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Micellar-Enhanced Ultrafiltration for the Removal of Anionic Nutrients from Aqueous Solutions

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Highlights

- CTAB was applied for nitrate and phosphate removal by MEUF
- The presence of co-anion (phosphate) did not affect nitrate removal
- Simultaneous removal of nutrients caused a 50% decrease in phosphate separation
- The higher the MWCO values the more intensive membrane fouling was observed
- Even 13 to 36% of the applied surfactant passed through the UF membrane

Graphical abstract
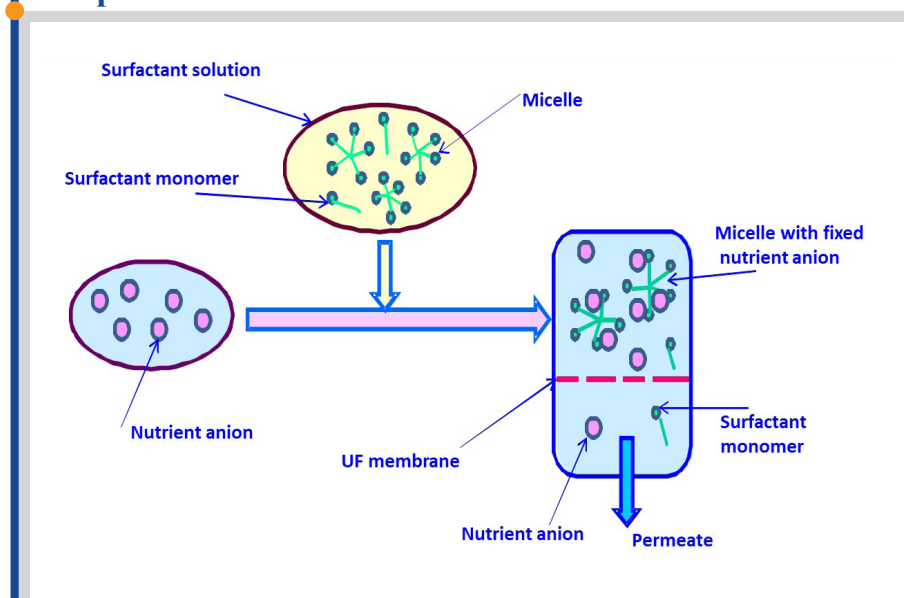
Abstract

The performance of micellar-enhanced ultrafiltration (MEUF) in removing nutrients from aqueous solutions was evaluated. The process was performed with the use of polyethersulfone (PES) and regenerated cellulose (RC) membranes that varied in terms of molecular weight cut-off values (4÷50 kDa). Nitrate and phosphate solutions containing 28 mg N-NO$_3$/dm^3 and/or 15 mg P-PO$_4^{3-}$/dm^3 were used in the tests. Cetyltrimethylammonium bromide (CTAB) was chosen as a surfactant to create cationic micelles in the tested solutions. The concentration of CTAB surfactant amounted to 2 and 3CMC (CMC - critical micelle concentration). The results of the study showed that the composition of the solution, membrane material, and membrane molecular weight cut-off influenced the efficiency of the process. The removal of nitrate and phosphate from single-component solutions was approximately 74÷93% and 15÷55%, respectively. The simultaneous removal of nutrients using MEUF revealed a deterioration in phosphate ion rejection - even by 50% when compared to the separation efficiency for single-component solutions. The worsening in nitrate rejection was seen to be insignificant. The adverse effect of nitrate ions on the phosphate ion removal was due to the greater affinity of the nitrate ions than phosphate ions towards CTAB micelles. Secondary contamination of the permeate by CTAB was also observed. The percentage of CTAB passing from the feed to the permeate ranged from 12.9 to 36.2%. The PES and RC membrane vulnerability to fouling varied to a great extent – the relative flux fluctuated from 0.16 to 0.95.

1. Introduction

Nitrogen and phosphorous are important elements for living organisms and they are natural parts of aquatic ecosystems and are important elements for living organisms. However, excess amounts of nutrients in water bodies often lead to eutrophication. The natural environment can be provided with inorganic

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nitrogen and phosphorous compounds by surface flows, including fertilizers, industrial wastewater from rainfall, and gas emission. A possible source of nutrients in the aquatic environment is very often uncontrolled discharges of municipal and industrial wastewater into water bodies.

