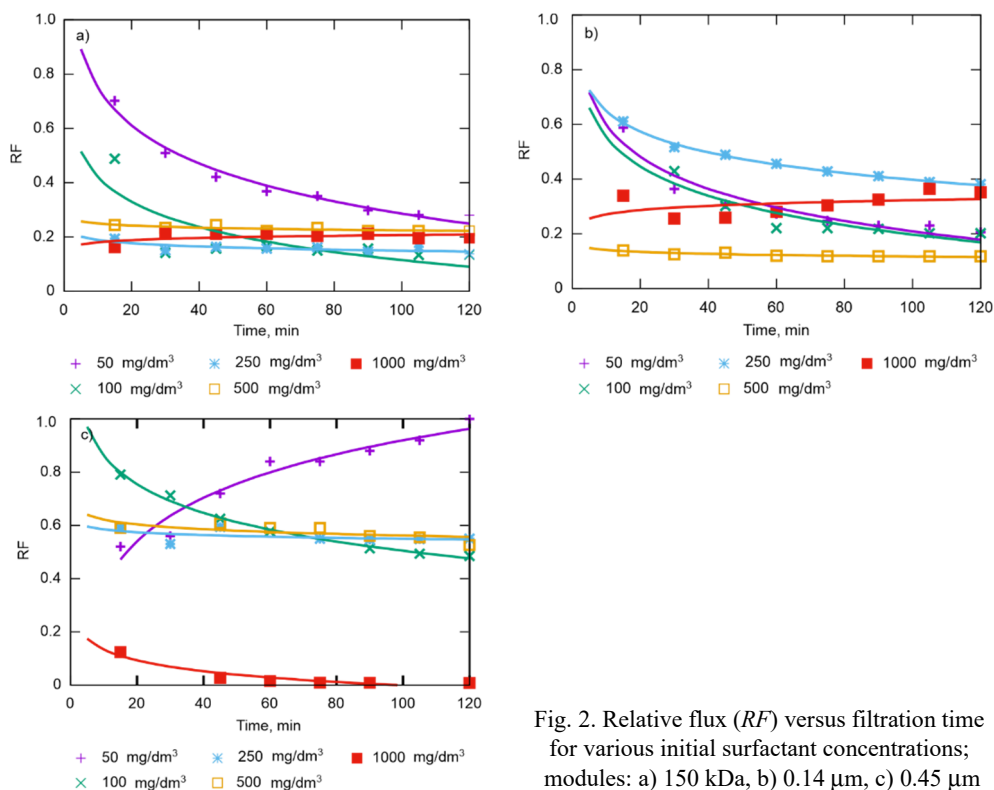


Fig. 2. Relative flux (RF) versus filtration time for various initial surfactant concentrations; modules: a) 150 kDa, b) 0.14 μm , c) 0.45 μm

It seems that the deterioration in membrane transport properties (compared to the distilled water flux) was also caused by the interaction between surfactant particles and the hydrophilic surface of the ceramic membranes. Surfactant molecules arrange hydrophilic heads near the hydrophilic surface, filling it one by one at very close distances between each other (Fig. 3). As a result, membrane hydraulic resistance increases. Moreover, TEAQ particles are adsorbed inside the pores causing a reduction in their sizes and, as a consequence, membrane permeability.

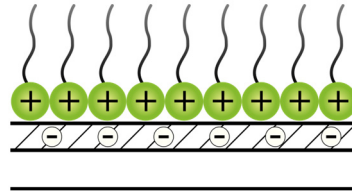


Fig. 3. Cationic surfactant particle arrangement on a hydrophobic membrane

3.2. MODIFICATION OF THE PROCESS AND FEED SOLUTION PARAMETERS

Due to the relatively high retention coefficients of surfactant, the MF module with the pore diameter of $0.14\ \mu\text{m}$ was chosen for the next part of the test that involved changes in the process parameters to limit the fouling phenomena. The parameters tested for this purpose were transmembrane pressure (TMP) and linear flow velocity (v). The tests were performed for the initial TEAQ concentration of $50\ \text{mg}/\text{dm}^3$. The first part was carried out under a constant TMP of 2 bar and for five values of linear velocity, i.e., 1.25, 1.80, 2.8, 4.4, and 5.7 m/s. The average retention coefficients and the relative flux values obtained during the 60-minute processes are plotted in Fig. 4a. It was noted that an increase in linear flow velocity did not bring any essential changes in TEAQ removal efficiency (retention coefficients were in the range from 87 to 92%). However, it should be stressed that in terms of fouling phenomena, an increase in this parameter to the value of 5.7 m/s gave a significant reduction in surfactant fouling. The relative flux value was about 0.72, which means that the drop in permeate flux did not exceed 30%. For the remaining values of linear flow velocity, the relative flux amounted approximately to 0.35. It can be stated that at turbulent flow, the fouling phenomena were limited due to surfactant washing out.

