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Separation of benzalkonium chloride using polymeric membranes

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ABSTRACT

The paper presents the findings of an experimental research employing tubular nanofiltration and ultrafiltration modules for cationic surfactant (benzalkonium chloride, BAC) removal from water solutions of initial concentration in the range from 50 to 1,000 mg/L. The study involved characteristics of the surfactant (critical micelle concentration CMC, micelle size distribution) and an assessment of the membrane filtration efficiency in terms of BAC separation and the volumetric flux. The effect of the modification of process parameters (transmembrane pressure and linear flow velocity) on surfactant retention and fouling intensity was evaluated. The experiments showed that the removal of benzalkonium chloride (CMC = 350 mg/L, micelle size 11.8 nm) with the use of nanofiltration module AFC40 exceeded 74% in all range of concentrations tested. The surfactant concentration was found as an important factor affecting the hydraulic performance of membrane filtration – increasing BAC concentration in the feed solutions resulted in permeability deterioration and the most significant drop in volumetric fluxes was noted for initial solutions of 1,000 mg/L. Moreover, the pore size, the hydrophilicity of the polymer and its net charge strongly affect the membrane fouling by the cationic surfactant particles. The most prone to pore blocking was the ultrafiltration membrane, while the nanofiltration membrane characterized by the lowest MWCO and pore sizes showed the least flux reduction.

Keywords: Pressure-driven membrane process; Cationic surfactant; Quaternary ammonium compound; Ultrafiltration; Nanofiltration

1. Introduction

Development of urbanisation and industrialisation is associated with anthropological pollution of water and soil. Improvement in the living standards leads to a growth in the production of detergents, cosmetic products, drugs or pesticides, which on the one hand secure human health but on the other bring the degradation of natural environment. Common feature of products mentioned is that all of them contain cationic surfactants which are toxic to aquatic life [1,2]. The main group of cationic surfactants are quaternary ammonium salts (QAS), whose biocidal activity is known since 1935 [3]. The positively charged QAS particles bind to negatively charged cell membranes, altering their physical properties and affecting their function which can result in cell death [4]. Benzalkonium chloride (BAC) is one of the most often used QAS, characterized by lethal action against many aquatic species [5,6], thus its penetration into the natural environment is particularly dangerous. Surfactant-contaminated wastewater may be generated in facilities producing detergents, laundries, textile facilities or households; however, the surfactant content in specific wastewater differs and may be in the range from a few to thousands g m^{-3} [7,8]. Literature data show such processes as biodegradation, coagulation, foaming, oxidation and adsorption methods [9–13] may be useful for surfactants removal from water solutions, however the cost-effectiveness of these methods is limited due to inability to recover and reuse valuable components contained in effluents.

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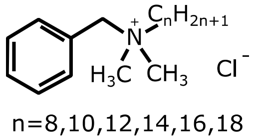
Pressure-driven membrane processes allow this goal to be achieved – during the membrane filtration, certain compounds of the treated solution do not pass through the membrane, while the other ones together with the solvent can permeate to the other side of the membrane. A selection of the membrane characterized by the smaller pore size than the contaminant particle size enables its retention on the membrane and as a result concentration in the feed stream. In case of surfactant wastewater, it is important to define whether the treated solution is in monomeric or micellar form. The concentration above which surfactant monomers agglomerate is named critical micelle concentration (CMC). Micelles consist of dozens of monomers, thus both their size and molecular weight are greater than that of the monomers. Basing on that, membranes characterized by the smaller pores and more compact structure (NF, RO) are suggested for monomeric solutions purification [14,15]; for more concentrated solutions (above the CMC) UF membranes are proposed as more effective ones. Surfactants are known to adsorb in the membrane pores affecting membrane permeability decline [16,17]. There are two main phenomena that contribute to lowering the permeate stream: concentration polarisation layer created near the membrane surface and adsorption of surfactants particles in the membrane pores [18]. Due to the positive charge of the cationic surfactants and negative charge of the majority of the membranes applied in wastewater treatment, the adsorption mechanism seems to be the crucial phenomenon for membrane fouling. Studies on removal of cationic surfactants from water solutions and their effect on the properties of the membranes are limited. Boussu et al. [18] reported cationic surfactant (cetrimide, feed solution of 40 mg/L) retention coefficients equal to 17%, 21%, 89% and 97% with the use of nanofiltration membranes NTR7450, NFPES10, NF270 and Desal51HL, respectively. Membrane filtration of cetrimide solution resulted in flux decline from 19 even up to 99% for NTR7450 membrane. Significant differences in the separation efficiency and susceptibility to pore blocking resulted from the characteristics of the membranes – surface charge and MWCO. Iqbal et al. [19] reported 95%–96% retention of hexadecyltrimethylammonium bromide (CTAB) with the use of ultrafiltration membranes. The solution tested was characterized by surfactant concentration exceeding 5 CMC. Our previous paper [20] showed that the correlation between membrane MWCO and surfactant particle size is important for nanofiltration course. Cationic surfactant CTAB solutions of concentration from 50 to 1,000 mg/L were purified with the use of two nanofiltration modules (AFC30, AFC80). Module with the greater MWCO value showed significant increase in CTAB concentration in the permeate over the filtration cycle, what evidence the adsorption of surfactant monomers in the membrane structure. Due to the adsorption capacity exhaustion, a greater number of the monomers passed through the membrane. In this study, we investigated the effectiveness of ceramic modules in terms of cationic surfactant (type of esterquat) removal from aqueous solutions.

