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Sequential process: membrane filtration and ion exchange as an effective method for water solution purification containing cationic surfactants

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ABSTRACT

Combination of the membrane process and ion exchange for the removal of cationic surfactants was investigated. Model solutions containing cetrimonium bromide (CTAB) and benzalkonium chloride (BAC) were treated. Polymeric nanofiltration and ultrafiltration modules were employed for the experiments. Ion-exchange tests were conducted in a batch mode with the use of two strongly acidic cation-exchange resins (C150H and Marathon 1200 Na). Tested solutions were characterized by a concentration range of surfactants below (50 mg/L), around (250 mg/L), and above (1,000 mg/L) the critical micelle concentration (CMC). In a sequential treatment, the permeate obtained over the membrane filtration cycle was directed to the ion exchange reactors. It was proved that the single purification process may not be sufficient in terms of both surfactant removal (in membrane processes due to the penetration of surfactant monomers into the permeate side) or economic aspects (in ion exchange due to a large amount of resin used). However, in the sequential purification system, both BAC and CTAB was removed with 100% efficiency from the solutions of initial concentrations below and around the CMC with the use of ultrafiltration and ion exchange. For highly concentrated BAC solutions, the best efficiency was seen when combining the ultrafiltration module and C150H resin (90% removal). In experiments with CTAB, for an initial surfactant concentration of 1,000 mg/L, the use of the ultrafiltration process, followed by ion exchange, allowed 99.6% of the surfactant to be removed.

Keywords: Pressure-driven membrane process; Surface active agent; Ultrafiltration; Nanofiltration; Ion-exchange resin

1. Introduction

In the 21st century, the problem of drinking water shortages has increased due to population growth and progressive urbanization and industrialization. In the last few years, Poland has faced the threat of a water crisis due to the drying up of rivers, which can be associated with climate change. Finding opportunities to acquire new water sources or save them for industrial purposes is nowadays a challenge for environmental engineers.

Surface active agents (surfactants) are applied in thousands of commercial products (e.g., personal care products, agricultural products, and cleaning agents), and their annual production is growing due to an increase in consumption. The global demand for surfactants in cosmetics and personal care products is likely to witness the fastest compound annual growth rate (CAGR) from 2019 to 2025 of 5.8%; and the global market for the main application of surfactants (soaps, detergents, and cleaners) is expected to reach US$14.4 billion by 2025 [1].

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Surfactants are classified into four groups: anionic, cationic, non-ionic, and zwitterionic, according to the charge of their hydrophilic group. Quaternary ammonium salts such as benzalkonium chloride (BAC) and cetrimonium bromide (CTAB) are the main and most abundant group of cationic surfactants. On an industrial level, cationic surfactants have found an application in oil recovery [2], bactericidal effects [3], and sugar decolorization [4]. These compounds are also constituents of personal care products. Cationic surfactants are commonly used as fabric softeners and are even used in the manufacture of fiberglass for sailboats [5,6]. There are also reports that the CTAB surfactant can be used as a component of the buffer for DNA extraction [7].

Biodegradation of cationic surfactants by bacteria tends to be poor – it takes longer than months, or even years. Biodegradation efficiency is also much lower when compared to other surfactants, according to the ranking: anionic surfactants > non-ionic surfactants > cationic surfactants [8]. Cationic surfactants persist in the aquatic environment and cause damage to aquatic species [9]. They foam in rivers, causing the eutrophication of reservoirs [10]. Polish legal regulations regarding the maximum allowable concentration of surfactants in industrial wastewater discharged into sewage systems give the permissible value of 15 and 20 mg/L for anionic and non-ionic surfactants, respectively [11]. It should be stressed that the permissible value was not given for cationic surfactants.