To prevent the intensive growth of algae in surface water there is a need to minimalize the content of nutrients in treated municipal and industrial wastewater. Nitrate and phosphate are the most ubiquitous nutrients in aqueous solutions. The most common techniques for removing them from reclaimed wastewater are biological methods, however, these methods are sensitive to variations in feed composition and seasonal changes in temperature [1]. Phosphate phosphorous can also be removed from the wastewater phase by chemical precipitation, but this method generates troublesome sediments [2]. Physical treatment methods such as ion exchange or reverse osmosis/nanofiltration are also suitable for nitrate and phosphate removal, but the main disadvantages of these processes are problems with ion-exchange resin regeneration, high-operational costs, a high energy demand, and the necessity of extensive pretreatment [3, 4]. Generally, most of the conventional methods of nutrient removal are costly or not very efficient, and therefore micellar enhanced ultrafiltration (MEUF) is being investigated with regards to the removal of anionic nutrient species.

The MEUF process is a separation technology that allows the removal of dissolved pollutants with the use of the ultrafiltration process and surfactants. It is characterized by high separation factors (as in the case of reverse osmosis) and high permeability at low transmembrane pressures (as in the case of ultrafiltration, UF). The advantage of MEUF with regards to the ultrafiltration technique is the result of surfactant usage, which facilitates the separation, among others, of ionic contaminants, by entrapping them into micelles. These micelles are created when the surfactant concentration is greater than the critical micelle concentration (CMC). The surfactant micelles are large enough to be retained by UF membranes. This arises from the application of UF membranes, which are characterized by a relatively high permeability at low transmembrane pressure. Ultimately, pollutants are concentrated in the retentate, with the permeate being practically clean water. However, the risk of surfactant monomers and unfixed pollutants passing into the permeate cannot be excluded [5].

Depending on the type of pollutants that should be separated by MEUF, various surfactants are applied. Cationic surfactants create micelles that can interact electrostatically with anionic pollutants [6, 7], for example, anionic dyes [8, 9], anionic heavy metals [10, 11], and anionic nutrients [1]. Cationic surfactants can also be used in the removal of organic substances, e.g. phenolic compounds [12], due to the solubilization of organic matter in the micelle's hydrophobic core. The MEUF process, using cationic surfactants, is mostly applied for wastewater treatment. Among various cationic surfactants, CTAB seems to be the most common surfactant used in practice. This surfactant belongs to a group of quaternary ammonium salts and is characterized by a relatively long hydrophobic tail group (with 16 carbons) and a low CMC value (0.92 mM/dm^3) [6]. The application of surfactants with low CMC values is advantageous for the MEUF process because a less contaminated permeate can be expected. Bielska and Prochaska [9] successfully applied CTAB surfactant in anionic dye removal, achieving almost 99% separation. However, the dosage of the surfactant was rather high (5CMC) and contamination of the permeate by the surfactant was noted (in a concentration of 335 mg/dm^3). Pollution of the permeate with CTAB was diminished by 50% when a binary mixture of surfactants (CTAB + non-ionic surfactant) was used. Moreover, the application of the surfactant mixture did not result in a significant reduction of dye separation. The CTAB surfactant was also successfully applied for chromate ion removal with the use of MEUF [11]. Chromate rejection of up to 99% was observed in the absence of electrolytes in the feed, whereas the NaCl presence deteriorated chromate removal by up to 82%. It should be noted that these satisfactory results were obtained when the CTAB concentration markedly exceeded the CMC value, i.e. for a surfactant concentration in the range of 10÷20CMC. Consequently, the relative flux decreased to 0.2÷0.4. The undesirable phenomenon of membrane low permeability was attributed to the deformation of surfactant micelles to small aggregates or the change of micelle shape from spherical to cylindrical. However, this explanation referred to the specific membrane in question, as only one membrane type was applied in the experiments (PES membrane with a molecular weight cut-off equal to 20 kDa).

Research has also focused on the removal of anionic nutrients (nitrate and phosphate) by applying various cationic surfactants at a wide concentration range. One of the first attempts to apply the MEUF in nitrate and phosphate removal was made by Baek et al. [13] almost 2 decades ago. They applied cellulose membranes, characterized by a molecular weight cut-off (MWCO) of 3 and 10 kDa, and cetylpyridinium chloride (CPC) in the treatment of model solutions containing both nitrate and phosphate ions. The removal efficiency of nutrients amounted to 90÷93%, however, the CPC was applied at rather high dosages (even up to 20 mM/dm^3, i.e. up to 22CMC). It was observed that with an increasing molar ratio of CPC to nutrient, the removal efficiency of