2. Materials and methodology

Quaternary ammonium compound benzalkonium chloride was selected for the experiments (Table 1) due to its wide range of applications. Solutions containing 50, 100, 250, 500 and 1,000 mg BAC/L were prepared with the use of distilled water of conductivity 2.5 µS/cm. The pH value of the prepared solutions was in the range 6.5–7.5.

Table 1
Characteristics of the surfactant

Parameter	Benzalkonium chloride
Molecular weight, g/mol	283.80–423.97
Type	Cationic
Purity, %	80
Carbon atoms in chain	8–18
Structural formula	
Water solubility	Soluble in all proportions

The cross-flow semi-pilot filtration set up was employed for the experimental research [20]. According to producer instructions, the maximum working transmembrane pressure (TMP) for this equipment amounted to 0.5 MPa. The installation was equipped with a membrane module (consisting of two polymeric membranes), feed tank of volume 10 L, circulation pump (Grundfos) and cooling system. The experiments were carried out with continuous recirculation of retentate and permeate to the feed tank (the surfactant concentration in the feed tank was kept constant). The membrane filtration was performed under the TMP of 0.3 MPa and the linear flow velocity was in the range from 0.6 to 0.8 m/s. The volume of the feed solution amounted to 8 L and its temperature was 20°C. 20 mL permeate samples were collected for measurements of surfactant concentration in the intervals of 15 min.

One ultrafiltration (UF) and three nanofiltration (NF) modules (PCI Filtration group) made of modified polyethersulfone and polyamide were examined (Table 2). The single module length was 0.3 m, inner diameter was 0.0125 m and filtration area amounted to 0.024 m^2. According to the recommendations of membrane module manufacturer, the safe operation conditions are up to a value of TMP of approximately 6 MPa for NF modules and 4 MPa for UF module. However, the membrane filtration set-up applied in the test was not able to achieve this level of TMP (mainly due to the type of pump used). Thus, it was decided to carry out the UF and NF process at the same TMP values, that is, 0.3 MPa (with the awareness that the TMP value for nanofiltration experiments should reach a higher level).

Benzalkonium chloride characteristics involving CMC value and micelle size distribution was determined with the use of dynamic light scattering (DLS, Malvern Zetasizer Nano ZS, UK, wavelength 532 nm) method. Spectrophotometric measurements (UV Mini 1200 Shimadzu, Japan, wavelength of 215 nm) were employed for BAC concentration monitoring. Additionally, total organic carbon (TOC) (HACH IL550 TOC-TN, US) concentration was determined in selected samples. BAC separation efficiency was assessed basing on the retention coefficient:

Table 2
Characteristics of the modules

Module	Material	MWCO, kDa	Salt retention, %	Mean pore size, nm	Hydrophilicity (1 is low 5 is high)
			UF		
ESP04	Modified PES	4	–	–	2
			NF		
AFC30	PA	0.2[21]	75% $CaCl_2$	0.6 ± 0.1[22]	4
AFC40		0.3[23]	60% $CaCl_2$	0.48 ± 0.069[24]	
AFC80		<0.2[25]	80% NaCl	0.262–0.315[26]	

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

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

Besides the separation properties, membrane permeability expressed as a volumetric flux is an important parameter for the membrane process performance evaluation. Volumetric flux was calculated according to the following equation:

$$J = \frac{V}{A \times t}, \frac{L}{\mathrm{m}^2 0} \tag{2}$$

where J is the permeate volume flux (L/m^{2}h); 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:

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

where RF is the normalized flux; J is the permeate volume flux after time t; J_0 is the distilled water permeate flux (L/m^{2}h).

During the membrane filtration, the permeability deterioration due to the changes in membrane total resistance may occur. The resistance depends on the membrane parameters (material, pore size) and feed solution composition [27,28]. In this paper, the approach of the Hagen–Poiseuille equation was used for the membrane resistance calculation. For filtration of distilled water, the below equation was employed:

$$J = \frac{\Delta P}{\mu R_{\mathrm{mem}}}, \frac{\mathrm{m}^3}{\mathrm{m}^2 h} \tag{4}$$

where ΔP is transmembrane pressure (TMP, Pa), μ is dynamic viscosity coefficient (Pa s) and R is membrane resistance (m^{-1}).

To describe the filtration of solutions containing organic compounds, the modified Hagen–Poiseuille equation was used:

$$J = \frac{\Delta P}{\mu (R_{\mathrm{mem}} + R_f + R_{\mathrm{cp}})}, \frac{\mathrm{m}^3}{\mathrm{m}^2 h} \tag{5}$$

where R_f is membrane resistance resulting from fouling phenomena (m^{-1}) and R_{cp} is membrane resistance resulting from polarisation concentration layer (m^{-1}).

3. Results and discussion

Analysis of benzalkonium chloride parameters (CMC value and micelle size distribution) was conducted via DLS measurements. Fig. 1a shows the mean scattering intensity (kcps) vs. surfactant concentration in the test sample. Based on this dependence, CMC was determined as the intersection point of the approximated line function below and above the CMC. Calculated value amounted to 350 ± 5 mg/L. According to the data presented in Fig. 1b, BAC micelle size distribution was 11.8 ± 1.0 nm. Taking into account that surfactant micelle diameter is twice the length of the monomer, the length of single BAC monomer was about 6.4 nm.