Due to the physico-chemical properties of cationic surfactants and their effect on the solvents in which they occur, the use of a single purification method may not be sufficient for their effective removal from effluents. Recent studies have established that the application of coagulation and flocculation [12], foaming [13], photocatalytic oxidation [14], and sorption [15] can reduce the concentration of surfactants in water solutions. The adsorption process also proved to be useful in fulfilling this purpose [16,17]. The ionic nature of surfactants has caused an interest in the process of ion exchange (IE) in the context of their removal from aqueous solutions [18,19]. According to Schuricht et al. [20], ion-exchange resins may be more effective in removing surfactants than conventional adsorbents. Ion exchange and hydrophobic interaction were found to be involved in the sorption processes on resins, while for activated carbon, surfactant removal was only due to physisorptively bounding on activated carbons. Nonetheless, it is impossible to recover the valuable surfactants in the techniques mentioned above. That possibility can be provided by using membrane-based treatment methods, that is, pressure-driven membrane processes. The literature data confirm the usefulness of this group of processes for surfactant removal from wastewater. Fernández et al. [21] reported the removal of anionic (SDS) and non-ionic (tergitol NP-9) surfactants in the range of 60%–70% using the ultrafiltration (UF) ceramic membrane Membralox®. Guilbaud et al. [22] investigated the possibility of laundry water recycling by direct nanofiltration (NF) with the use of the tubular polymeric membranes AFC30, AFC40, and AFC80 (PCI filtration group). The processes were conducted at 35 bar and 25°C and the treated laundry solutions were characterized by a chemical oxygen demand (COD) value of 1,340 mg/L. The authors reported a very high COD recovery rate – around 98.0% for AFC30 and AFC40, and 99.7% for the AFC80 membrane. The concentration of the COD in the permeate amounted to 134, 116, and below 25 mg/L for AFC30, AFC40, and AFC80, respectively. Wendler et al. [23] modeled anionic surfactant sodium dodecylether sulfate (SDES) removal with the use of a spiral-wound NF module (D5K by Osmonics, material PA/PPA on polyester). The published data described a SDES retention exceeding 99.9%. The combination of the membrane processes with conventional methods is increasingly being employed in surfactant-contaminated wastewater treatment. In recent years, the purification of laundry wastewater or graywater has seen a particularly high amount of interest [24,25]. Nascimento et al. [12] reported the efficiency of methylene blue active substances (MBAS) surfactant removal with the use of a microfiltration membrane (hollow fiber, material poly(imide), and pore diameter 0.4 μm) at the level of 12%. When integrated technology involving coagulation, flocculation, sedimentation, and microfiltration was applied, the removal efficiency increased up to 70%. In the same article, UF (hollow fiber, material polyethersulfone, and MWCO 50 kDa) and MF (hollow fiber, material poly(imide), and pore diameter 0.4 μm) membranes were compared in terms of surfactant removal from laundry wastewater containing 9.5 mg/L of surfactants. The authors reported retention coefficients in the range from 6% to 9% for the MF module, and from 28% to 36% for the UF module, depending on the TMP value (0.6, 1, and 1.4 bars).

In this paper, we investigated the effectiveness of the membrane process and ion exchange, which worked as unit purification processes for the removal of cationic surfactants. These techniques were then combined into a sequential purification system.

2. Material and methods

2.1. Chemicals

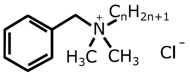
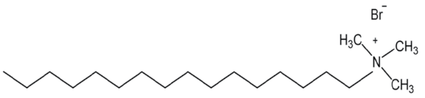
Quaternary ammonium-type cationic surfactants: BAC and CTAB were selected for the experiments. The physical properties of the surfactants (critical micelle concentration and micelle size distribution) were determined via dynamic light scattering (DLS, Malvern Zetasizer nano ZS, wavelength 532 nm, UK). A summary of the characteristics of the surfactants is presented in Table 1.

The surfactant concentration in the model solutions amounted to 50, 250, and 1,000 mg/L, which, in relation to the CMCs, indicates that the solutions differed in terms of the form of the prevalent surfactants (monomer or micellar). During the tests, the concentration of the surfactants in the samples was measured by means of spectrophotometric measurements (at wavelength of 215 nm) and potentiometric titration (785 DMP Titrino, Metrohm, Switzerland) for the BAC and CTAB solutions, respectively.

2.2. Membrane process

The scheme of the laboratory set-up is presented in Fig. 1. The surfactant solutions (initial concentrations of 50, 250, and 1,000 mg/L) were first purified by membrane filtration in a 180 min cycle. The cross-flow semi-pilot filtration set

Table 1
Characteristics of the surfactants

Name	Benzalkonium chloride (BAC)	Hexadecyltrimethylammonium bromide (CTAB)
Molecular weight, g/mol	283.80–423.97	364.5
Type	Cationic	Cationic
Purity, %	80	96
Carbon atoms in chain	8–18	19
Structural formula	 n=8,10,12,14,16,18	
Critical micelle concentration (CMC), mg/L	350 ± 5	368.7 ± 131.4
Micelle size distribution, nm	11.8 ± 1.0	6.5 ± 0.5
Water solubility	Soluble in water in all proportions	100 mg/mL

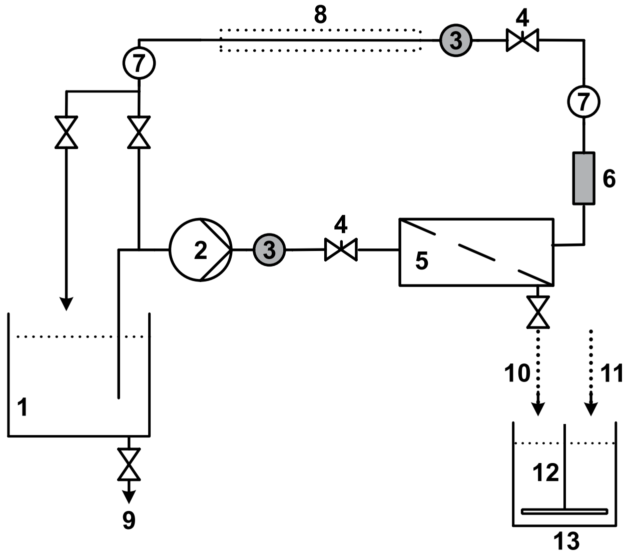


Fig. 1. Schematic diagram of the laboratory set-up: (1) feeding tank, (2) circulation pump (Grundfos, Denmark), (3) manometer, (4) pressure regulation valve, (5) membrane module, (6) rotameter, (7) thermometer, (8) cooler, (9) drain valve, (10) permeate, (11) ion-exchange resin, (12) stirrer, and (13) ion-exchange reactor.

