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ULTRAFILTRATION CONCENTRATION OF MODEL DETERGENT SOLUTIONS

The efficiency of ultrafiltration allowing model detergent solutions to be purified and concentrated was evaluated. The tests were performed with the use of flat-sheet polyethersulfone and polysulfone membranes (with a cut-off of 5, 10 and 30 kDa) and flat Pellicon module with polyethersulfone membranes (with a cut-off of 5 kDa).

The lowest separation of anionic surfactant and total organic carbon was achieved at surfactant concentration below the critical micelle concentration (CMC). Around and above the CMC value the membrane selectivity and hydraulic performance slightly increased in comparison to the lowest concentration.

The retention coefficient of anionic surfactant for all the membranes tested was stable during concentration processes and ranged from 75% (PS30) to 90% (PES5 and PS5). Also concentration tests on Pellicon ultrafiltration module enabled efficient removal of anionic surfactant (about 90%) from model solutions.

1. INTRODUCTION

From the environmental point of view, there is a need to safeguard the quality of freshwater resources and therefore they ought to be better managed [1], [2]. It is desirable to develop an intensive water recycling and to minimize the emission of pollutants by implementing high-performance treatment technology.

Detergent products are used in large quantities in such industrial branches as textiles, food processing, paints, polymers, cosmetics, pharmaceuticals, mining, and pulp and paper production.

The consumption of surfactants has resulted in their worldwide production of approximately 17 million tonnes in 2000 (including soap), with expected future growth rates of 3–4% per year globally and of 1.5–2.0% in the European Union [2]. Anionic surfactants are commercially the most important product, and their market share ap-

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proaches 50% [2] of total production.

Environmental risk associated with detergent manufacture, its use and disposal is of great interest because detergent products and its core ingredients (surfactants) can be relatively toxic to aquatic ecosystems. Moreover, detergents present in water are responsible for “cultural eutrophication” (phosphates) and hence for stimulation of algal propagation; they prevent carbon dioxide from leaving the water and at the same time prevent oxygen from dissolving in the water (the conditions unfavourable to biodegradation). Detergents also affect selection of microorganisms (anaerobes prevail) and foam formation. Synthetic detergents may have a negative impact on aquatic organisms, especially those who depend on surface tension [3].

Due to the diversity of detergent wastewater it is difficult to develop a single and effective treatment method. From among conventional techniques which were presented in this research [4]–[14] we can list biodegradation, coagulation, foaming, oxidation, adsorption and ion exchange. Numerous reports indicate that membrane technology is considered to be one of a highly competitive method for recovering water and concentrated products from the rinsing waters used in the batch production of surfactants and detergents. It can also be used as a polishing step before effluents are discharged [15]–[19]. Membrane-based separation processes – because of the selectivity of the membrane – create the possibility of recovering chemical agents and process water as well as of reducing high organic load of the wastewater.

The ultrafiltration efficiency for purification and concentration of model detergent solutions was evaluated. The tests were performed with the use of flat-sheet polyethersulfone and polysulfone membranes (with a cut-off of 5, 10 and 30 kDa) and flat Pellicon module with polyethersulfone membranes (with a cut-off of 5 kDa).

2. EXPERIMENTAL

2.1. SOLUTIONS

Experiments were carried out on model detergent solutions prepared from tap water and liquid detergent. The concentration of anionic surfactant (sodium laureth sulphate (SLES) in model solutions amounted to 100, 300 and 600 g/m³).

2.2. MEMBRANES AND MODULES

The ultrafiltration tests were performed with the use of flat-sheet polyethersulfone and polysulfone Intersep Nadir membranes (the cut-off of 5, 10 and 30 kDa) (table 1) and a flat Pellicon module with polyethersulfone membranes (with the cut-off of

5 kDa) (table 2).

Table 1

Characteristic of Intersep Nadir membranes

Membrane type	Description	Contact angle (°)	Cut-off (kDa)	Mean pore radius (nm)
Polyethersulfone (PES)	moderately hydrophilic	50.01	5	0.62
			10	2.04
			30	8.38
Polysulfone (PS)	chemically modified to be hydrophilic	67.6	5	0.80
			10	3.20
			30	9.54

Table 2

Characteristic of ultrafiltration module

Parameter	Module type
	Pellicon
Configuration	flat
Cut-off (kDa)	5
Membrane area (m ²)	0.1

2.3. EXPERIMENTAL SYSTEMS

Flat-sheet membranes were tested in a laboratory set-up (figure 1), whose main part was an Amicon 8400 UF cell with a total volume of $0.350 \times 10^{-3} \text{ m}^3$ and an effective surface area of the membrane of $4.54 \times 10^{-3} \text{ m}^2$. The Pellicon module was tested in Pro-Flux system (a total volume of $3 \times 10^{-3} \text{ m}^3$) (figure 2). The experiments were run at the pressure of 0.20 MPa.

