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SECONDARY POLLUTION OF PERMEATE DURING MICELLAR ENHANCED ULTRAFILTRATION OF PHOSPHATE AND NITRATE SOLUTIONS

The pollution of permeate with surfactant during nutrients removal from aqueous solutions by micellar enhanced ultrafiltration (MEUF) was evaluated. The process was performed with the use of polyethersulfone (PES) and regenerated cellulose (RC) polymer membranes, as well as ceramic membranes that varied in terms of molecular weight cut-off (MWCO) values (1–50 kDa). Three cationic surfactants (cetyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC), octadecylamine acetate (ODA)) were chosen to bind nitrate or phosphate anions to surfactant micelles. The results of the study showed that the composition of the solution, membrane material, and membrane MWCO influenced the intensity of the secondary pollution of the permeate. The percentage of surfactant leakage from the feed to the permeate varied from 0.3 to 90.9% (CTAB), from 11.1 to 26.6% (ODA), and from 10.5 to 58.4% (CPC). The lowest intensity of the secondary pollution of MEUF permeates was observed when nitrate solutions were treated by CTAB surfactant and PES membranes were used. It was also proved that acidification of the permeate followed by ultrafiltration (UF) enabled reduction of the surfactant content in the post-treated permeate by 32–60% (in relation to the surfactant content in the initial MEUF permeate).

1. INTRODUCTION

Micellar enhanced ultrafiltration (MEUF) is a hybrid separation technology that enables the removal of dissolved pollutants (also in ionic form) with the use of ultrafiltration (UF) and surfactants. It combines the benefits of UF, such as high permeate fluxes at low transmembrane pressures, and the advantages of reverse osmosis (RO), such as high separation factors of low-molecular-weight pollutants. The MEUF underlying

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principle relies on increasing the size of the pollutant by creating a complex of pollutant and surfactant micelle, which cannot pass through UF membranes. The surfactant micelles are formed on condition that the surfactant concentration is higher than the critical micelle concentration (CMC). Basically, most pollutant particles or undesired ions are concentrated in the retentate, and the obtained permeate is characterized by good quality. However, there is a risk that some surfactant monomers and unfixed contaminants can pass through the UF membrane into the permeate.

The MEUF technology for contaminants removal from aqueous solutions has been studied for more than 30 years. It has been proven to be a viable separation process for removing various pollutants from water/wastewater, such as heavy metals (nickel, cadmium, chromium, arsenic, lead), dyes, nutrients, and some harmful organic compounds (phenol and its derivatives, organic acids, aniline, aromatic alcohols) [1, 2].

Although the idea of the MEUF process seems to be simple, in fact, it is a very complex process. Its efficiency depends on a variety of parameters (membrane type, surfactant type, operating conditions, and added solutes). The surfactant type is crucial for the success of a given MEUF application. Based on the electrical charge of the hydrophilic head group, surfactants are classified into four types: anionic, cationic, nonionic, and amphoteric. Thus, micelles of cationic surfactants can interact electrostatically with anionic pollutants, whereas micelles of anionic surfactants can form complexes with cationic pollutants. The MEUF process, using cationic surfactants, is mostly applied for wastewater treatment. Among various cationic surfactants, cetyltrimethylammonium bromide (CTAB) seems to be the most widely used in practice due to its low CMC value (0.92 mM) [3]. Other cationic surfactants, which are also characterized by low CMC values, are: hexadecylpyridinium chloride (CPC, 0.9 mM) and octadecylamine acetate (ODA, 0.9 mM) [4]. The high CMC values are considered a disadvantage because of the intensified secondary pollution of permeate, as well as problems with the management of the retentate containing high organic load. Thus, suitable and cost-effective techniques for permeate post-treatment and surfactant recovery from retentate should be available to make the MEUF process economical. Surfactant monomers that passed through the UF membranes to permeate can be removed by chemical methods combined with UF [5, 6], whereas surfactants retained in the retentate can be recovered by changing temperature or pH, as well as by an ion-exchange method [7].

The leakage of the surfactant monomers into the UF permeate can be a serious obstacle, especially when high water quality is expected. However, the scale of this problem can vary depending on the surfactant type and process parameters. Some researchers stated that the secondary pollution of permeate was negligible [3]. On the other hand, Bielska and Prochaska [8] found that in the course of anionic dye removal by MEUF, the CTAB concentration in the permeate amounted to 335 mg/dm^3 when the surfactant dosage was equal to 5 CMC. A similar level of permeate pollution (i.e., around 240 mg/dm^3)

was observed by Baek et al. [9] for the MEUF process aimed at anionic nutrients removal with the use of CPC surfactant at an extremely high dosage of 22 CMC. On the contrary, Camarillo et al. [10] noted rather minor concentration of CTAB surfactant in the permeate (around 17 mg/dm³) after phosphate removal by MEUF with very low surfactant dosage (0.09 CMC).