up, purchased from J.A.M. INOX (Poland) and equipped with a membrane module (consisting of two polymeric membranes), a 10 L volume feed tank, a circulation pump (Grundfos, Denmark), and a cooling system, was set in a continuous batch concentration mode. One ultrafiltration (UF) and one nanofiltration (NF) module (PCI Filtration group, UK) made of modified polyethersulfone and polyamide were examined (Table 2). The effective surface area of the module was 0.024 m^2 and the initial volume of the feed amounted to 8 L. The tests were performed under the transmembrane pressure of 3 bar and at the cross-flow velocity of approximately 0.6 m/s. During the filtration processes, the permeate samples were collected in intervals of 30 min for the surfactant concentration measurements. The volumetric flux of the permeate was monitored during the process and calculated according to the following formula:

$$J = \frac{V}{A \cdot t}, \quad \frac{\text{L}}{\text{m}^2\text{h}} \tag{1}$$

where V is the volume of the collected permeate sample, L; t is the time, h; and A is the effective membrane surface area, m^2.

Additionally, to evaluate the intensity of surfactant fouling, the relative flux was calculated:

$$\text{RF} = \frac{J}{J_0}, - \tag{2}$$

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

2.3. Ion exchange

Four cation exchange resins were used in the IE experiments (Table 3). Brand new resins C150H (Purolite, Poland), Dowex 88 (Dow Chemicals, US), and Marathon 1200 Na (Dow Chemicals, US) were regenerated with the use of 12% NaCl solution and soaked in distilled water until the regeneration agent vanished. A weakly-acidic C104 plus (Purolite, Poland) resin was applied in hydrogen form.

The initial experiment involved determination of the resins' maximum exchange capacity ($q_{\max}$) values. For evaluation of this parameter, a constant dose of the resins (1 mL) was added to the reactors (250 mL), which contained surfactant solutions in a wide range of concentrations (50–1,000 mg/L). After 24 h of mixing (Heidolph Unimax 1010 shaker, 200 rpm, Germany), the concentration of the surfactants was determined. For the ion exchange discussion, a classical approach of the linear-form of the Langmuir model was analyzed in this paper:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{3}$$

where q_e (mg/mL) is the equilibrium amount of surfactant exchanged on a resin volume of 1 mL, calculated from the following equation:

Table 2
Characteristics of the modules

Module	ESP04 (UF)	AFC40 (NF)
Material	Modified PES	PA
MWCO, kDa	4	0.3 [26]
Salt retention	–	60% $CaCl_2$
Mean pore size, nm	–	0.48 ± 0.069 [27]
Distilled water flux (at 3 bar), LMH	47.5	14.5
Hydrophilicity (1 is low 5 is high)	2	4

Table 3
Characteristics of cation exchange resins

Resin	Type	Structure	Functional group	Grain size, μm	Exchange capacity*, eq/L
C150H	Strongly acidic	Polystyrene-DVB, macroporous	Sulfonate	600–850	1.7
Dowex 88	Strongly acidic	Styrene-DVB, macroporous	Sulfonate	300–1,200	1.8
Marathon 1200 Na	Strongly acidic	Styrene-DVB, gel	Sulfonate	535–635	≥2.0
C104 plus	weakly acidic	Polyacrylic crosslinked with DVB, gel	Carboxylic	300–1,200	4.2

$$q_e = \left(C_i - C_e\right)\frac{V}{V_J} \quad (4)$$

where C_i (mg/L) is the initial surfactant concentration, C_e (mg/L) is the equilibrium surfactant concentration, V (L) is the solution volume, V_J (mL) is the resin volume, $q_{\max}$ (mg/mL) is the maximum uptake of surfactant exchanged on a resin volume of 1 mL, K_L (L/mg) is the Langmuir constant.

Based on the data obtained in the first step of the tests, two resins were selected for the subsequent parts of the study, which was the ion exchange process in a batch mode. The tests were carried out in 2 L reactors, containing 1 L of the surfactant solution (50, 250, and 1,000 mg/L), and charged with the resins in doses of 2.5, 5, 10, and 20 mL. The reactors were placed on the Velp Scientifica FC6S flocculator and stirred at a rotational speed of 150 rpm, which ensured the uniform distribution of the resin within the entire volume of the solution. After pre-defined mixing periods (5–120 min), the samples were collected for measurements of the surfactant concentrations.

2.4. Sequential treatment: membrane process – ion exchange

Permeates collected after 180 min of the membrane filtration were then directed into ion exchange reactors. The ion exchange purification was carried out after 40 min, with the dose of resin equal to 5 mL/L. In this part of the test, two resins (C150H, Marathon 1200 Na) were used, selected on the basis of the preliminary experiments. In order to verify the effectiveness of the purification of the solutions, the removal ratio was calculated:

$$R = \frac{C_0 - C}{C_0} \cdot 100\% \quad (5)$$

where C_0 and C represent the initial and final values of the surfactant concentration (mg/L).