nitrate/phosphate improved. However, the permeate flux was reduced due to the gel layer formed on the surface of the membrane. The fouling phenomenon occurred with great intensity, which was because the dead-end UF system was used. The applied surfactant was present in the permeate in a concentration equal to approximately 0.75 mM/dm^3 (i.e. below the CMC). The same authors [14] performed similar experiments on both nitrate and phosphate removal using MEUF, but they used the cross-flow UF installation. The obtained results were quite satisfactory – 86÷91% of nutrients were removed, however, the high molar ratios of the CPC surfactant to the pollutant (>3-5) were still applied. As a consequence of high surfactant dosages, the permeate flux constituted only 20-30% of the pure water flux. Camarillo et al. [1], during their study on phosphate removal from real wastewater a few years later, obtained rather unexpected results. They employed the cetyltrimethylammonium bromide (CTAB) surfactant and found that for the 95% removal of phosphate ions, the optimal CTAB concentration was only 0.1 mM/dm^3 (i.e. 9 times lower than the CMC for CTAB). This phenomenon was explained by surfactant accumulation near the membrane surface, which meant that the formation of micelles was possible - even when the bulk surfactant concentration was lower than the CMC value. Nevertheless, the pollution of the permeate by a surfactant (at the concentration of 0.05 mM/dm^3) was observed.

Most recently, the available literature on nutrient removal using the MEUF process is limited. Bahmani et al. [15] evaluated the removal of nitrate from single-component solutions, as well as under the presence of arsenate ions, using the MEUF process with polyacrylonitrile (PAN) membranes. They found that efficient nitrate removal (90.5%) from a single-component solution was possible when the surfactant (CPC) concentration was equal to 5 mM/dm^3. The presence of arsenate ions in the solution decreased the nitrate separation efficiency from 90.5 to about 75%, which was explained by the preferential binding of As(V) to CPC micelles. Chen and Jafvert [16] confirmed the absence of studies regarding the removal of specific anions from complex ionic mixtures, such as natural water or wastewater. They, therefore, investigated the relative association affinities of common anions, including nitrate and phosphate, towards micelles formed with two common surfactants (CPC and CTAB). They also developed a model to predict anion removal. They reported that up to 84% of NO$_3^-$ and up to 91% of HPO$_4^{2-}$/H$_2$PO$_4^-$ were removed from nutrient-enriched water, however, the surfactant (CPC) was dosed at a relatively high concentration (10 mM/dm^3). Nevertheless, they concluded that the MEUF process may be a potential technology for nutrient removal from natural or effluent water. This statement encouraged the authors of the current study to verify the suitability of the MEUF process for nitrate and phosphate removal from aqueous solutions.

A review of the literature on the MEUF process generally indicates membrane fouling (due to high surfactant dosages) as the key aspect of applying the process for environmental remediation. However, in most studies reported to date, UF membranes with poorly differentiated MWCO values (5 or 10 kDa) were applied. Taking into account the dynamics of the formation of surfactant micelles in the membrane boundary layer, as well as in the bulk solution, the impact of diversified MWCO values on the membrane flux seems to be worth investigating. It should also be noted that in the majority of MEUF applications, rather high surfactant dosages (from 10 to 20CMC) were used. High surfactant amounts are disadvantageous with regards to permeate quality and membrane permeability, and therefore efforts to use low surfactant dosages in MEUF can be seen to be desirable. According to a few already published papers, the main factors influencing nutrient removal by MEUF were (besides operating conditions), membrane and surfactant properties. Moreover, the aspect of co-existing anions has not been analyzed in great detail. Thus, CTAB surfactants characterized by a low CMC value, low CTAB dosages, and hydrophilic polymeric membranes that vary in terms of MWCO were chosen for the study. The mutual effect of the presence of nitrate and phosphate in the feed on their rejections was evaluated. The nitrate and phosphate retention coefficients and the permeate fluxes were estimated concerning the membrane MWCO and the membrane material. The extent of permeate pollution by surfactant concerning the membrane cut-off was also analyzed.

2. Materials and methods

2.1. Materials

Commercially available UF flat membranes (Microdyn Nadir®) made of polyethersulfone (PES) and regenerated cellulose (RC) were used in the experiments. The membranes varied in terms of their MWCO values (4, 5, 10, 20, 30, 50 kDa) and hydrophilicity. The characteristics of the investigated membranes are given in Table 1. The Microdyn Nadir® membranes are chemically resistant and permanently hydrophilic, and they are manufactured

in a specially developed process [17]. The active surface area of a membrane was equal to 0.0045 m².

Sodium nitrate (NaNO₃, CAS: 7631-99-4) and potassium phosphate (KH₂PO₄, CAS: 7778-77-0) were purchased from Chempur (Poland). Cetyltrimethylammonium bromide (CTAB, CAS: 57-09-0), a cationic surfactant also known as hexadecyltrimethylammonium bromide, was purchased from Sigma-Aldrich (Poland) (Table 2). Deionized distilled water was used in all the experiments.