The aim of this paper was to evaluate the pollution level of the MEUF permeate with surfactant monomers during nutrients removal from aqueous solutions. The effect of surfactant type, membrane material, and membrane MWCO on surfactant concentration in the permeate was established. The output of permeate and retentate post-treatment was also reported.

2. MATERIALS AND METHODS

Materials. Commercially available polymer and ceramic UF membranes were used in the experiments. The flat polymer membranes (Microdyn Nadir®) were made of polyethersulfone (PES) and regenerated cellulose (RC) and were characterized by a wide range of MWCO values (from 4 to 50 kDa). The active surface area of a polymer membrane was equal to 0.0045 m². Tubular ceramic membranes (CéRAM INSIDE®, Tami Industries) were of a multi-channel type with MWCO values of 1, 15, and 50 kDa. The active surface area of a ceramic membrane amounted to 0.011 or 0.032 m², depending on the number of channels (1 or 7) in the ceramic module. The characteristics of the investigated membranes are given in Table 1 (flat polymer membranes) and Table 2 (tubular ceramic membranes).

Table 1

Characteristics of Microdyn Nadir® membranes [11]

Membrane	MWCO [kDa]	Membrane material	Water flux ^a [m ³ /(m ² ·day)]	Water flux ^b [m ³ /(m ² ·day)]
PES4	4	polyethersulfone (moderately hydrophilic)	> 0.48	0.48
PES10	10		> 3.6	3.40
PES20	20		> 4.8	4.42
PES30	30		> 2.4	3.82
PES50	50		> 6	10.75
RC5	5	regenerated cellulose (highly hydrophilic)	> 0.6	1.05
RC10	10		> 0.96	1.82
RC30	30		> 7.2	13.83

^a Measured under 0.3 MPa (according to the manufacturer).

^b Determined experimentally under 0.2 MPa.

Sodium nitrate (NaNO_3 , CAS: 7631-99-4) and potassium phosphate (KH_2PO_4 , CAS: 7778-77-0) were purchased from Chempur (Poland). Three cationic surfactants: cetyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC), and octadecylamine acetate (ODA) were chosen for MEUF experiments (Table 3). Deionized distilled water was used in all experiments.

Table 2

Characteristics of CéRAM INSIDE[®] ceramic modules [12]

Parameter	Specification		
Configuration	tubular (1-channel)/clover (7-channel)		
Symbol	1 kDa 1C	15 kDa 7C	50 kDa 7C
MWCO, kDa	1	15	50
Water flux, m ³ /(m ² ·day) ^a	0.73	2.04	19.84
Membrane material	titanium dioxide/zirconium oxide		
Effective surface area, m ²	0.011	0.032	
Number of channels	1	7	
Internal channel diameter, mm	6	2	
External membrane diameter, mm	10		
Membrane length, mm	600		

^aDetermined experimentally under 0.2 MPa.

Table 3

Characteristics of experimental cationic surfactants

Surfactant	CMC ^a [mM]	Molecular mass [g/mol]	Chemical formula	$\log K_{\text{OW}}$	Manufacturer CAS
Cetyltrimethyl-ammonium bromide (CTAB)	0.92	364.46	$\text{C}_{19}\text{H}_{42}\text{NBr}$	3.18 ^b	Aldrich 57-09-0
Cetylpyridinium chloride (CPC)	0.90	358.01	$\text{C}_{21}\text{H}_{38}\text{CN}$	1.71 ^c	Sigma-Aldrich 6004-24-6
Octadecylamine acetate (ODA)	0.90	329.57	$\text{C}_{20}\text{H}_{41}\text{NO}_2$	6.99 ^d	TCI 2190-04-7

^a [10].

^b <https://www.carlroth.com>

^c <https://pubchem.ncbi.nlm.nih.gov>

^d ChemSrc (<http://m.chemsrc.com/en/index.jsp>).