3. Results and discussion

3.1. Membrane test

Table 4 summarizes the results obtained in the single membrane processes. The averaged values of the concentration of the surfactants in the permeates collected during the 180 min membrane filtration cycle are contained in the table. As can be seen, the membrane processes reduced the surfactant concentration (by 55%–97% and 60%–96% for the BAC and CTAB, respectively), but not as much as one might expect when taking into account the molecular weight cut-off (MWCO), pore sizes of the membranes, and the dimensions of the particles being removed. The low values of the modules' relative permeability (Table 5, average value for the 180 min filtration cycle) indicate significant membrane fouling with surfactant particles. The higher the initial surfactant concentration, the greater the observed decline in permeability. For example, the UF module ESP04 showed an 80% drop in permeability (in comparison with the distilled water flux) for the solution of 1,000 mg/L. For the same module and the solution of 250 mg/L, a 40% and 50% drop in membrane permeability was noted for the BAC and CTAB solutions, respectively. The intensity of membrane fouling may be reduced by implementation of several actions, for example, by increasing the cross-flow velocity or application of strongly hydrophilic membranes.

As described in detail in our previous studies [28,29], the separation of cationic surfactants using polymer modules, as well as the course of membrane fouling, can be attributed to the following phenomena:

- hydrophilic interaction between surfactant particles and the surface of membranes;

Table 4
Summary results: surfactant concentration (mg/L) in the UF/NF permeate and after batch ion exchange

	Membrane process		Ion exchange							
	ESP04	AFC40	C150 H dose, mL/L				Marathon 1200 Na dose, mL/L			
			2.5	5	10	20	2.5	5	10	20
BAC										
Feed 50 mg/L	1	4	0	0	0	0	0	0	0	0
Feed 250 mg/L	40	95	107	34	0	0	120	69	0	0
Feed 1,000 mg/L	255	446	776	688	332	23	934	817	651	77
CTAB										
Feed 50 mg/L	7	8	4	0	0	0	2	0	0	0
Feed 250 mg/L	32	101	146	92	17	0	126	29	0	0
Feed 1,000 mg/L	44	150	838	764	612	246	828	719	456	31

- surfactant adsorption within the membrane structure due to the electrostatic attraction resulting from the potential difference between the membrane surface and the surfactant molecules;
- the creation of micelles and pre-micelles in the polarization layer near the membrane surface;
- the sieve mechanism.

At the end of the filtration cycle, the concentration of surfactant in the concentrate stream was determined. The final concentration in the feed tank amounted to 52, 245, and 954 mg/L, and 46, 233, and 824 mg/L for the BAC and CTAB, respectively, which indicated that the solution was not concentrated. For the AFC40 module, analogous results were obtained. Therefore, one may suspect the surfactant particles deposited in the membrane structure and installation components that confirm the thesis made.

The experiments showed that the membrane filtration was insufficient for surfactant separation from water solutions. Only in the case of the low concentrated solutions did the modules achieve good separation. It should be noted that the application of another NF module (even with lower MWCO value a higher density) may be purposeless due to the unsatisfactory permeability of those modules and the fact that penetration of the surfactant particles through the membrane occurs even when the membrane MWCO should theoretically provide a good separation. As the membrane filtration processes do not provide a total or satisfactory level of surfactant removal, the post-treatment step should be implemented.

3.2. Ion exchange – preliminary tests

Maximum exchange capacity values ($q_{\max}$, maximum uptake of surfactant macroions exchanged on a resin volume unit) were calculated based on the linear-form of the Langmuir model (Eqs. (1) and (2)) and the tangent of the slope angle of the curve $f(C_e) = C_e/q_e$ (Fig. 2). The maximum exchange capacity values are compared in Table 6.

As can be read from the obtained data, the ion exchange resins can be arranged from the highest to the lowest value of maximum exchange capacity ($q_{\max}$) as follows:

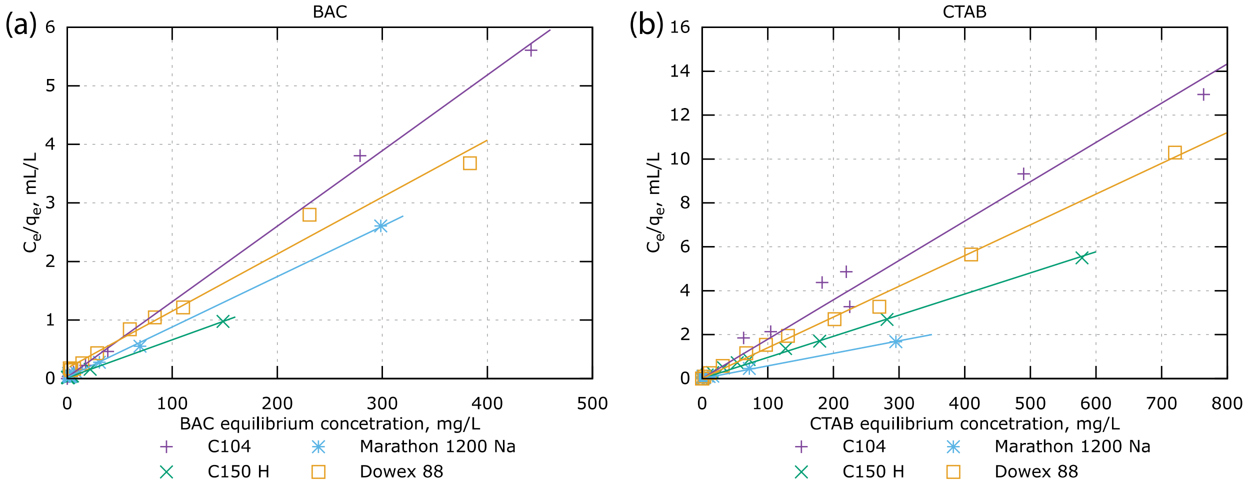


Fig. 2. Linear form of (a) BAC and (b) CTAB ion exchange isotherms.

Table 5
Relative permeability vs. initial surfactant concentration

Surfactants	BAC			CTAB		
Initial concentration, mg/L	50	250	1,000	50	250	1,000
Module UF ESP04	0.89	0.63	0.21	0.74	0.46	0.22
Module NF AFC40	0.65	0.28	0.18	0.73	0.39	0.47

C150H > Marathon 1200 > Dowex 88 > C104 plus; and Marathon 1200 Na > C150H > Dowex 88 > C104 plus for the BAC and CTAB, respectively. It was noted that the highest values were achieved for strongly acidic resins with similar and rather low grain sizes (600–850 µm for C150H and 535–635 µm for Marathon 1200 Na). The lower grain diameters result in the shortening of both the duration of the diffusive transport of the ion from the ionite grain surface to the exchange site, and the duration of the diffusive transport of the displaced ion to the grain surface.

Two types of resins can be ascribed due to the degree of polymer cross-linking: macroporous and gel. Macroporous resins have similar pores with diameters in the range of 20–200 nm, and are much larger when compared to the distance between adjacent hydrocarbon chains of gel-type materials (0.5–20 nm) [30]. Thus, due to the lower porosity of gel ion exchange resins, access to their active sites may be restricted. However, it can be observed that the strongly acidic gel resin Marathon 1200 Na achieved the highest value of CTAB exchange capacity, while – the strongly acidic macroporous resin C150H achieved the highest value of BAC exchange capacity. Taking into account the length of the surfactant monomer (approx. a half of the micelle diameter), which was 5.9 and 3.3 nm for the BAC and CTAB, respectively, it may be concluded that the gel resin is more effective for the macroions with a smaller particle size, that is, CTAB. For larger macroions, the macroporous structure of the resins is more accessible. Moreover, the exchange capacity values (given by the manufacturers) show that Marathon 1200 Na is able to exchange more ions than macroporous strongly acidic resins (C150H and Dowex 88). This may indicate that the Marathon 1200 Na resin has a larger number of functional groups than the other resins, which may explain the high value of $q_{\max}$ for the CTAB. Dowex 88 showed worse results than the previously mentioned strongly acidic resins, which may be explained by its large and heterogeneous grains. Due to the gel structure of the C104 resin, the access of monomers to the active sites may be restricted. This contributes to the lower selectivity of the weak acid cations and the lowest value of the $q_{\max}$ parameter in comparison with the other resins. One may also suspect that the value of $q_{\max}$ is affected not only by the "pure" ion exchange process, but also by the sorption between hydrophobic surfactant chains and polymer chains.

3.3. Ion exchange – batch experiments

According to the $q_{\max}$ values obtained in the preliminary tests, two of the resins (C150H and Marathon 1200 Na) were selected for the test with ion exchange in batch mode (applied as a single treatment method) and for integrated purification system involving membrane process as a first (main step) and ion exchange as a post-treatment process. The changes in the concentration of the surfactants in the 120 min processes are plotted in Fig. 3. In order to present the aggregation diversity of the surfactant particles, the results for the monomeric (50 mg/L) and micellar (1,000 mg/L) solutions were presented. As can be seen, an enhancement in process efficacy was noted along with mixing time and with an increase in resin dose. However, for the initial surfactant concentration equal to 50 mg/L, the almost total removal of the surfactants can be observed after the contact time of 60 min for all of the applied resin doses, not including Marathon 1200 Na in a dose of 2.5 mL/L. When focusing on the course of the ion-exchange curves for the highly concentrated solutions (1,000 mg/L), significant differences in surfactant removal can be seen for each resin dose. For both of the surfactants and resins tested, the quasi-linear courses of the curves are visible for the doses of 2.5, 5, and 10 mL/L; however, for the highest dose, the ion exchange takes a non-linear course and becomes more dynamic vs. contact time. This means that the equilibrium of ion exchange can be achieved faster for high doses of resin.