Table 1
Characteristics of Microdyn Nadir® membranes [17]

Membrane	MWCO, kDa	Membrane material	Water flux[a], m³/m²day	Water flux[b], m³/m²day
PES4	4		>0.48	0.48
PES10	10	Polyethersulfone (moderately hydrophilic)	>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 information from the producer)
[b] determined experimentally under 0.2 MPa

2.2. Preparation of model solutions

In the experiments, aqueous model solutions containing sodium nitrate (NaNO₃) and/or potassium dihydrogen phosphate (KH₂PO₄) were used. The concentration of the nitrate nitrogen and phosphate phosphorous was equal to 28 mg N- NO_3^-/dm³ (124 mg NO_3^-/dm³) and 15 mg P- PO_4^{3-}/dm³ (47.5 mg PO_4^{3-}/dm³), respectively. The model solutions containing nitrate and/or phosphate were prepared by dissolving 170 mg of NaNO₃ and/or 66 mg of KH₂PO₄ in 1 dm³ of distilled water, respectively. The feed solutions were prepared at room temperature with the use of a magnetic stirrer to ensure the complete dissolution of the salts. Both mineral salts were used without any further purification.

In the MEUF experiments, a cationic-type surface active agent (cetyltrimethylammonium bromide, CTAB) was applied. The concentration of the CTAB amounted to 2CMC and 3CMC. The critical micelle concentration (CMC) of CTAB surfactant in pure water corresponds to 335.30 mg/dm³ (Table 2). The applied CTAB concentration was considerably higher than 1CMC, which should have guaranteed the transformation of surfactant monomers into micelles. The predetermined amounts of CTAB were added in 1 dm³ of the model solutions containing nitrate and/or phosphate.

Table 2
Characteristics and concentration of the CTAB

Company/ CAS	Molecular mass, g/mol	Chemical formula	LogK$_{OW}$[a]	CMC[b] mM/dm³	1CMC	2CMC	3CMC
						mg/dm³	
Sigma-Aldrich 57-09-0	364.46	C₁₉H₄₂NBr	3.18	0.92	335.30	670.60	1005.9

[a] https://www.carlroth.com
[b] according to [1]

2.3. MEUF process

The MEUF process was performed in a dead-end ultrafiltration cell (Amicon 8400). The total volume of the UF cell amounted to 350 cm³. The used membranes had a diameter of 76 mm. The aqueous solutions containing phosphate and/or nitrate and surfactant were subjected to the UF process under a pressure difference of 0.15 MPa. The pressure was generated by nitrogen delivered from a gas cylinder. To ensure a constant concentration of the feed solution, the permeate was periodically recirculated to the UF cell. Due to the constant mixing of the feed with a magnetic stirrer, the risk of membrane fouling was minimized. The used UF installation was described in detail in other research [7].

Before the MEUF tests, the new membranes were conditioned with distilled water at 0.2 MPa until a constant permeate flux was established. The permeate fluxes and retention coefficients were analyzed with respect to the solutions of nitrate and/or phosphate after steady conditions of permeation were

achieved. All measurements were made in duplicate, and the average values of fluxes, nitrate, and phosphate concentrations were considered in the discussion of the obtained results.

The permeation measurements were carried out with distilled water, nitrate solutions, phosphate solutions, and solutions containing nitrate and phosphate. The MEUF tests were conducted under conditions of steady flow.

The permeate/water flux was calculated according to Eq. (1):

$$J = \frac{V}{A.t} \tag{1}$$

where, J is the permeate/water flux (m³/m²day), V is the volume of permeate/water (m³), t is the time (day) and A is the surface area of the membrane (m²).

The degree of fouling was assessed by calculating the relative flux:

$$RF = \frac{J}{J_0} \tag{2}$$

where RF is the relative flux, J is the permeate flux of the N/P solution (m³/m².day) and J_0 is the flux of the water (m³/m² day).

The nitrate/phosphate retention coefficient was calculated according to Eq. (3):

$$R_{N/P}[\%] = \frac{C_i - C_p}{C_i} \times 100 \tag{3}$$

where $R_{N/P}$ is the nitrate or phosphate retention coefficient (%), C_i is the nitrate or phosphate concentration in the feed/concentrate (mg/dm³) and C_p is the nitrate or phosphate concentration in the permeate (mg/dm³).

The nitrate concentration in aqueous solutions was analyzed using a spectrophotometric method with NitraVer® 5 Reagent Powder Pillows. To determine the nitrate content, a HACH model DR/2900 spectrophotometer was used (method no. 8039, program no. 355, and wavelength: 500 nm). The method's accuracy amounted to ±5%. The phosphate concentration (in the form of orthophosphate) in aqueous solutions was determined using a spectrophotometric method (at a wavelength of 690 nm). The method is based on the reaction between orthophosphate and ammonium molybdate in the aqueous acidic condition, followed by its reduction by ascorbic acid. Determination of the phosphate was carried out with the use of a WTW model MPM 3000 spectrophotometer. The method's accuracy amounted to ±5%. Both nitrate and phosphate concentrations were analyzed in the model solutions before and after the MEUF process.