Preparation of model solutions. Aqueous model solutions containing sodium nitrate (NaNO_3) and/or potassium dihydrogen phosphate (KH_2PO_4) were used. The concentration of the nitrate nitrogen and phosphate phosphorus was equal to $28 \text{ mg NO}_3^- \text{-N/dm}^3$ ($124 \text{ mg NO}_3^- \text{/dm}^3$) and $15 \text{ mg PO}_4^{3-} \text{-P/dm}^3$ ($47.5 \text{ mg PO}_4^{3-} \text{/dm}^3$), respectively. The feed

solutions were prepared at room temperature with the use of a magnetic stirrer to ensure complete dissolution of the salts.

In the MEUF experiments, various cationic surfactants such as CTAB, CPC, and ODA were added to the model nutrient solutions in concentrations of 2 CMC, 3 CMC, and 6 CMC.

MEUF process. The MEUF process with polymeric membranes was performed in a dead-end ultrafiltration cell (Amicon 8400) under a pressure difference of 0.1–0.2 MPa. To maintain a constant concentration of the feed solution, the permeate was periodically recirculated to the UF cell. The applied UF dead-end installation was described in detail in other research [13].

The MEUF process with ceramic membranes was examined in a cross-flow ProFlux M12 (Millipore) installation [14], under a pressure difference of 0.04–0.1 MPa. The nitrate and phosphate retention coefficients were calculated according to the procedure described elsewhere [15]. All measurements were done in duplicate, and the average nitrate and phosphate concentrations were considered in the discussion of the obtained results.

The nitrate concentrations in aqueous solutions were determined by a spectrophotometric method with NitraVer® 5 Reagent Powder Pillows. The phosphate concentrations (in the form of orthophosphate) in aqueous solutions were determined by a spectrophotometric method with ammonium molybdate and ascorbic acid. Both nitrate and phosphate concentrations were analysed in the model solutions before and after the MEUF process. The total carbon (TC) content was monitored in the feed/concentrate and permeate with the use of a HACH IL550 TOC-TN analyser.

3. RESULTS AND DISCUSSION

3.1. NITRATE AND PHOSPHATE REMOVAL EFFICIENCIES DURING MEUF WITH CATIONIC SURFACTANTS

The main aim of the research was to evaluate the pollution of the MEUF permeate with surfactant monomers during nutrient removal. However, for better clarity, the removal efficiencies of nitrates and phosphates by MEUF with the use of various cationic surfactants and various UF membranes are also presented. Based on the MEUF results [13–16], the minimum and maximum values of the NO_3^- and PO_4^{3-} rejection coefficients obtained for variable process parameters are shown in Fig. 1. The nitrate and phosphate retention coefficients were calculated for single-component solutions, i.e., for surfactant solutions containing 28 mg NO_3^- -N/dm³ or 15 mg PO_4^{3-} -P/dm³.