In the first stage of the filtration experiments, membrane permeability under various values of the TMP was examined for distilled water. As can be seen from Fig. 2, the ultrafiltration membrane achieved much greater volumetric flux than nanofiltration membranes. AFC80 which has the smallest pores showed the worse permeability. Under the TMP of 0.3 MPa, distilled water flux amounted to 47.5, 15.8, 14.5 and 5 L/m^{2}h for ESP04, AFC30, AFC40 and AFC80 module, respectively. The calculated values of hydraulic resistance for the brand-new modules at the TMP of 0.3 MPa amounted to 1.88 × 10^{14}, 6.48 × 10^{14}, 5.96 × 10^{13} and 1,98 × 10^{14} 1/m for AFC80, AFC40, AFC30 and ESP04, respectively.

3.1. Purification

Averaged retention coefficients obtained during 120 min filtration cycles are plotted in Fig. 3. As can be seen, high retention coefficients of BAC, that is, 82% and 77% from solutions of concentration 50 and 100 mg/L were achieved with the use of ultrafiltration module. Shi et al. [29] indicated that cationic surfactant particles adsorb on the surface and inside the pores of ultrafiltration membranes due to the strong electrostatic interaction between positively charged monomers and the membrane. As a consequence, high surfactant retention from solutions of low concentrations (below the CMC) can be achieved with the use of UF membranes which pores are much greater in comparison with nanofiltration membranes. The large pores of UF

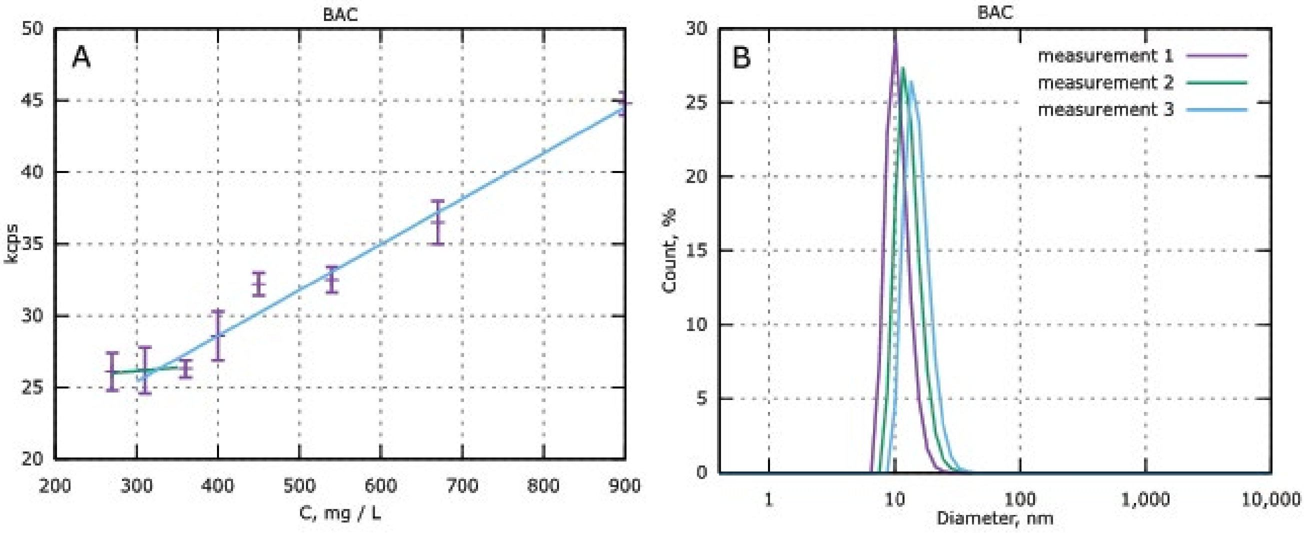


Fig. 1. (a) Mean scattering intensity (kcps) vs. BAC concentration, (b) BAC micelle size distribution.