The total carbon (TC) content was monitored in the feed and permeate with the use of a HACH IL550 TOC-TN analyzer. The method's accuracy amounted to ±2%.

2.4. Determination of the Critical Micelle Concentration (CMC)

The CMC values of the CTAB for various solution compositions were determined according to the procedure described by Benito et al. [18] by plotting the electrical conductivity versus the concentration of the surfactant. The applied concentration range of the CTAB varied from 50 to 3000 mg/dm³. The measurements were carried out at the temperature of 25 ºC with the use of an Elmetron CC-411 conductometer. The measurement accuracy was equal to ±0.2%.

3. Results and discussion

3.1. The effect of mineral salt on the CMC values of the CTAB surfactant

The CMC value of the applied CTAB surfactant was determined and then compared with literature data. Furthermore, the variation in the CMC values due to the presence of mineral salt in the surfactant solution was also analyzed. The CMC values were determined (by electrical conductivity measurements) for the following solutions: CTAB only; CTAB + 28 mg N- NO_3^-/dm³; CTAB + 15 mg P- PO_4^{3-}/dm³, and CTAB + 15 mg P- PO_4^{3-}/dm³ + 28 mg N- NO_3^-/dm³. The obtained CMC values are presented in Table 3. It was noted that there was almost no difference between the experimentally determined CMC and the literature CMC value of the CTAB surfactant.

Generally, an increase in the ionic strength of a solution containing ionic surfactant causes a reduction in the CMC value [5, 19, 20]. In the presence of mineral salt, the electrostatic forces between the polar head groups of the surfactant are significantly diminished. This leads to a facilitated micelle formation at the lower surfactant concentration than in cases without the

addition of salt. The phenomenon of CMC reduction is evident when nitrate is present in the CTAB solution as single salt, or together with phosphorous salt (Table 3). The noted CMC$_s$ values (when nitrate was present in the CTAB solution) were lower by approximately 30-50% in comparison with the CMC value for the pure CTAB solution. Interestingly, the presence of phosphate (as single salt) in the concentration of 15 mg P- PO_4^{3-}/dm^3 did not affect the CMC value of the CTAB surfactant. It is generally assumed that the degree of counter-ions binding increases with an increase in ion valence and with a decrease in the hydrated radius [21]. The hydrated radii of the ions present in the CTAB model solutions were equal to: 0.340 nm (NO_3^-) [22]; 0.327 nm (HPO_4^{2-}) and 0.302 nm ($H_2PO_4^-$) [23]. Thus, the presence of phosphate ions in the CTAB solutions should cause the lowering of the CMC value. On the other hand, Chen et al. [6] ascertain that the CMC value of cationic surfactants increases due to the presence of counter ions according to the sequence: NO_3^- < Br^- < Cl^-. However, the most reasonable explanation of the observed effects of the presence of phosphate and nitrate on the CMC value is a too-low phosphate ion concentration in comparison to the equivalent nitrate concentration.

Table 3
The CMC values for the CTAB with regard to the solution's composition

Solution composition	CMC, g/dm³	Solution pH, -	
		2CMC	3CMC
CTAB	0.3353[a]	-	-
CTAB	0.3357[b]	5.80	5.85
	CMC$_s$[c], g/dm³	CMC$_s$/CMC	
CTAB + 15 mg P- PO_4^{3-}/dm^3	0.3541	1.06	5.8	5.7
CTAB + 28 mg N- NO_3^-/dm^3	0.2419	0.72	6.0	6.4
CTAB + 15 mg P- PO_4^{3-}/dm^3 + 28 mg N- NO_3^-/dm^3	0.1732	0.52	5.9	5.8

[a] according to [1]
[b] this study
[c] the CMC value due to salt presence

3.2. Nitrate and phosphate removal efficiency by MEUF

The research aimed to evaluate the efficiency of MEUF in removing nitrate and phosphate, especially when both ions are present in the treated solution. The effect of membrane MWCO, membrane material, and surfactant dosage on the ion retention and membrane flux was analyzed. The nitrate and phosphate retention coefficients for PES and RC membranes, when nitrogen or phosphorous salt was present in the solution (single-component solution), are shown in Figs. 1 and 2, respectively.