The concentrations of surfactants in the samples, taken after 120 min of the ion exchange process, are shown in Table 4. As can be seen, for the lowest initial concentrations (50 mg/L), every dose of tested resin provided total BAC removal. For CTAB, such a result was noted for doses equal to or above 5 mL/L. When the initial surfactant concentration increased to the value of 250 mg/L, resin doses of 10 and 20 mL/L allowed the BAC solution to be effectively purified. In the CTAB experiments, application of Marathon 1200 Na brought lower final concentrations when compared to C150H. It can generally be stated that the data obtained, which is compared in Table 6, corresponds to the preliminary tests. Marathon 1200 Na, due to a higher value of the $q_{\max}$ parameter, proved to be more suitable for CTAB removal when compared to C150H, and conversely – C150H characterized by a higher value of maximum exchange capacity value toward BAC, allowed to reduce its concentration to a greater extent. The use of the highest resin dose (20 mL/L) effectively removed the surfactant, even from a highly concentrated solution (1,000 mg/L) – 23 mg BAC/L for C150H and 31 mg CTAB/L for Marathon 1200 Na.

The results proved that the ion exchange process can be an effective alternative for the purification of surfactant solutions. However, the mixing time and the resin dose strongly affect the efficiency of the process. For the purification of solutions containing large amounts of surfactants, it is necessary to use a sufficiently high dose of resin and to ensure a sufficiently long contact time, which involves , mg/mL)

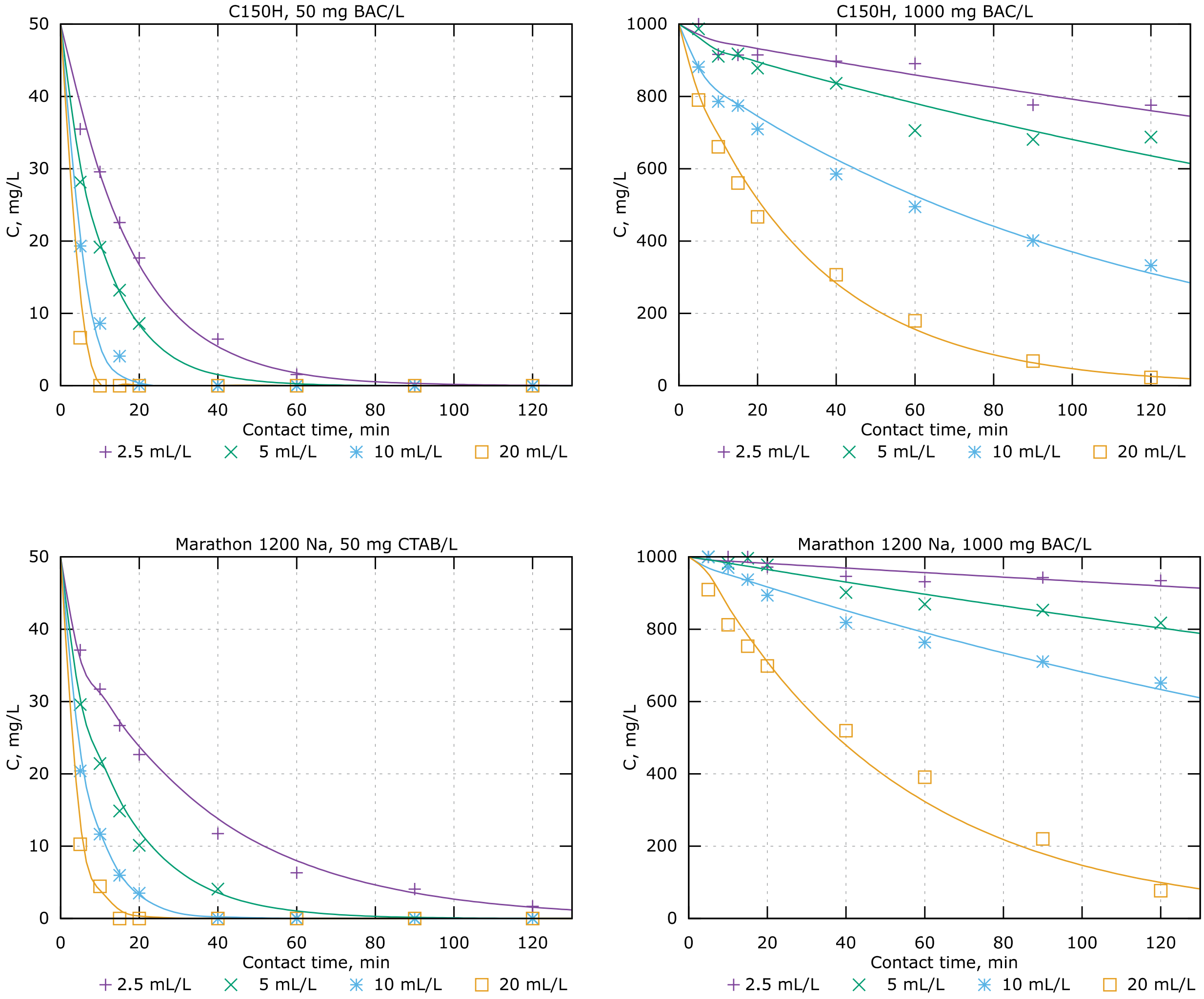


Fig. 3. Changes in surfactant concentration vs. contact time.