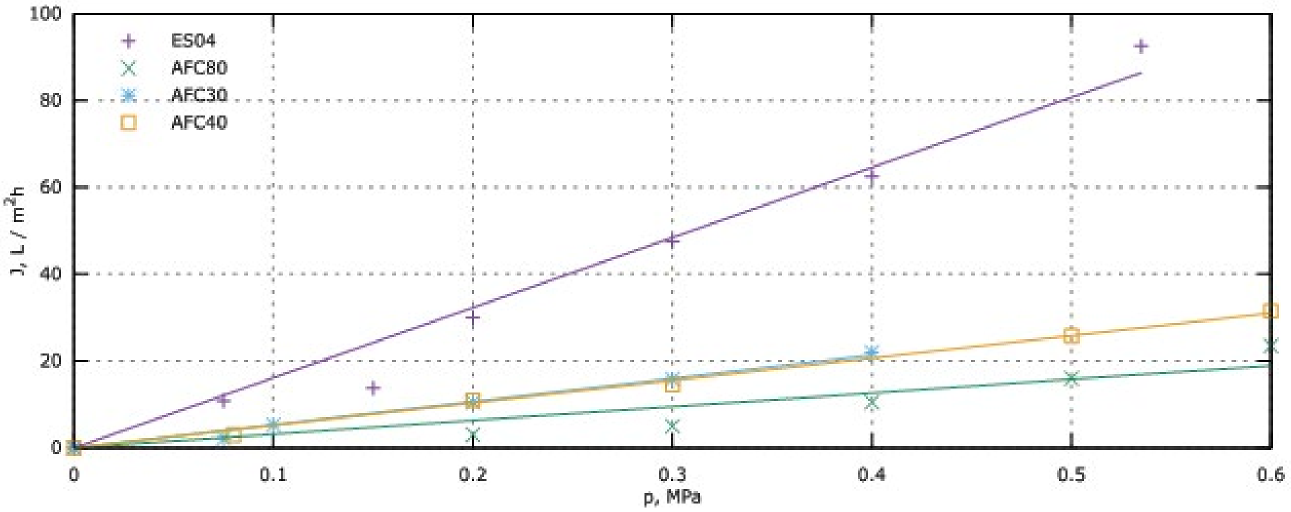


Fig. 2. Volumetric flux vs. transmembrane pressure for distilled water.

membranes contribute to the binding of a large amount of surfactant monomers, which is reflected in high retention coefficients for solutions below CMC.

However, for the solution of 1,000 mg BAC/L ESP04 module showed the worse separation from all tested modules – 59%. When NF modules were employed, retention coefficient increased to 67%, 74% and 77% for AFC30, AFC40 and AFC80, respectively. Good separation properties (retention coefficients in the range 74%–91%) in all range of the surfactant concentrations showed module AFC40, however a slight decrease in BAC removal with increasing its initial concentration can be observed. During all experimental studies complete removal of surfactants was impossible due to the BAC structure. Despite the fact that the molecular weight of the surfactant monomer exceeds the MWCO value of the NF membranes, its penetration through membrane is possible due to the structure of benzalkonium chloride particle which is long and slender. The same dependency in terms of surfactant particle size and membrane pore radius can be observed. Even if the monomer length (6.4 nm) is 10-fold greater than the mean pore size of membrane (ex. 0.6 nm, AFC30), its permeation occurs. It should be also noted that BAC monomers in water solutions differ in alkyl chain lengths and as a result in molecular weights. The literature reports the major share of BAC_{12} and BAC_{14} homologs in BAC products [30]. Diversified particle size should be considered as one of the factors affecting BAC separation in membrane processes.

Fig. 4 presents BAC concentration in the permeate streams measured during 120-min membrane process. Tested modules exhibited worsening in the permeate quality (increase in contaminant content) over the filtration cycle, however module AFC80 achieved the most stable BAC concentration – for example. for solutions of initial

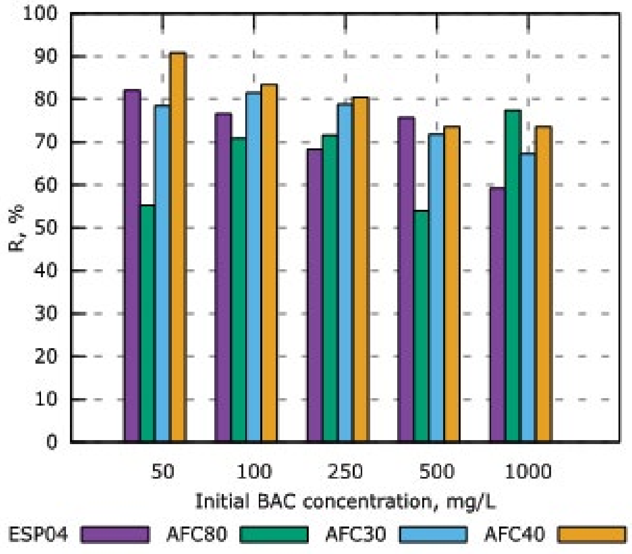


Fig. 3. Averaged retention coefficients vs. initial BAC concentration (TMP = 0.3 MPa, linear flow velocity 0.6–0.8 m/s).

surfactant concentration of 50 and 500 mg/L, after 30 min from the process run, BAC concentration in the permeate was in steady-state and amounted to about 23 mg/L for the feed solution of 50 mg/L and about 250 mg/L for the feed of 500 mg/L. Such course of the experiments indicates a share of mechanism of surfactant particles adsorption within membrane pores. Establishing the constant quality of the permeate (proceeded by increasing in contaminant concentration in the permeate) was due to membrane adsorption capacity exhaustion and further contribution of a sieve mechanism in surfactant separation on the membrane. AFC80 module has the lowest pore sizes in comparison with the other modules, thus its adsorption capacity is significantly smaller than that of the modules characterized by the greater pore diameters.

It should be stressed that for the highly concentrated solutions (exceeding CMC) no significant enhancement in BAC removal was seen. Even for surfactant solutions of concentration exceeds CMC value, significant number of monomers, dimers or trimers still exist in treated medium and can easily pass through the membrane. According to the literature data [31], application of UF module was associated with the worse separation comparing with the NF modules – for the solution of the initial surfactant concentration equal to 1,000 mg/L, after 60 min of the filtration, permeate from ESP04 contained approximately twice as much of surfactant (493 mg/L) than that obtained from AFC80 module (277 mg/L). Generally, results indicate that only for the low BAC concentration, modules achieved satisfactory surfactant separation (especially AFC40). In all experiments, application of a single membrane process is not sufficient for complete purification.