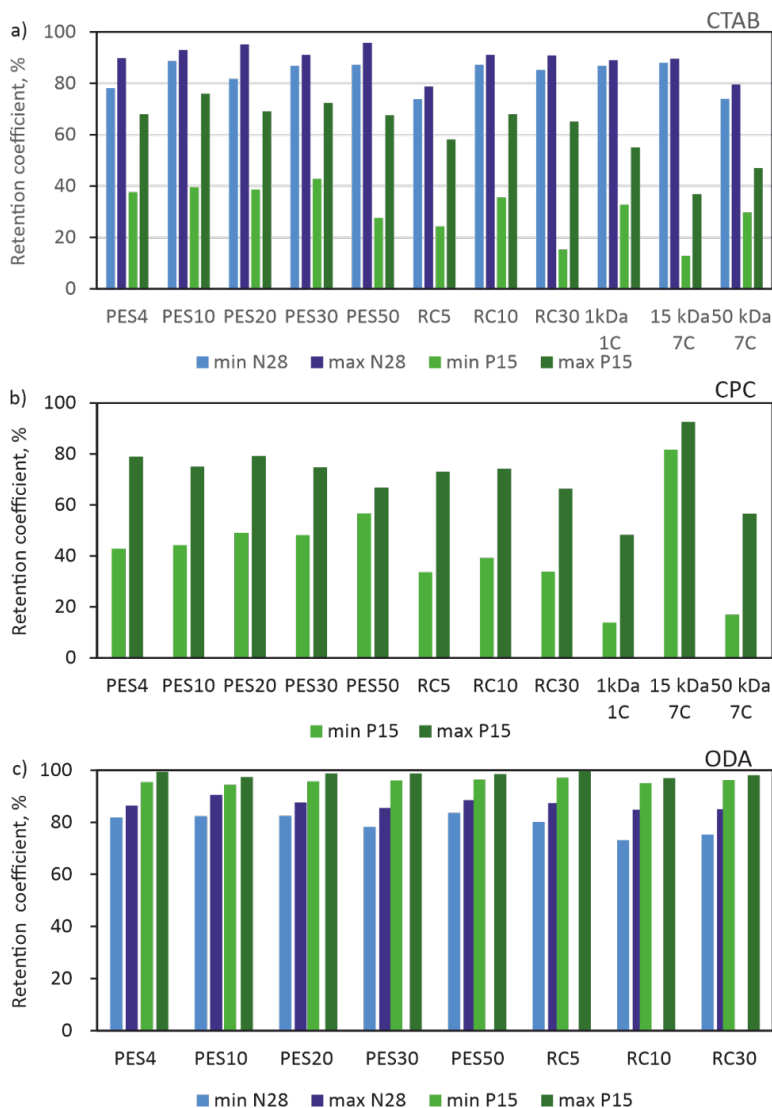


Fig. 1. Minimum and maximum nitrate and phosphate retention coefficients for MEUF with various surfactants: a) CTAB, b) CPC, and c) ODA ($P15 - 15 \text{ mg PO}_4^{3-}\text{-P/dm}^3$, $N28 - 28 \text{ mg NO}_3^-\text{-N/dm}^3$)

According to the presented results (Fig. 1a), it was concluded that the MEUF process with the CTAB surfactant and PES membranes was suitable for nitrate removal from aqueous solutions. The nitrate retention coefficients were quite satisfactory and varied from 78.15 to 95.86%, regardless of the PES membrane cut-off. Acceptable results of nitrate removal were also obtained for the MEUF process with the CTAB and

RC membranes (retention coefficient varied from 73.82 to 91.10%), as well as for ceramic membranes (retention coefficient from 73.93 to 89.66%). However, the application of the CTAB surfactant to phosphate removal gave rather moderate results, especially for ceramic membranes – the phosphate retention coefficients amounted to 27.54–75.99% (PES membranes), 15.34–67.97% (RC membranes), and 12.75–55.15% (ceramic membranes). The substitution of the CTAB with the CPC surfactant resulted in a slight improvement of the phosphate removal for polymeric membranes (by 5–8%) in comparison to the phosphate removal by the MEUF with the CTAB surfactant (Fig. 1b). It is interesting to note that in the case of the ceramic membrane (cut-off 15 kDa), several-fold upgrading of the phosphate rejection was observed for the MEUF with the CPC (instead of the CTAB surfactant). Generally, the CPC surfactant demonstrated better removal efficiency for phosphate anions than the CTAB surfactant, since the initial anion in CTAB was Br^- , which had a greater affinity for the surfactant micelles than Cl^- (the initial anion in CPC) [1].

Application of ODA surfactant gave the best results in phosphate removal by MEUF with polymeric membranes (Fig. 1c). The phosphate retention coefficient varied in a narrow range (from 95 to 99.8%), irrespective of the membrane material and membrane cut-off. These retention coefficients were 20–40% higher than retention coefficients for the MEUF with CTAB and CPC surfactants. Probably, significant membrane fouling by the ODA surfactant contributed to the high removal efficiency of the PO_4^{3-} ion. Interestingly, the phosphate removal efficiency was higher than the nitrate removal efficiency by 10–30%. Presumably, this observation can be attributed to the smaller hydrated radius of the phosphate ion compared to that of the nitrate ion and the stronger binding of the phosphate ion than of the nitrate ion by the ODA micelles [17–19].

3.2. PERMEATE POLLUTION WITH SURFACTANT

In the MEUF process, the removal efficiency of undesired pollutants as well as the high surfactant rejection are important. The applied surfactant dosages should enable the creation of high-molecular-weight micelles, which are then successfully rejected by UF membranes. However, in practice, some amount of surfactant is present in the treated solution as monomers, substantially worsening the UF permeate quality. It is well-known that some experimental conditions (temperature, solution pH, the presence of electrolytes, salinity) as well as the chemical structure of surfactant can influence the value of the CMC for a given surface-active agent. For this reason, the UF permeate quality (determined as the content of the total organic carbon, TC) was evaluated in the course of nitrate and phosphate removal by MEUF conducted with the use of various membranes and various cationic surfactants. The comparison of the TC concentration in the feed solution and in the MEUF permeate allowed for the assessment of the scale of the permeate pollution problem.