According to the obtained results, the nitrate retention coefficient varied only slightly, especially for the PES membranes, and amounted to 84.3-93% (PES membranes) and 73.8-91.1% (RC membranes). For both membranes (PES and RC), a better separation efficiency was observed when the CTAB was applied in a dosage of 3CMC than when applied in a dosage of 2CMC. Unexpectedly, the membrane MWCO had a minor impact on the nitrate rejection in the case of the PES membranes, whereas when the RC membranes were applied a better nitrate rejection was noted for the RC10 membrane (cut-off 10 kDa) than for the RC5 membrane (cut-off 5kDa). Generally, the membranes made of regenerated cellulose exhibited slightly worse nitrate rejection than the membranes made of polyethersulfone – this observation was especially visible when membranes of low MWCO values (4, 5, and 10 kDa) were considered. This was probably caused by the greater pore size of the RC5 and RC10 membranes (0.82 nm and 5.01 nm, respectively) when compared to the pore size of the PES4 and PES10 membranes (0.62 nm and 2.04 nm, respectively) [24]. In the case of more open membranes (cut-off 30 kDa), the difference between pore size is less distinct (4.89 nm for the RC30 membrane and 8.38 nm for the PES30 membrane) [24, 25], with nitrate rejections being comparable for both membrane types.
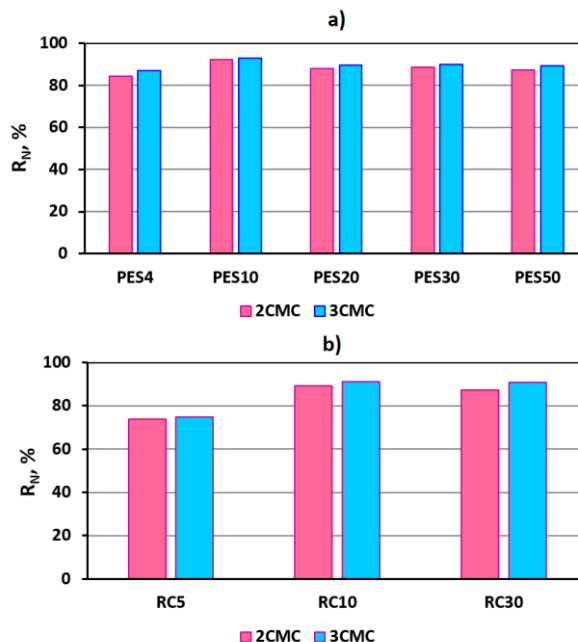

Fig.1. Nitrate retention coefficient (R_N) versus membrane MWCO and CTAB dosage for the PES (a) and RC (b) membranes: C_i = 28 mg N-NO_3^-/dm^3 (single-component solution); ΔP = 0.15 MPa

When analyzing phosphate removal by MEUF, a rather poor rejection was found for both membrane types. When polyethersulfone membranes were applied, the rejection coefficient of PO_4^{3-} ions varied from approximately 37 to 55%. A slightly better separation was observed for a surfactant dosage of 3CMC than for a surfactant dosage of 2CMC when the membrane cut-off amounted to 4÷30 kDa. Nevertheless, the worst phosphate ion rejection was noted for the PES50 membrane (i.e. for the membrane with the highest MWCO value). For the MEUF process with membranes made of regenerated cellulose, the phosphate rejection was extremely poor and amounted to 15÷47%. Again, the best rejection was monitored for the RC10 membrane. The increase in the CTAB dosage brought about an improvement in phosphate ion rejection even two-fold (for the RC30 membrane).
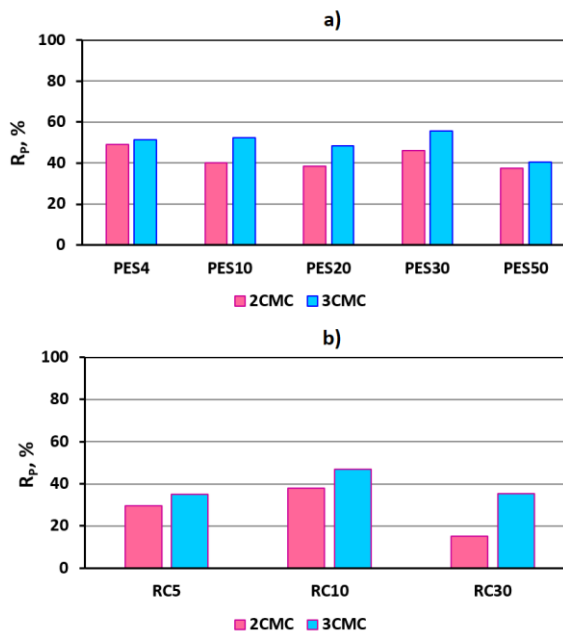

Fig.2. Phosphate retention coefficient (R_P) versus membrane cut-off and CTAB dosage for the PES (a) and RC (b) membranes: C_i = 15 mg P-PO_4^{3-}/dm^3 (single-component solution); ΔP = 0.15 MPa