Table 6
Langmuir isotherms parameters (q_{max}, mg/mL) for BAC and CTAB ion exchange

Resin	BAC	CTAB
C150 H	153.8	107.5
Dowex 88	103.1	71.9
Marathon 1200 Na	116.3	178.6
C104	87.7	59.9

significant operating costs. Thus, in this paper ion exchange process is being proposed as a final purification step for surfactant solutions preceded by the membrane filtration.

3.4. Integrated purification system

An UF/NF – IE integrated system was investigated in terms of the removal of cationic surfactants. Membrane permeate was directed to the ion exchange reactors, where the resins were then dosed in an amount of 5 mL/L. The samples were then mixed for 40 min. Fig. 4 presents the results of the combined processes, expressed as the surfactant removal ratio. Integration of the UF module ESP04 and gel resin Marathon 1200 Na enabled complete CTAB removal (retention 99.6%–100%) in all ranges of the initial surfactant concentration. Moreover, for other CTAB experiments, the surfactant concentration was significantly reduced – retention exceeded 89%. Purification of the BAC solutions was very effective (100% removal) for both tested combinations when its initial concentration amounted to 50 and 250 mg/L. However, an increase in the initial BAC concentration to the value of 1,000 mg/L resulted in a visible disproportion in the effectiveness of the used processes. Combination of the ESP04 module with ion exchange allowed the BAC concentration to be reduced by approximately 90% (C150H) and 88% (Marathon 1200 Na). Moreover, when the AFC40 module was applied, the BAC concentration declined by only 74% (C150H) and 67% (Marathon 1200 Na). It should be stressed that poor BAC removal in the integrated process from highly concentrated solutions (1,000 mg/L) is

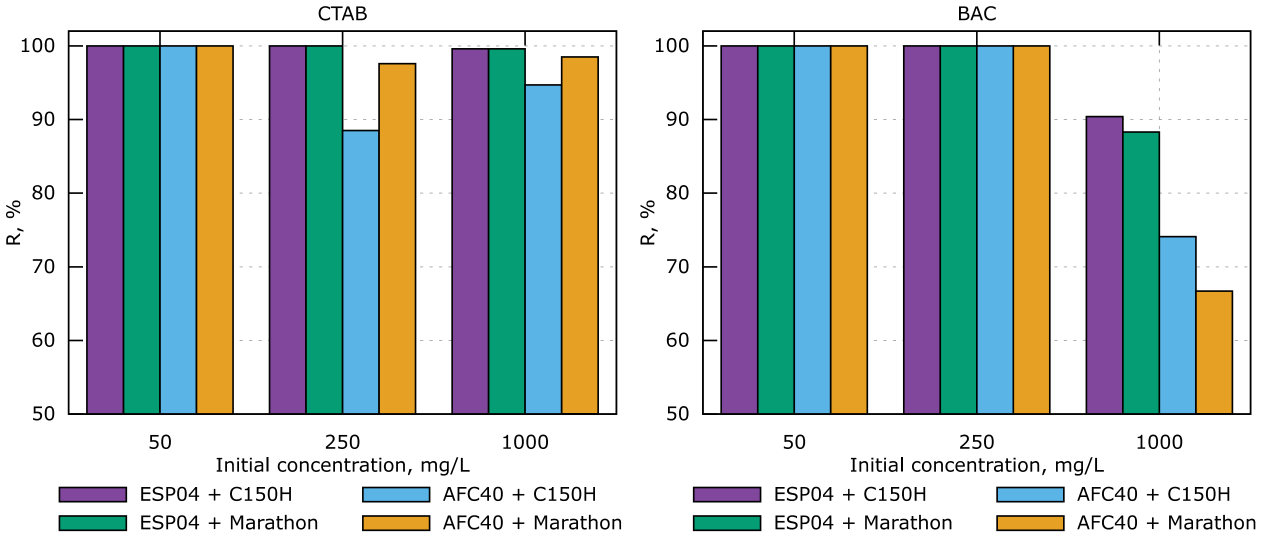


Fig. 4. Surfactants removal coefficients for integrated purification processes.