The TC concentrations in the permeate for chosen MEUF experiments are given in Tables 4–6 (MEUF with CTAB, CPC, and ODA, respectively). The percentage passage of the given surfactant from the feed to the permeate was also given (values in brackets).

Table 4

TC content in the permeate relative to the feed composition
and membrane used in the MEUF with CTAB

Feed composition ^a	Initial TC in the feed [mg C/dm ³]	TC in the permeate [mg C/dm ³] ^b (CTAB transported from the feed to the permeate [%]) ^c				
		PES membranes				
		4 kDa	10 kDa	20 kDa	30 kDa	50 kDa
15P + 28N + 2CMC	474	103 (21.7)	76 (16.0)	80 (16.9)	85 (17.9)	86 (18.1)
15P + 28N + 3CMC	628	108 (17.2)	85 (13.5)	81 (12.9)	83 (13.2)	85 (13.5)
15P + 2CMC	474	98 (20.7)	100 (21.1)	89 (18.8)	123 (26.0)	99 (20.9)
15P + 3CMC	628	98 (15.6)	114 (18.2)	87 (13.9)	122 (19.4)	96 (15.3)
15P + 6CMC	1258	127 (10.1)	147 (11.7)	135 (10.7)	128 (10.2)	141 (11.2)
		RC membranes				
		5 kDa		10 kDa		30 kDa
15P + 28N + 2CMC	474	121 (25.5)		147 (31.0)		139 (29.3)
15P + 28N + 3CMC	628	121 (19.3)		171 (27.2)		227 (36.2)
15P + 2CMC	474	150 (31.6)		159 (33.5)		162 (34.2)
15P + 3CMC	628	156 (24.8)		180 (28.7)		163 (26.0)
		Ceramic membranes				
		1 kDa		15 kDa		50 kDa
15P + 28N + 2CMC	474	110 (23.2)		74 (15.6)		217 (45.8)
15P + 28N + 3CMC	628	105 (16.7)		99 (15.8)		224 (35.7)
28N + 2CMC	474	28 (5.9)		74 (15.6)		389 (82.1)
28N + 3CMC	628	51 (8.1)		97 (15.4)		533 (84.8)
15P + 2CMC	474	37 (7.8)		356 (75.1)		370 (78.1)
15P + 3CMC	628	28 (4.5)		517 (90.9)		532 (84.7)
15P + 6CMC	1258	38 (0.3)		958 (76.2)		973 (77.3)

^a15P – 15 mg PO₄³⁻-P/dm³, 28N – 28 mg NO₃⁻-N/dm³.

^bThe mean values for Δp from 0.1 to 0.2 MPa for polymeric membranes.

^cCalculated in relation to the initial TC in the feed solution.

According to the data given in Tables 4–6, it can be concluded that the used surfactants contaminated the UF permeate to varying degrees, depending on the feed composition, membrane type, membrane MWCO and surfactant type. Generally, the amount of surface-active agent passing through the UF membranes varied from a few percent to around 85% of the initial surfactant amount in the feed solution (measured as TC).

Table 5

TC content in the permeate in relation to the feed composition and membrane used in the MEUF with CPC

Feed composition ^a	Initial TC in the feed [mg C/dm ³]	TC in the permeate [mg C/dm ³] ^b (CPC transported from the feed to the permeate [%]) ^c				
		PES membranes				
		4 kDa	10 kDa	20 kDa	30 kDa	50 kDa
15P + 2CMC	468	121 (25.9)	111(23.7)	127 (27.1)	124 (26.5)	108 (23.1)
15P + 3CMC	666	140 (21.6)	119(17.9)	133 (20.0)	142 (21.3)	147 (22.1)
15P + 6CMC	1353	180 (13.3)	120 (8.9)	141 (10.5)	176 (13.0)	188 (13.9)
		Ceramic membranes				
		1 kDa	15 kDa	50 kDa		
15P + 2CMC	468	54 (11.5)	99 (21.2)	254 (54.3)		
15P + 3CMC	666	113 (17.0)	163 (24.5)	360 (54.1)		
15P + 6CMC	1353	176 (13.0)	272 (20.1)	790 (58.4)		

^a15P – 15 mg PO₄³⁻-P/dm³, 28N – 28 mg NO₃⁻-N/dm³.^bThe mean values for Δp from 0.1 to 0.2 MPa for polymeric membranes and from 0.04 to 0.1 MPa for ceramic membranes.^cCalculated in relation to the initial TC in the feed solution.