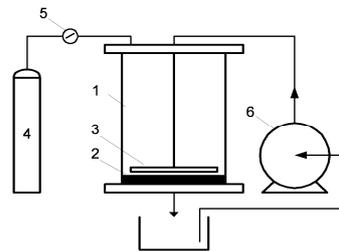


Fig. 1. Laboratory set-up: 1 – ultrafiltration cell, 2 – membrane, 3 – stirrer, 4 – gas cylinder, 5 – reducer, 6 – recirculation pump

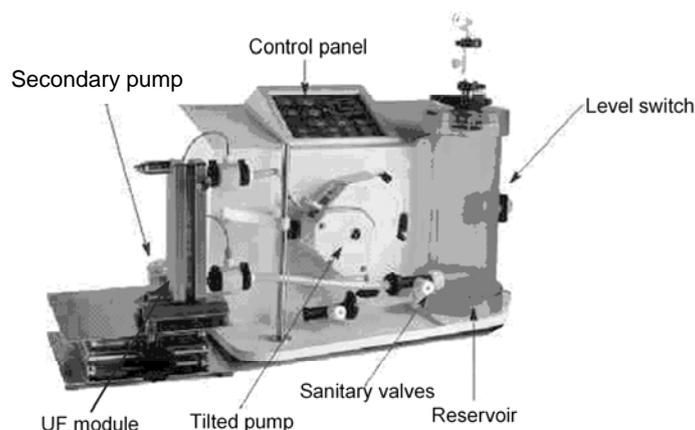


Fig. 2. Pro-Flux M12 system (Millipore)

2.4. ANALYTICAL METHODS

The concentration of anionic surfactant (AS) was measured spectrophotometrically (colour reaction using the Rhodamine G6 indicator and measurements of the absorbance at a 565 nm wavelength using UV-MINI-1240 spectrophotometer (Shimadzu) and 0.5×10^{-2} m glass cuvettes). The detectability limit of was around 0.1×10^{-3} g.

The concentration of total organic carbon (TOC) was measured with TOC 5050 Analyser (Shimadzu).

The efficiency of the ultrafiltration process was determined based on the following expression:

$$R = \frac{C_0 - C_p}{C_0} \cdot 100 \quad (\%),$$

where R is the retention coefficient, and C_0 and C_p are the concentration of the feed and permeate, respectively.

The effluent concentration was determined according to the following formula:

$$CF = \frac{V_0}{V_t},$$

where CF is the concentration factor, and V_0 and V_t denote an initial volume of feed and the volume of concentrate after the time t , respectively.

During the experiments the normalized fluxes were determined:

J/J_{H_2O} – the ratio of the permeate flux (J) after the time t to the flux of distilled water (J_{H_2O});

J/J_0 – the ratio of the permeate flux (J) after the time t to the permeate flux (J_0) at the beginning of the concentration process.

3. RESULTS AND DISCUSSION

Figure 3 presents retention coefficient of anionic surfactant and total organic carbon as well as normalized flux of PES and PS membranes versus anionic surfactant concentration during ultrafiltration process. As can be seen, the lowest separation of AS was achieved for the solution of 100 g of SLES/m³. However, for the surfactant concentration around and above the critical micelle concentration (300 g/m³ [20]) the improvement in membranes selectivity was observed. For example, the retention coefficient obtained for the PES5 membrane amounted to 70%, 90% and 92% for 100 g/m³, 300 g/m³ and 600 g/m³, respectively. In the case of TOC separation (figure 3b), the similar trend, depending on surfactant concentration, was noticed. Below the CMC value, the TOC retention coefficient of the PES5 and PS5 membranes amounted to 60%; however, for the solution of the highest surfactant concentration the reduction of the TOC was on a level of 87%.