Table 3 shows the TOC concentration in the permeate samples collected during the membrane filtration with the use of ESP04 module. Comparing the TOC values with the concentrations measured by the spectrophotometric method, the linear correlation between the parameters was determined. Based on equation shown in Fig. 5, the TOC content in other BAC samples may be calculated with high accuracy ($R^2 = 97.9\%$).

Averaged values of the normalized flux obtained in the 120 min experiments are shown in Fig. 6. A general trend of deterioration of the module permeability can be observed with the increase of the initial concentration of the surfactant. Particularly the filtration of the highly concentrated solution (1,000 mg/L) resulted in achievement of averaged fluxes at very low levels, that is, 0.04, 0.29, 0.35, 0.54 for ESP04, AFC30, AFC40 and AFC80, respectively. Generally, the AFC80 module due to the small pore sizes proved to be the most fouling resistant one from all of the tested modules – the biggest drop in the permeability noted for BAC concentration of 1,000 mg/L did not exceeded 50%.

The course of normalized flux over the membrane filtration for monomeric and micellar solutions is plotted in Fig. 7. As can be observed, the presence of a highly concentrated BAC solution drastically reduced ESP04 module permeability. After the first 15 min of the filtration test, module achieved only 10% of its initial permeability. Continuation of the membrane filtration brought a 96% drop in flux. As a result of modules blocking, their hydraulic resistance increased significantly – after 120 min of 1,000 mg BAC/L solution filtration, ESP04 resistance growth to the value of 1.47×10^{14}. Resistance of remaining modules (under the TMP of 0.3 MPa) amounted to 2.94×10^{14} (AFC40), 5.6×10^{14} (AFC30) and 6.17×10^{14} 1/m.

The aforementioned BAC adsorption into the membrane pores plays a crucial role in the fouling phenomena course. Due to the opposite charges of the surfactant molecules (+) and the membrane surface (–), the attraction of contaminant to the membrane' skin layer is intensive. Benzalkonium chloride solutions are positively charged due to cationic character of the surfactant. White et al. [32] reported zeta potential of cationic surfactant hexadecyltrimethylammonium bromide (CMC = 350 mg/L, quaternary ammonium compound, concentration 30xCMC) solution equal to +61.5 mV. The isoelectric point (pzc), defined as the pH for which the net charge of the membrane is equal to zero, for PES and PA is located around 3 [33,34]. Hence, at the pH range of the tested solutions (6.5–7.5), both types of the polymers were negatively charged. Boussu et al. [35] reported zeta potential equal to –19 and –12 mV (tests at the pH 7) for membranes made of PA and PES, respectively.

It may be stated that differences in susceptibility to blocking of the tested modules result from their pore sizes (the greater the pore sizes, the more particles can bind inside the pores) and diversified hydrophilic properties. According to the producer data, the hydrophilicity of PES membrane is lower than that of PA ones. As a consequence, surfactant particles orientation at the membrane's active layer may be different – when the top layer is strongly hydrophilic (e.g., PA), hydrophilic heads of the cationic surfactants are located near the hydrophilic surface, filling it one by one in very close distances between each other (Fig. 8a). As a result, membrane surface becomes more hydrophobic. When the membrane polymer is more hydrophobic (PES), surfactant particles may arrange alternately (Fig. 8b), increasing the hydrophilicity of the surface [17].