Table 6

TC content in the permeate in relation to the feed composition and membrane used in the MEUF with ODA

Feed composition ^a	Initial TC in the feed [mg C/dm ³]	TC in the permeate [mg C/dm ³] ^b (ODA transported from the feed to the permeate [%]) ^c				
		PES membranes				
		4 kDa	10 kDa	20 kDa	30 kDa	50 kDa
15P + 28N + 2CMC	467	67 (14.4)	68 (14.6)	64 (13.8)	63 (13.5)	61 (13.1)
15P + 28N + 3CMC	625	86 (13.8)	82 (13.1)	89 (14.2)	85 (13.6)	91 (14.6)
28N + 2CMC	467	58 (12.4)	54 (11.5)	59 (12.6)	59 (12.5)	63 (13.5)
28N + 3CMC	625	80 (12.8)	74 (11.8)	76 (12.2)	85 (13.6)	78 (12.5)
15P + 2CMC	467	84 (18.0)	100(21.4)	100 (21.4)	90 (19.3)	93 (19.9)
15P + 3CMC	625	121 (19.4)	114(16.2)	125 (20.0)	114 (18.2)	115 (18.4)
15P + 6CMC	1270	203 (16.0)	196(15.4)	123 (9.7)	165 (13.0)	192 (15.1)
		RC membranes				
		5 kDa	10 kDa	30 kDa		
15P + 28N + 2CMC	467	70 (15.0)	71 (15.2)	60 (12.8)		
15P + 28N + 3CMC	625	94 (15.1)	95 (15.2)	79 (12.6)		
28N + 2CMC	467	70 (15.0)	71 (15.2)	52 (11.1)		
28N + 3CMC	625	93 (14.8)	78 (12.5)	79 (12.6)		
15P + 2CMC	467	124 (26.6)	119 (25.5)	83 (17.8)		
15P + 3CMC	625	142 (22.7)	114 (18.2)	83 (13.3)		

^a15P – 15 mg PO₄³⁻-P/dm³, 28N – 28 mg NO₃⁻-N/dm³.^bThe mean values for Δp from 0.1 to 0.2 MPa for polymeric membranes and from 0.04 to 0.1 MPa for ceramic membranes.^cCalculated in relation to the initial TC in the feed solution.

Considering the MEUF process with CTAB (Table 4), it was observed that the lowest amount of CTAB passed through the PES membranes, from 10.1 to 26% (in relation to the initial CTAB concentration in the feed). In the case of the feed solutions containing both nitrate and phosphate ions, the TC concentrations in permeates were similar, irrespective of the MWCO of the PES membranes. This may indicate that the CTAB micelles are rejected by all PES membranes, whereas only single surfactant monomers are transported to permeates. Definitely more CTAB passed through the RC membranes – the percentage of the CTAB amount in permeate varied from 19.3 to 36.2% (in relation to the CTAB initial concentration). The membranes made of regenerated cellulose (RC) are characterized by a larger pore size and higher flux than that of the PES membranes [13], and therefore, more monomers/pre-micelles can be transported to the MEUF permeate. The increase of the TC in permeate with increasing MWCO of the RC membranes was also noted. In turn, among the ceramic membranes tested, the most permeable for CTAB was the membrane with the MWCO of 50 kDa. This would prove about too large a membrane pore size in relation to the size of the CTAB micelle.

In the case of the MEUF with the CPC surfactant (Table 5) and ceramic membranes, the membrane MWCO had an evident influence on the permeate quality – with increasing MWCO, the TC content in permeate increased, reaching more than 50% of the initial TC content in the feed for a ceramic membrane with the MWCO of 50 kDa. For this reason, as well as due to poor phosphate rejection (Fig. 1b), this ceramic membrane cannot be recommended for nutrient removal by MEUF with CPC surfactant. On the contrary, the CPC surfactant passed the PES membranes to a low extent (8.9–27.1%) irrespective of the membrane cut-off.

In the course of the MEUF process with the ODA surfactant (Table 6), the PES membranes behaved similarly to those during the MEUF process with the CTAB surfactant. The TC content in permeate constituted from 9.7 to 21.4% of the initial TC concentration in the feed. What is more, TC concentrations in permeates were similar, irrespective of the MWCO of the PES membranes. The RC membranes also allowed the ODA passage in a rather low degree (11.1–26.6%), regardless of the feed composition and the membrane MWCO. However, it should be noted that the ODA surfactant has a great potential for membrane fouling [15], thus its transport to permeate (as single monomers or micelles) could be hampered.