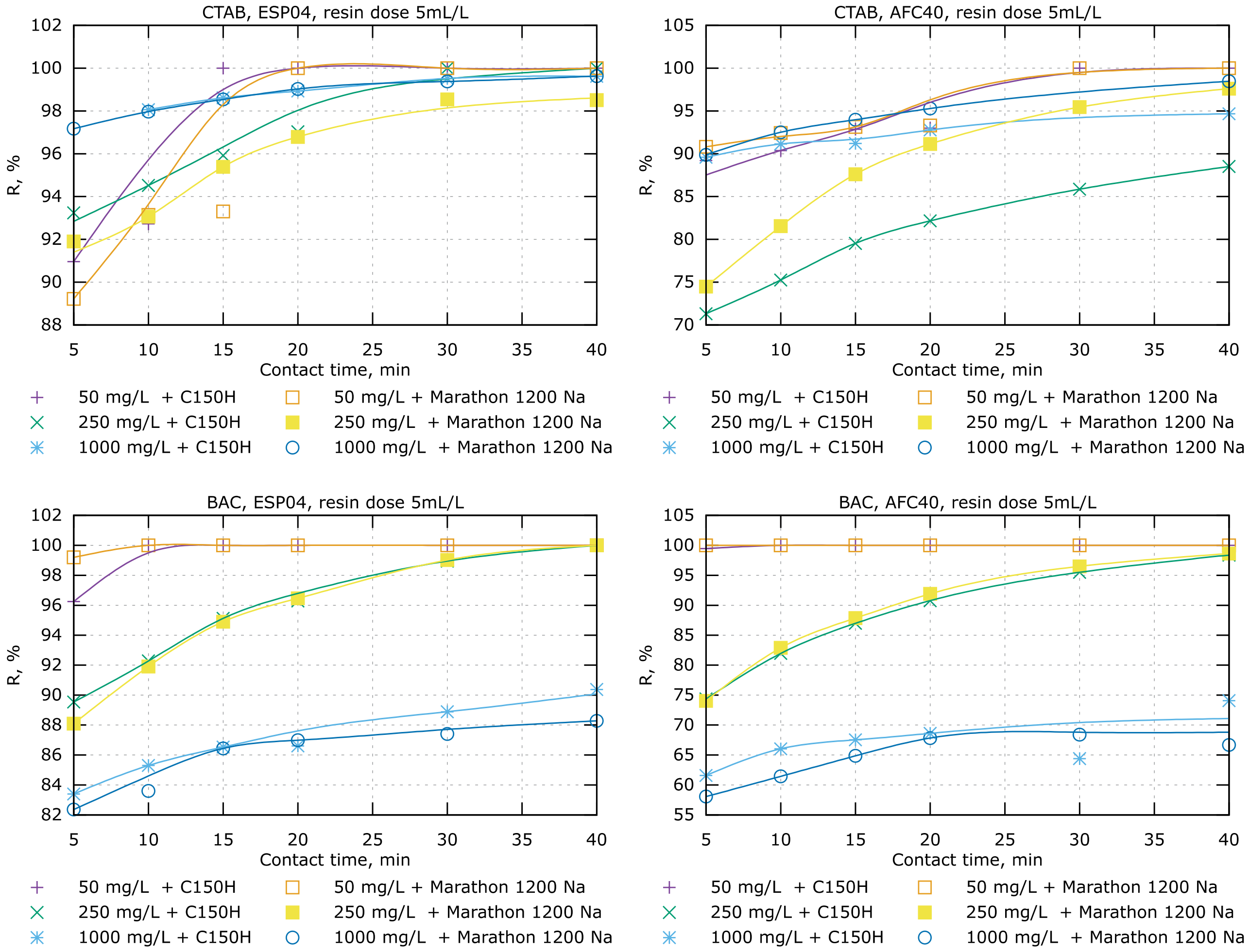


Fig. 5. Surfactant removal efficacy in a sequential UF/NF-IE system vs. mixing time.

mainly due to the low selectivity of the NF module, which in the first step of the purification retained only about 56% of BAC. Discussing the results in terms of legislative values (the same maximum permissible concentration was adopted as for anionic surfactants, i.e., 15 mg/L), in a large number of the variants performed, the final concentration of the surfactants was acceptable. In the CTAB experiments, only the combination of the AFC40 module with the C150H ion exchange resin resulted in the permissible concentration value (in the experiments with the feed solution containing 250 and 1,000 mg CTAB/L) being exceeded. The final BAC concentration did not comply with legal standards (i.e., 15 mg/L) for all solutions with the initial concentration equal to 1,000 mg/L.

Fig. 5 presents the efficiency of the sequential purification system (expressed as the removal ratio) determined by the mixing time. It can be noted that complementation of the membrane treatment by the ion exchange process significantly improved the quality of the solutions, especially for the CTAB ones. The process efficacy was better when there was a longer contact time. Due to the dynamic course of CTAB curves, one might expect that the extension of mixing time would bring an enhancement in surfactant removal.

4. Conclusions

The investigations confirm the potential of the proposed sequential purification technology for the separation of cationic surfactants from water solutions. The integration of two processes (the pressure-driven membrane process and ion exchange), working on different removal mechanisms, enabled the following:

- the removal of a significant amount (above 55%) of the surfactants in the first purification step;
- the enhancement of the quality of the permeate by adding the ion exchange resins – complete CTAB removal (retention 99.6%–100%) was achieved;
- the obtaining of a high-quality water stream that meets the legal requirements;
- the reduction of the consumption of ion exchange resins by dispensing smaller doses in comparison with the batch mode ion exchange.

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