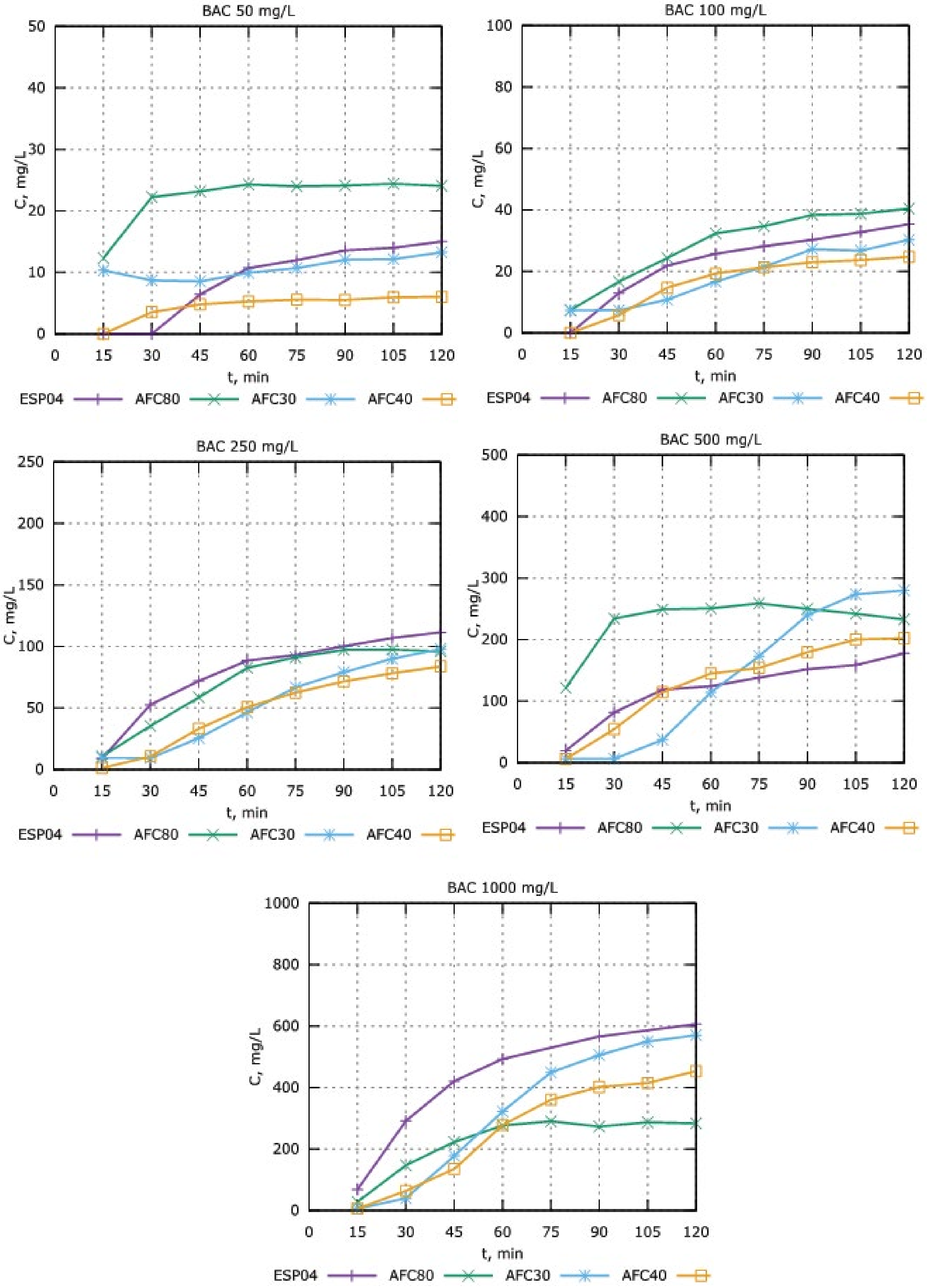


Fig. 4. BAC concentration in the permeate vs. filtration time (TMP = 0.3 MPa, linear flow velocity 0.6–0.8 m/s).

Table 3
TOC concentration (mg/L) in the permeate vs. filtration time (ESP04 module, process parameters: TMP = 0.3 MPa, linear flow velocity 0.6 m/s)

Time,	Initial BAC concentration, mg/L				
min	50	100	250	500	1,000
30	4.98 ± 0.09	16.76 ± 0.16	35.44 ± 0.46	37.02 ± 0.36	228.66 ± 0.13
60	12.47 ± 0.08	25.92 ± 0.15	38.88 ± 0.23	127.70 ± 2.70	336.66 ± 0.69
90	16.23 ± 0.09	25.34 ± 0.13	58.14 ± 0.81	110.20 ± 0.33	384.66 ± 1.19
120	15.20 ± 0.01	15.20 ± 0.04	52.71 ± 0.94	115.60 ± 0.12	–

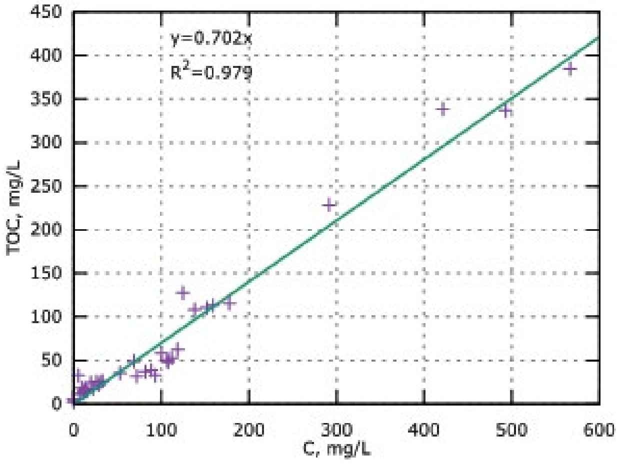


Fig. 5. TOC concentration vs. concentration obtained from spectrophotometric measurements.

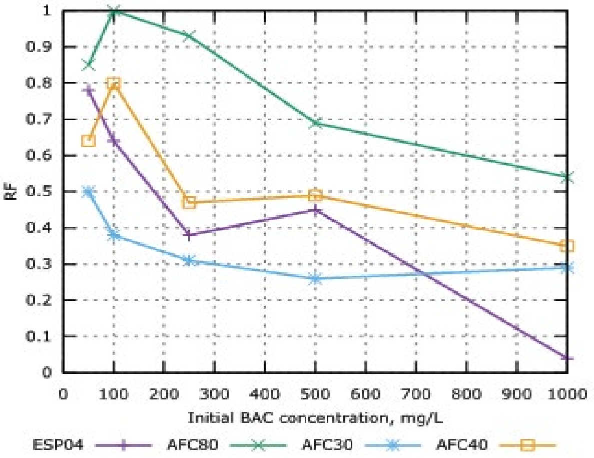


Fig. 6. Relative flux vs. initial BAC concentration (TMP = 0.3 MPa, linear flow velocity 0.6–0.8 m/s).