Based on the results listed in Tables 4–6, it can be stated that the permeate quality (in view of the TC content) in the course of phosphate removal from single-salt solutions was slightly worse than the permeate quality for the remaining MEUF experimental series. This phenomenon can be explained by the increased CMC of the applied surfactants due to the presence of phosphates in the tested solutions [15]. Thus, a greater number of surfactant monomers can be expected in solutions containing phosphates than in solutions containing only nitrates or a nutrient mixture (i.e., NO_3^- and PO_4^{3-}).

3.3. THE IDEA OF PERMEATE AND RETENTATE POST-TREATMENT

The evaluation of the permeate quality in the course of nutrient removal by MEUF indicated rather a high degree of pollution with surfactants (measured as the TC concentration). Although the removal efficiency of nitrates and phosphates was quite satisfactory, the obtained permeates are not suitable for, e.g., drinking water supply. Thus, the lowering of the surfactant concentration in the MEUF permeate should be addressed when the practical application of the MEUF is considered. This aim can be achieved by overdosing an electrolyte in the surfactant solution. Gzara et al. [20] found that the increase of NaCl concentration from 1 to 500 mM resulted in the decrease of CPC concentration in MEUF permeate from 1 to 0.15 mM. It is also possible to use a surfactant that is characterized by a low value of CMC.

In this study, preliminary experiments aiming at the TC reduction in the MEUF permeate were undertaken. For this purpose, permeates after MEUF with the PES10 membrane and the CTAB surfactant were used, since for this MEUF variant, the nitrate and phosphate removal efficiencies were satisfactory, while the intensity of membrane fouling was moderate [15].

Considering the information found in literature [20–22], the surfactant concentration in the MEUF permeate was lowered by its acidification to $\text{pH} < 1$ (with the use of 0.1 M HCl solution). The obtained acidified permeate (MEUF+HCl permeate) was subjected to the UF process with the PES10 membrane under a pressure difference of 0.1, 0.15, and 0.2 MPa. Then, the pH adjustment of the UF permeate to $\text{pH} > 7$ was conducted with 0.1 M NaOH solution.

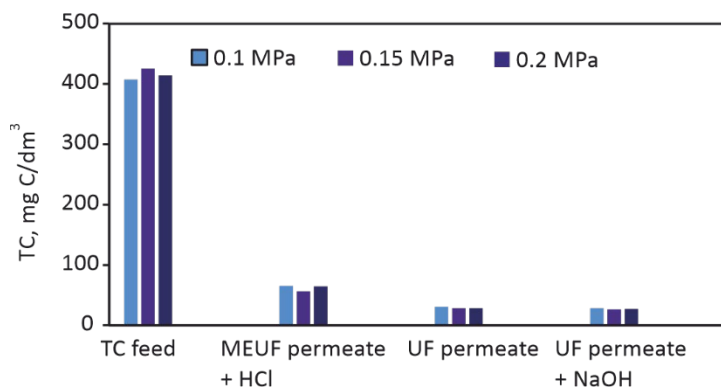


Fig. 2. The TC content in each stage of the post-treatment of the MEUF permeate; feed composition: $28 \text{ mg NO}_3^- \text{-N/dm}^3$ + 2CMC CTAB; PES10 membrane

In Figure 2, exemplary effects of the applied procedure are shown. The feed solution contained $28 \text{ mg NO}_3^- \text{-N/dm}^3$ and CTAB in a concentration of 2CMC. Permeate acidification and subsequent UF process brought about the reduction of surfactant content

by 49–56% in relation to the initial MEUF permeate. The final TC concentration in the post-treated MEUF permeate amounted to 29–30 mg/dm³. In turn, the decrease of TC content in the final MEUF product (in relation to the initial TC concentration in the feed) achieved even 92–93%. Similar results were obtained for the remaining experimental MEUF series with the CTAB surfactant – the TC concentration in the post-treated MEUF permeate was reduced by 32–60% (in relation to the TC concentration in the initial MEUF permeate).

The idea of the MEUF permeate acidification is closely related to the phenomenon of the CMC value decreasing for cationic surfactants in the presence of electrolytes. Assuming that the high pollution of the MEUF permeate may arise from the passage of the surfactant monomers through UF membranes, the addition of a strong electrolyte to the permeate should cause the formation of surfactant micelles. Application of the UF process for treatment of this modified MEUF permeate allows retention of surfactant micelles in the retentate [20]. Moreover, the increase of the CTAB micelle size in solution of pH < 2, as well as the change of micelle shape from spherical to ellipsoidal [20], enhance the CTAB separation by UF.