Based on the results obtained it should also be stressed that during UF process the permeability of membranes deteriorated (figure 3c). The biggest drop in permeate volume flux (in comparison to the distilled water) was observed for the 30 kDa membranes and amounted to 45%, 55% and 53% for 100 g/m³, 300 g/m³ and 600 g/m³, respectively. While the reduction in hydraulic capacity of the 5 kDa membranes did not exceed 20%.

A worse permeability of detergent solutions through membranes can be attributed to the concentration polarisation at the membrane surface. The compounds present in the solution accumulate at the membrane surface and in the membrane pores. It can be anticipated that the greater the molecular weight cut-off of the membrane (the more spongy the structure and the larger the pore size), the more intensive the membrane clogging.

For the concentration close to CMC value, as a result of the micelle creation, the separation slightly increased and simultaneously the improvement in transport properties was observed. Because the micelle surface is hydrophilic, it has a greater affinity to the solvent than to the UF membranes. At the same time the electrostatic repulsion between negatively charged micelles results in the less compact polarization layer and thereby the solvent transport was facilitated [17].

During the next stage of the study the concentration processes of model solutions (in the dead-end regime) were carried out (figure 4). A decrease in the permeate volume flux of 5 and 10 kDa membranes did not exceed 14% (in comparison to the permeate volume flux at the beginning of the process) for the 14-fold concentration factor. The 30 kDa membranes, because of their less compact polymer structure, were