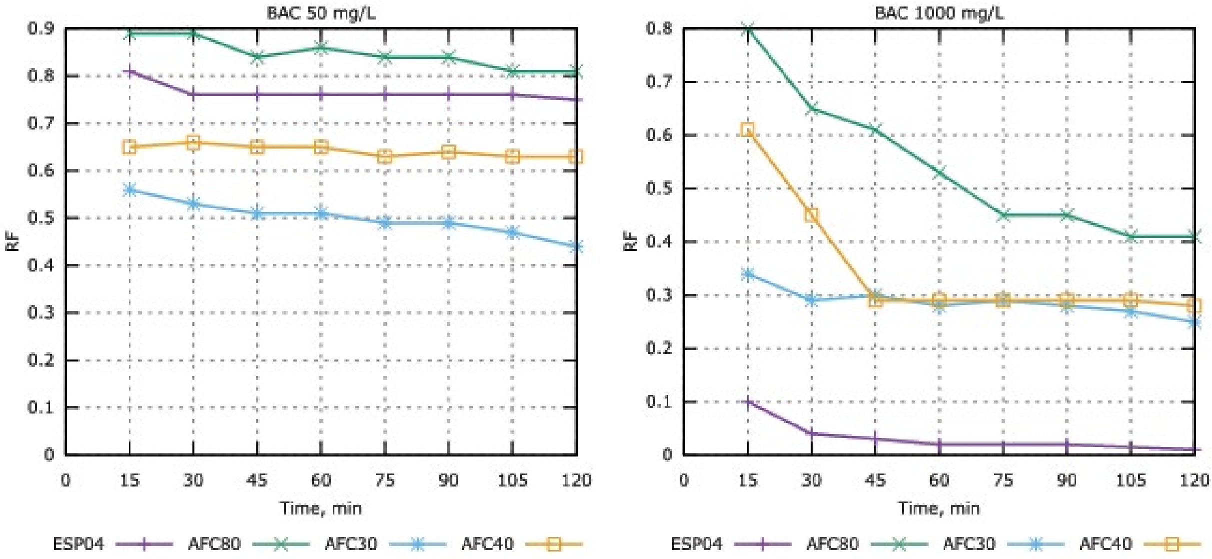


Fig. 7. Relative flux vs. filtration time (TMP = 0.3 MPa, linear flow velocity 0.6–0.8 m/s).

3.2. Modification of the process parameters

In order to limit the fouling phenomena, changes in the process parameters (e.g., linear flow velocity or TMP) may be introduced. The tests were performed for AFC40 module and the initial BAC concentration of 250 mg/L. The first part was performed under the constant linear velocity of 0.7 m/s and at the TMP of 0.15, 0.25, 0.35 and 0.45 MPa. 120-min filtration cycle was performed under the TMP of 0.15 MPa, then TMP value was increased to 0.25 and next

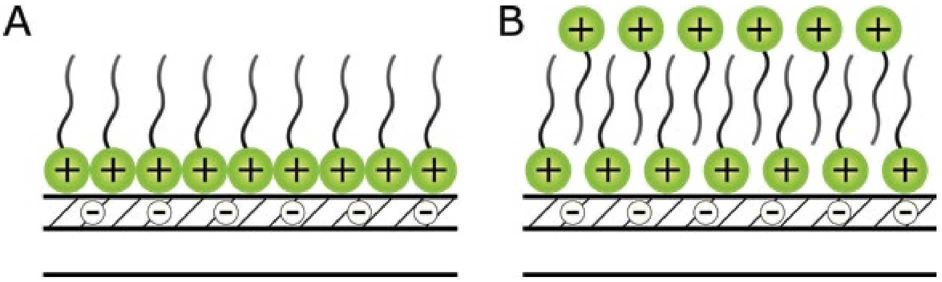


Fig. 8. BAC orientation at the membrane top layer: (a) hydrophilic membrane polymer; (b) hydrophobic membrane polymer.

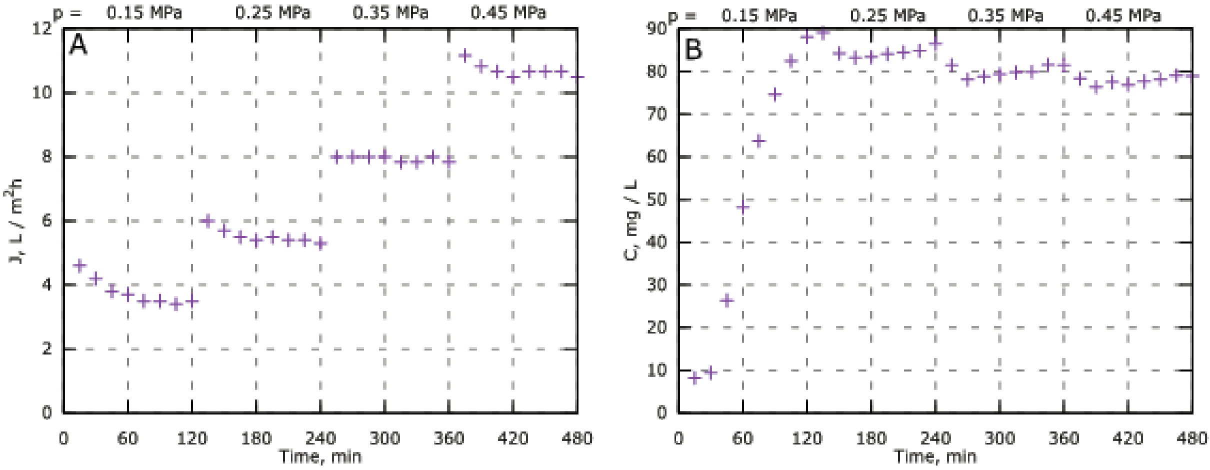


Fig. 9. Volumetric flux (a) and BAC concentration in the permeate (b) vs. filtration time and TMP (AFC40 module; initial BAC concentration 250 mg/L, linear velocity 0.6 m/s).