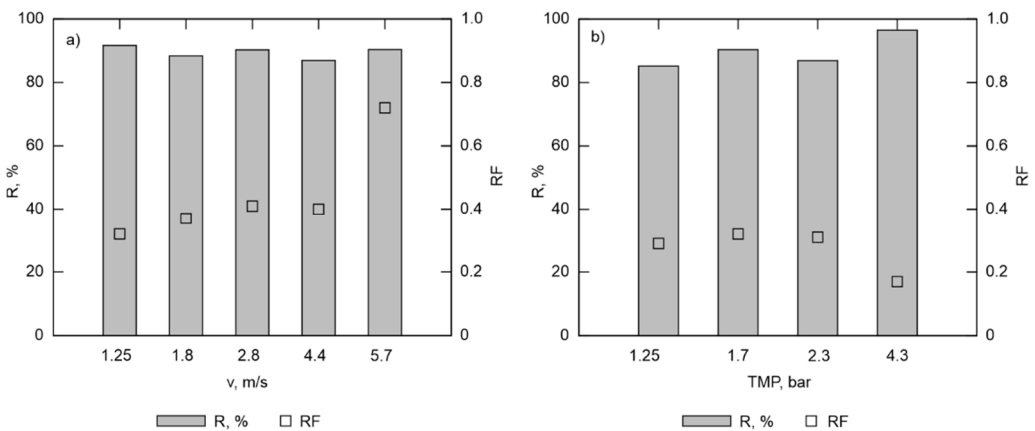


Fig. 4. Retention coefficients (R) and relative flux (RF) versus linear flow velocity (a) and transmembrane pressure (b) for the $0.14\ \mu\text{m}$ module and the initial TEAQ concentration of $50\ \text{mg}/\text{dm}^3$

The second part of the test included an evaluation of the effect of *TMP* on relative flux. Linear flow velocity was at the level of 4.1–4.5 m/s and the *TMP* values were equal to 1.25, 1.7, 2.3, and 4.3 bar. It was found (Fig. 4b) that increasing *TMP* resulted in relative flux deterioration. Simultaneously, a slight improvement in the retention coefficient (by about 10%) can be observed with the increasing value of *TMP*.

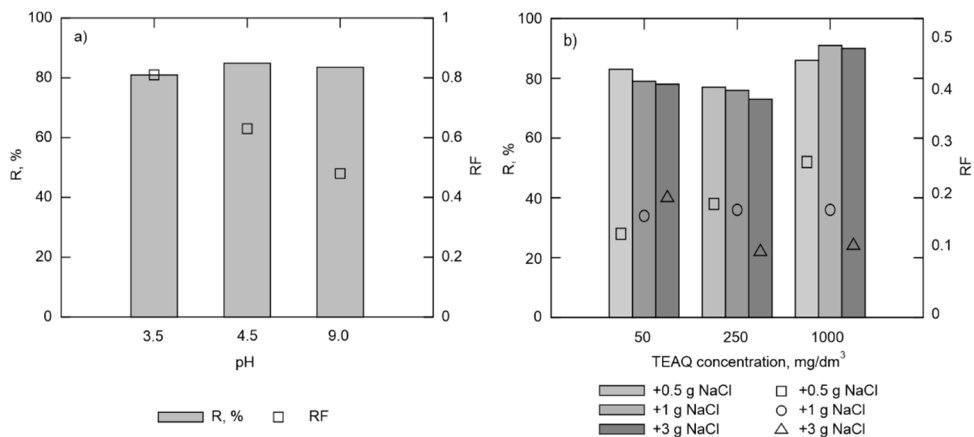


Fig. 5. Retention coefficients (*R*) and relative fluxes (*RF*) for the 0.14 μm module: a) versus pH for an initial TEAQ concentration of 50 mg/dm³, b) for various salt additions and initial TEAQ concentrations

The effect of pH on the process efficiency was also investigated. For this purpose, TEAQ solutions with a concentration equal to 50 mg/dm³ and various pHs were filtered on the 0.14 μm module for 60 min. The evident influence of solution pH on module permeability was observed (Fig. 5a). Purification of the strongly acidic solution (pH = 3.5) yielded a relative flux of about 0.80. When the pH was increased to 4.5, there was a decrease in relative permeability to about 0.62. Increasing the pH to 9 resulted in further deterioration of the permeability to the value of 0.48. According to de la Casa et al. [14], the isoelectric point (pzc), defined as the pH for which the net charge of the membrane is equal to zero, for amphoteric ceramic membranes Céram Inside 25 (pore radius 0.14 μm) with a zirconium dioxide active layer is located at around 6.9. Thus, the deterioration of the modules' permeability at pH 9 may result from the electrostatic attraction between the negatively charged membrane surface and the positively charged cationic surfactant particles. At pH 3, the membrane surface exhibits a positive charge load, and the less intensive membrane blocking can be ascribed to the strong electrostatic repulsion.