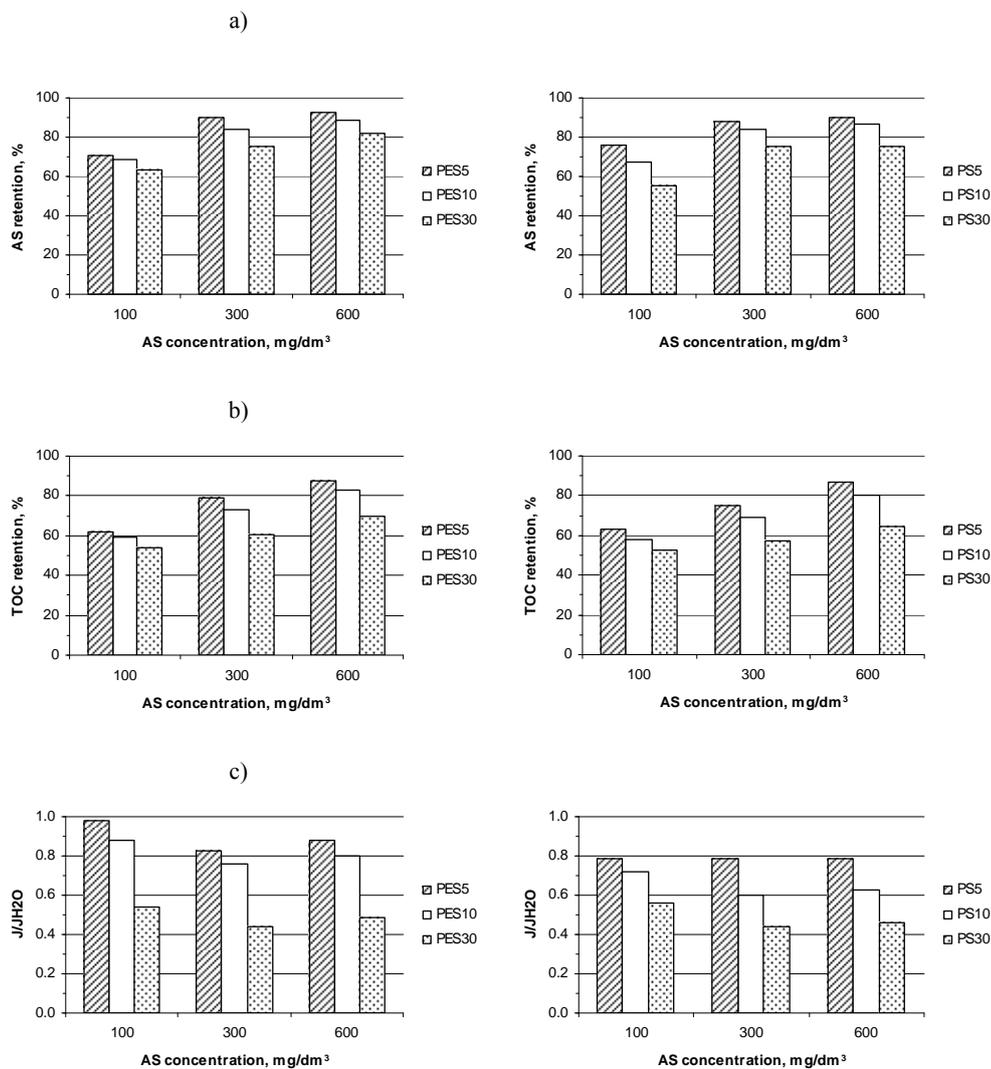


Fig. 3. Retention coefficient of anionic surfactant and total organic carbon and normalized flux of PES and PS membranes vs anionic surfactant concentration ($\Delta p = 0.20$ MPa)

more susceptible to fouling and therefore the drop in membrane permeability was more pronounced: 27% and 31% for PES and PS, respectively. The retention coefficient of AS for all the membranes tested was stable during concentration process and amounted to about 90% for 5 and 10 kDa membranes. In the case of 30 kDa membrane, the retention coefficient was lower, i.e., 80% and 75% for PES30 and PS30,

respectively. It should be noted that the retention coefficient of polysulfone and polyethersulfone in each series of membranes was very similar and depended on the membrane properties (table 2). Both polymers were characterized by similar hydrophilic-hydrophobic properties (moderately hydrophilic) and the pore radius.

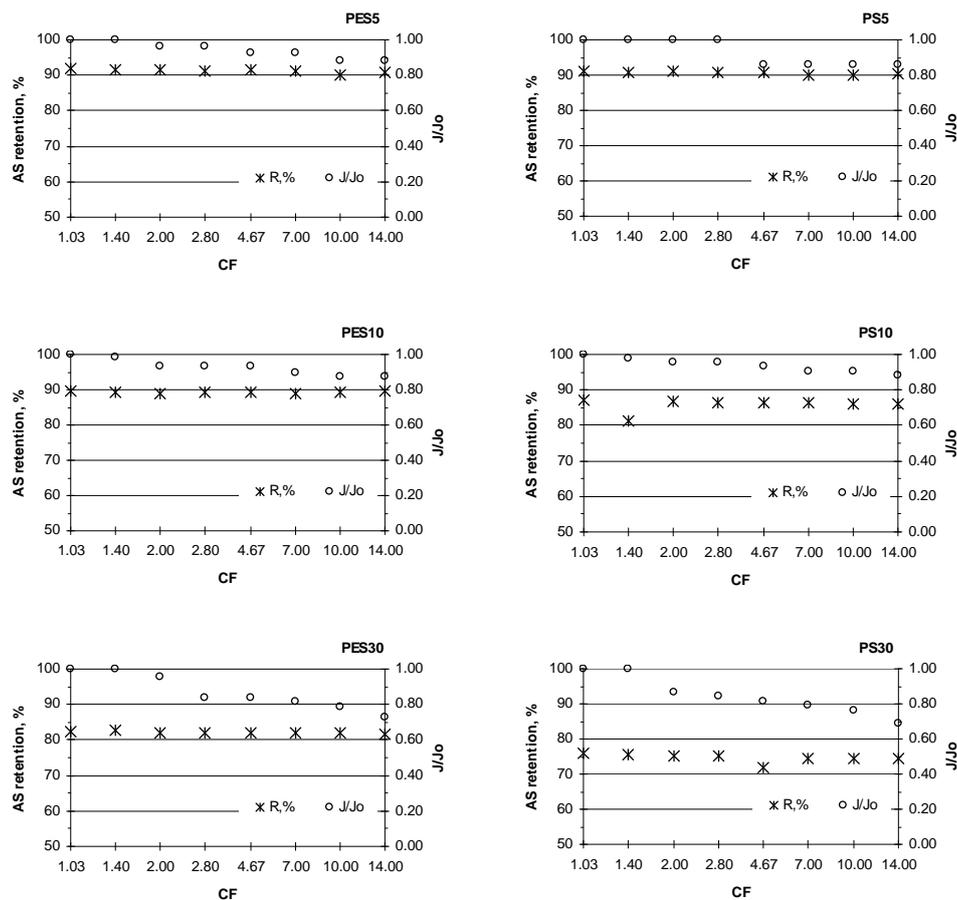


Fig. 4. Retention coefficient of anionic surfactant and normalized flux vs concentration factor of model solution for flat-sheet PES and PS membranes (initial surfactant concentration, 600 g/m^3 ; $\Delta p = 0.20 \text{ MPa}$)

As can be seen from figure 5, the concentration tests on the Pellicon ultrafiltration module (in the cross-flow regime) enabled efficient removal of AS at the retention coefficient approaching 90%. It was also inferred that a decrease in the permeate volume flux for the Pellicon module with PES5 membranes was more pronounced than that for flat-sheet PES5 membranes and amounted to 30% of the permeate volume flux

at the beginning of the process.