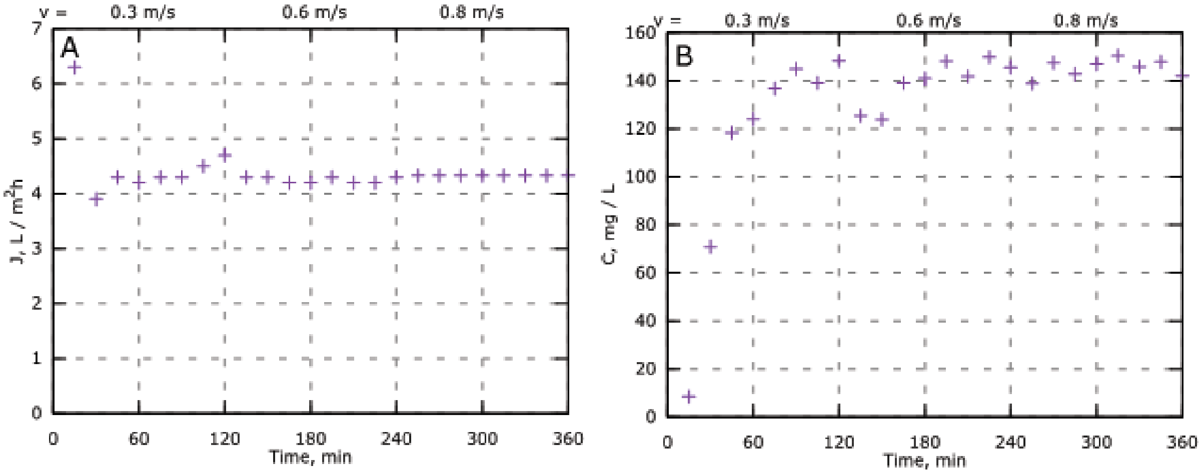


Fig. 10. Volumetric flux (a) and BAC concentration in the permeate (b) vs. filtration time and linear flow velocity (AFC40 module; initial BAC concentration 250 mg/L, TMP = 0.3 MPa).

120-min cycle was conducted. The same procedure was repeated till the last value of the TMP. During this part of the tests, surfactant concentration in the permeate as well as volumetric flux was monitored each 15 min. Fig. 9a presents volumetric flux achieved by AFC40 module depending on filtration time and TMP. It can be observed a temporary increase in permeate volume noticed during the first 15 min of filtration after increasing value of TMP. However, comparing data obtained for volumetric fluxes examined for the brand new module and distilled water (Fig. 2) it was noted that permeability decreased from 7.8 to ~3.8; from 12.9 to ~5.5; from 18.1 to ~7.9 and from 23.3 to ~10.7 L/m^{2}h in the presence of BAC for TMPs of 0.15, 0.25, 0.35 and 0.45 MPa, respectively. Calculated normalized flux values (0.49, 0.43, 0.44, 0.46) are similar and indicate that the change in TMP during the membrane filtration has no significant impact on permeability of the membrane. BAC concentration in the permeate is shown in Fig. 9b. During the first 105 min of the experiment, surfactant concentration was growing and stabilized after 120 min, achieving the value of about 80 mg/L. The data obtained corresponds to the previous part of the tests (Fig. 4). After exhausting the adsorption capacity, membrane separates the BAC particles due to the sieve mechanism. Further increasing in TMP brought a slight improvement in the permeate quality – the lowest BAC concentration amounting 76.4 mg/L was noted for the TMP of 0.45 MPa.

The second part involved experiments under the TMP of 0.3 MPa and variable linear flow velocity (0.3, 0.6 and 0.8 m/s). Analysis of the results (Fig. 10) indicates that lowering of the permeate flux occurred at the very beginning of the filtration and further increase in linear velocity did not bring any change in membrane permeability. After 15 min of the filtration, volumetric flux was in the range from 3.9 to 4.6 L/m^{2}h – averaged normalized flux amounted to 0.3. Moreover, at the low value of linear flow velocity, the drop in module selectivity resulted in the increase in BAC concentration in the permeate (comparing with the data obtained for v = 0.7 m/s) was noted. After linear velocity change to the higher values, the same separation ratios were still noted.

4. Summary

Membrane-based processes may find application in cationic surfactants removal from wastewater; however, several issues have been identified:

- Initial surfactant concentration affects the hydraulic efficiency of the membranes – the higher surfactant content, the more pronounced fouling phenomenon.
- Membrane permeability deterioration over the filtration process occurred for all tested modules and surfactant concentrations. The adsorption of surfactant monomers inside the membrane pores and hydrophilic interaction between the top layer of the membrane and surfactant particles play an important role in the fouling intensity.
- Modifications in operating parameters did not enhance the efficiency of membrane filtration. The performance was established at the initial stage of the process and further changes in TMP and linear flow velocity did not affect the separation and hydraulic properties of the membrane.
- The distinct correlation between two methods (TOC measurements and spectrophotometric methods) was found in terms of benzalkonium chloride concentration determination.

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