In natural water, both nitrate and phosphate ions are usually present, and it was thus worth investigating the separation efficiency of these ions from their aqueous mixtures. The rejection coefficients of PO_4^{3-} and NO_3^- ions from a solution containing 15 mg P- PO_4^{3-}/dm^3 and 28 mg N- NO_3^-/dm^3 are shown in Fig. 3 (PES membranes) and Fig. 4 (RC membranes). Generally, a great difference between biogenic ion removal was observed, irrespective of the membrane type. Both ion rejections worsen when compared to the separation efficiency from single-component solutions. However, this worsening in nitrate rejection was insignificant (by 5-10%), whereas the deterioration in phosphate ion removal (from solutions containing also nitrate ions) reached even 50% and was more pronounced for the polyethersulfone membranes with a cut-off ranging from 4 to 30 kDa.
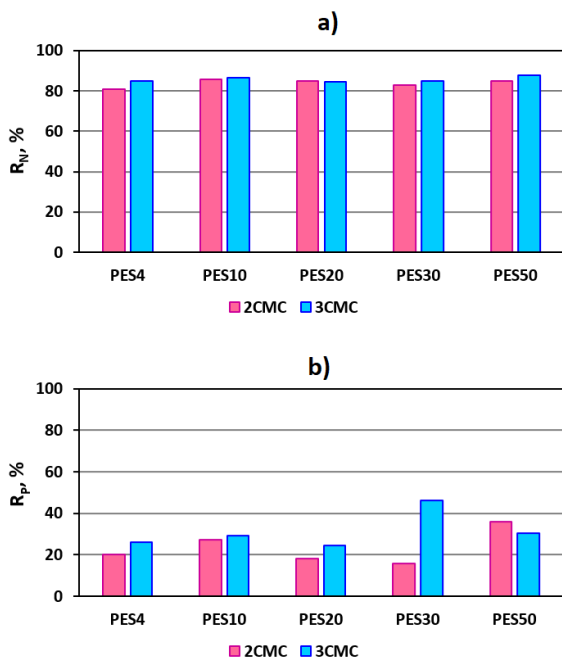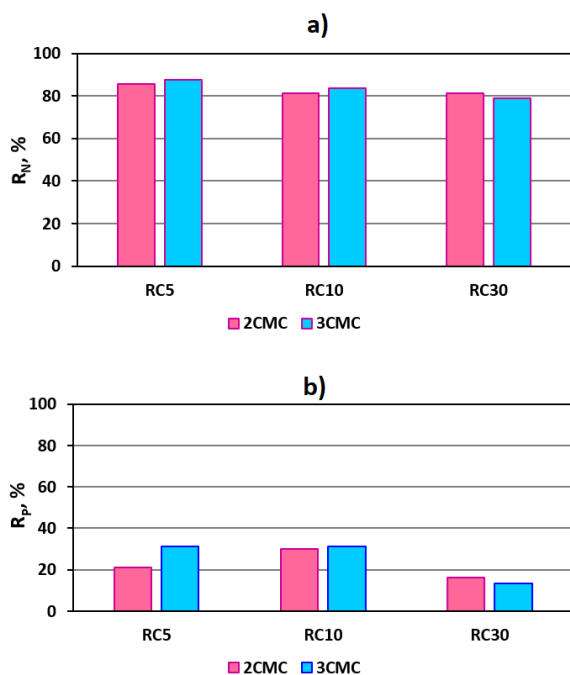

Fig.3. Nitrate retention coefficient, R_N (a) and phosphate retention coefficient, R_P (b) versus membrane cut-off and CTAB dosage for the PES membranes: C_i = 28 mg N- NO_3^-/dm^3 + 15 mg P-PO_4^{3-}/dm^3 (two-component salt solution); ΔP = 0.15 MPa

Fig.4. Nitrate retention coefficient, R_N (a) and phosphate retention coefficient, R_P (b) versus membrane cut-off and CTAB dosage for the RC membranes: C_i = 28 mg N- NO_3^-/dm^3 + 15 mg P- PO_4^{3-}/dm^3 (two-component salt solution); ΔP = 0.15 MPa

Based on the obtained results, it was concluded that the presence of phosphate ions had a minor impact on the nitrate rejection, whereas nitrate ions