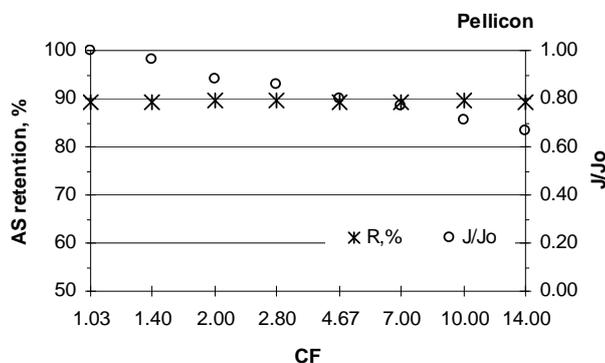


Fig. 5. Retention coefficient of anionic surfactant and normalized flux vs concentration factor of model solution for Pellicon module (initial surfactant concentration, 600 g/m^3 ; $\Delta p = 0.20 \text{ MPa}$)

The efficiency of AS separation from the model solution was very satisfactory (particularly in relation to cut-off value and mean pore radius of the membranes investigated) and similar for all the membranes tested and the flat Pellicon module. High retention coefficient of SLES is probably caused by creation of pre-micells and micelles above the CMC value. The results obtained indicate that the sieving mechanism of these particles of high-molecular weight could be sufficient to explain the separation of anionic surfactant by UF membranes. However, the interaction between surfactant particles and the remaining compounds of the solution can be regarded as a factor supporting the efficiency of surfactant removal from water solution by ultrafiltration.

4. CONCLUSIONS

1. Ultrafiltration, a low-pressure membrane process, was effective in AS and TOC reduction.

2. The lowest separation of AS and TOC was achieved at surfactant concentration below the CMC value. Around and above the CMC value the membrane selectivity and hydraulic performance slightly increased in comparison to the lowest concentration.

3. The 30 kDa membranes, because of the less compact polymer structure, were more susceptible to fouling and therefore the drop in membrane permeability was more pronounced in comparison to the 5 kDa and 10 kDa membranes.

4. The coefficient of retention of AS from model solutions for all the membranes tested was stable during concentration processes and ranged from 75% (PS30) to 90% (PES5 and PS5). Also concentration tests on Pellicon ultrafiltration modules

enabled efficient removal of anionic surfactants (about 90%) from model solutions.

ACKNOWLEDGEMENTS

The financial support of the Ministry of Science and Higher Education, grant no. N523 089 32/3477, is greatly appreciated.

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ULTRAFILTRACYJNE ZATĘŻANIE MODELOWYCH ROZTWORÓW DETERGENTÓW

Zbadano efektywność ultrafiltracyjnego oczyszczania i zateżenia modelowych roztworów detergentów. W badaniach wykorzystano płaskie membrany ultrafiltracyjne o granicznej rozdzielczość (*cut-off*) wynoszącej 5, 10 i 30 kDa oraz moduł Pellicon z płaskimi membranami wykonanymi z polietersulfonu (5 kDa).

Stwierdzono, że separacja anionowa substancji powierzchniowo czynnej oraz ogólnego węgla organicznego była najmniej efektywna dla roztworów poniżej krytycznego stężenia micel (CMC). Po zwiększeniu stężenia substancji powierzchniowo czynnej w roztworze powyżej wartości CMC w niewielkim stopniu wzrastała selektywność i hydrauliczna wydajność membran.

Proces ultrafiltracji umożliwiał zateżanie roztworów ze stałą i wysoką skutecznością separacji. Użytkiwane współczynniki retencji mieściły się w zakresie od 75% (na membranie PS30) do 90% (na membranach PES5 i PS5). Zateżanie prowadzone w układzie przepływu krzyżowego w module płaskim z membranami polietersulfonowymi (5 kDa) gwarantowało usunięcie anionowej substancji powierzchniowo czynnej na poziomie 90%.