The next step of the research was to evaluate the effect of electrolyte on surfactant retention and module permeability. TEAQ solutions at the concentrations of 50, 250, and 1000 mg/dm³ were prepared with the addition of NaCl of 0.5, 1, and 3 g/dm³. The results obtained in 60-minute processes are plotted in Fig. 5b. Comparing the data ob-

tained in the tests with the presence of an electrolyte to the results with single-component solutions (Table 2), it can be seen that the salt caused a slight drop in the retention coefficient. For example, for TEAQ concentrations of 1000 mg/dm^3 , the average retention coefficient amounted to 95%. When NaCl was present in the treated solution, this ratio was 86–91%. Focusing on the relative permeability, the negative effect of the electrolyte can be seen. In the first stage of the tests (Fig. 2), the average relative fluxes amounted to 0.30, 0.50, and 0.35 for solutions 50, 250, and 1000 mg/dm^3 , respectively. The addition of the electrolyte to the feed solutions resulted in relative fluxes below 0.26 for all variants. According to Bargeman et al. [15], an electroviscous effect connected with the presence of salt ions inside the pores most likely limits the stream flow through the small pores. Thus, mainly the larger pores have their share in the mechanism of the sieve separation of surfactants.

3.3. CONCENTRATION MODE

To verify the possibility of surfactant solution concentration, the last part of the research was performed with the use of two microfiltration modules. As the *CMC* of TEAQ is very low (0.026 mg/dm^3), the initial surfactant concentration (50 mg/dm^3) was almost 2000CMC . In this stage, the TOC concentration was monitored both in the concentrate (feeding tank) and the permeate. Figure 6 presents TOC content in process streams and the relative flux versus permeate recovery ratio. To obtain 43% permeate recovery on the $0.14 \mu\text{m}$ module, the membrane filtration proceeded for 9.5 h; for the $0.45 \mu\text{m}$ module, a recovery ratio of 31% was achieved 7 h after the process started. The processes were performed until the growth of the module's resistance prevented the maintenance of the constant parameters, i.e., *TMP* and linear flow velocity.

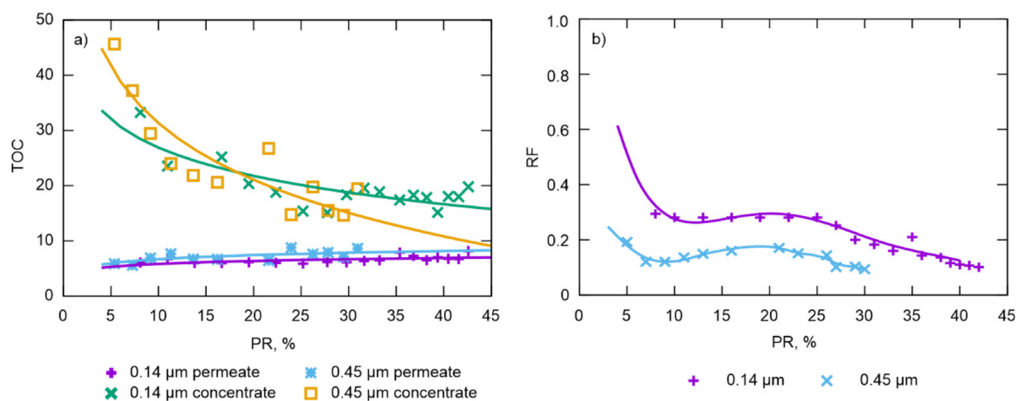


Fig. 6. TOC concentration in permeate and concentrate (a) and relative flux (b) versus permeate recovery ratio for microfiltration modules

It was noted that for both modules, the quality of the permeate was at a constant level over all experiments (TOC concentration was in the range from 5.1 to 8.2 mg/dm³ and from 5.6 to 8.8 mg/dm³ for the 0.14 µm and 0.45 µm modules, respectively). The goal of this experiment (i.e., maximum concentration of the surfactant solution) was not achieved. Over the filtration cycle, the TOC content in the feeding tank decreased from 33 and 37 mg/dm³ at the beginning of the process to 19.8 and 19.5 for the 0.14 µm and 0.45 µm modules, respectively. These results indicate the accumulation of surfactant particles within the membrane pores or their deposition on installation elements. This mechanism should be investigated to understand the interaction between the surfactants and the membrane. The course of the relative permeability curves confirms the thesis about the deposition of the surfactant inside the membrane; over the experiment, a relative flux decline was observed. Opposite to the previous part of the research, the module with the greater pore size was more susceptible to surfactant fouling. For a 30% permeate recovery ratio, the relative flux amounted to 0.10; when for the same value of the PR parameter, the 0.14 µm module achieved a value of 0.20.

4. CONCLUSIONS

- Ultrafiltration and microfiltration ceramic membranes proved to be useful in cationic surfactant removal. Above 70% of TEAQ was removed from the solutions regardless of the initial compound concentration.
- The presence of surfactant in treated solutions was associated with deterioration of the module's permeability. The fouling phenomena were most pronounced for the modules characterized by having pore diameters similar to the surfactant particle size.
- Correction of the process parameters affected the hydraulic performance of the membranes. The induction of the turbulent flow significantly reduced the intensity of surfactant fouling.
- The inefficient concentration of the surfactant solutions proved that TEAQ particles were deposited inside the membrane pores, making it impossible to obtain concentrate with a high content of surfactant.

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