Bearing in mind the economic aspects of the MEUF process, the possibility of surfactant recovery was verified. The recovery experiments were performed with the use of MEUF retentates received after the separation process with the PES10 membranes and the CTAB surfactant. The MEUF retentates were acidified with 0.1 M solution of HCl to reach pH < 1. Then, the modified retentates were subjected to the UF process through a PES10 membrane.

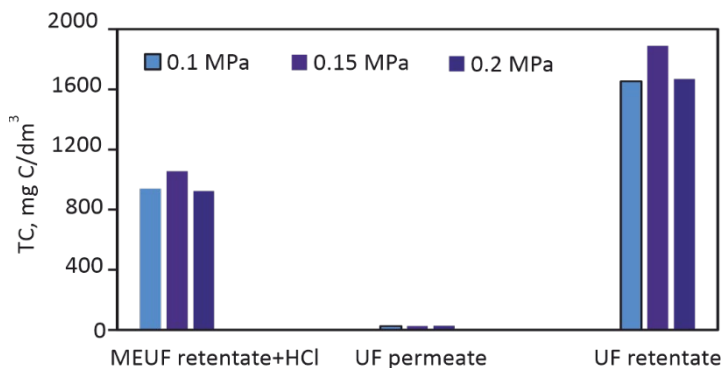


Fig. 3. The TC content in each stage of the post-treatment of the MEUF retentate; feed composition: 28 mg NO₃⁻-N/dm³ + 2CMC CTAB; PES10 membrane

Exemplary results of the applied procedure for the feed solution containing 28 mg NO₃⁻-N/dm³ and the CTAB surfactant in a concentration of 2 CMC are presented in Fig. 3. The TC concentration in the MEUF retentate just after the process varied from 923 to 1055 mg C/dm³. Acidification of this retentate and subsequent UF with a 2-fold

concentration factor (i.e., 2-fold decrease of the feed volume) enabled a significant increase in the TC content in the retentate. The TC concentration in the treated retentate was in the range of 1654–1890 mg C/dm³. At the same time, the TC content in the permeate amounted to 26–27 mg C/dm³. For the remaining MEUF experimental series with the CTAB surfactant, comparable results were obtained – the TC content in the concentrated retentate was around 1.6–2.3 times greater than the TC content in the retentate obtained directly after the MEUF process. Simultaneously, the TC concentration of the UF permeate constituted merely 2–3% of the TC concentration of the MEUF retentate.

The usage of a strong electrolyte (acid) in the applied recovery procedure aimed at the replacement of nitrates or phosphates trapped in the surfactant micelles by “stripping” anions of the electrolyte [21]. As a result, UF separation of the micellar phase from the nutrient phase was possible. It should be noted that single surfactant monomers present in the MEUF retentate can be built into surfactant micelles, thus enhancing the efficiency of surfactant recovery.

4. CONCLUSIONS

The surfactant leakage to MEUF permeates during nutrient removal was evaluated. The percentage of the initial dosage of CTAB, ODA, and CPC passing from the feed to the permeate ranged from 0.3 to 90.9%, from 11.1 to 26.6%, and from 10.5 to 58.4%, respectively, depending on the membrane type and membrane MWCO, as well as the feed composition. Generally, the permeate quality in view of TC content and membrane MWCO was less differentiated for polymeric membranes (PES and RC membranes) than for ceramic membranes. It was also found that the permeate quality was slightly worse when phosphates were present in the treated solution (in comparison to the feed solutions containing nitrates). It was also proved that the TC concentration in MEUF permeates increased with surfactant dosage. The lowest intensity of the secondary pollution of MEUF permeates was observed when nitrate solutions were treated by the CTAB surfactant (at the dosage of 2CMC) and the PES membranes were used.

The possibility of lowering the surfactant concentration in MEUF permeates was examined by permeate acidification followed by ultrafiltration. This procedure enabled the reduction of the TC concentration in the post-treated MEUF permeate by 32–60% (in relation to the TC concentration in the initial MEUF permeate). In turn, surfactant recovery experiments performed by the MEUF retentate acidification and subsequent UF concentration resulted in around a 2-fold increase of the TC in the post-treated retentate.

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