notably made the phosphate ion separation worse for both membrane types. Generally, the rather low phosphate ion removal (also from single-component solutions) probably arises from the low affinity of HPO_4^- ions towards CTAB micelles [16]. Among two possible speciation forms of phosphorus in the model solution ($H_2PO_4^-$ and HPO_4^{2-}), the speciation form HPO_4^- is dominant at the solution pH of 5.8-5.9 (Table 3). The adverse effect of nitrate ions on phosphate ion removal is exacerbated in binary-salt solutions due to the greater affinity of nitrate ions than phosphate ions towards CTAB micelles [16]. Moreover, the fact that the equivalent concentration of phosphate ions was lower than the equivalent concentration of nitrate ions can be seen to be insignificant. It can also be assumed that the anion affinity for surfactant micelles decreases with an increase in hydrated radii among anions of the same valence [6]. However, thorough research made by Chen and Jafvert [16] showed some exceptions to the above rule. Although the hydrated radii of the NO_3^- ion (0.340 nm) [22] are higher than the hydrated radii of the $H_2PO_4^-$ ion (0.302 nm) [23], the calculated selectivity coefficients gave rise to establishing the overall affinity of various monovalent anions towards CTAB micelles in the following decreasing order: $NO_3^- > Br^- > NO_2^- > Cl^- > HCO_3^- > H_2PO_4^- > F^-$.

3.3. Membrane permeability in the MEUF treatment of nitrate and/or phosphate solutions

The hydraulic capacity of the MEUF process, besides its separation efficiency, is a crucial parameter for possible practical applications. The water permeability of the used membranes was listed in Table 1. It is evident that membranes made of regenerated cellulose (RC) are characterized by higher permeate fluxes than the fluxes of polyethersulfone (PES) membranes. This observation can be attributed to the high hydrophilicity of RC membranes (in comparison to the moderate hydrophilicity of PES membranes), which is due to the high density of hydroxide groups in the polymer membrane matrix. However, it should be taken into consideration that the used RC membranes were additionally modified by the producer in order to be extremely hydrophilic. It is well known that the permeate flux of the treated solution is lower than the pure water flux (due to membrane fouling). The relative permeability (equation 2) is often used to evaluate the degree of membrane fouling. This parameter is determined as the ratio of the permeate flux to the pure water flux.

The relative fluxes for the PES and RC membranes in the course of the MEUF removal of nitrate and/or phosphate ions are shown in Figs. 5-7. When analyzing the obtained values of J/J_0 ratios, it can be concluded that both the PES and RC membranes were characterized by a differentiated vulnerability to fouling. The RF values were strongly dependent on the membrane MWCO and, to a lesser extent, on the composition of the treated solution. Unexpectedly, the membranes' hydrophilicity was not reflected in the relative permeability.

For single-component solutions containing nitrate or phosphate salt, the RF values for the PES membranes varied from 0.16 to 0.91 and 0.61 to 0.95, whereas the RF values for the RC membranes amounted to 0.5-0.88 and 0.61-0.83, respectively. The lowest RF values were generally noted for the membranes of the highest cut-off (PES50 and RC30), whereas the less hydrophilic PES50 membrane was almost completely fouled (J/J_0=0.16) when the nitrate solution was treated. This significant flux decline was probably due to pore blocking by CTAB micelles. A meaningful drop in membrane permeability (J/J_0 = 0.56) was also observed for the PES4 membrane (the lowest cut-off value) when the nitrate solution was treated. In this case, membrane fouling was possibly caused by the penetrating of the surfactant monomers into membrane pores, with the high-molecular-weight micelles (> 25 kDa) [26] being retained at the membrane surface. A visible trend of the fouling impact with an increasing membrane MWCO was observed for the PES membranes and phosphate solution, as well as for the RC membranes and nitrate solutions. Interestingly, the increased dose of CTAB (3CMC) brought about less fouling intensity (in comparison to the fouling degree noted for 2CMC) in most of the experimental tests.

When analyzing the relative flux values obtained for the MEUF of the solutions containing both N and P salts, it was evident that fouling was more intense than in the case of single-component salt solutions - but only for the PES membranes (the J/J_0 ratio amounted to 0.22-0.86). Moreover, when the RC membranes were applied in the MEUF of the N and P salt mixture, the fouling intensity was diminished (in comparison to the single-component salt solutions) and the RF values amounted to 0.53-0.97. Thus, the results obtained for N and P removal from the two-component solutions were according to the expectations, i.e. the RC membranes (more hydrophilic) exhibited less fouling vulnerability in comparison to the PES membranes (less hydrophilic).

As was already mentioned, the PES and RC membranes' vulnerability to fouling in the course of the MEUF process varied significantly. The lack of univocal relationships between process parameters and the RF values indicates

the complex nature of fouling. It seems that the fouling intensity in the course of nitrate and phosphate removal by MEUF with CTAB depends not only on the membrane's hydrophilic properties but also on the difference between the size of the surfactant monomer/pre-micelle/micelle and the membrane's pore size. Small CTAB monomers/pre-micelles may penetrate membrane pores, whereas big micelles will be deposited at the membrane surface. It is also possible, especially in the case of more open membranes (high cut-off values), that all CTAB structures (monomers, pre-micelles, and micelles) will penetrate membrane pores with partial migration to the permeate.
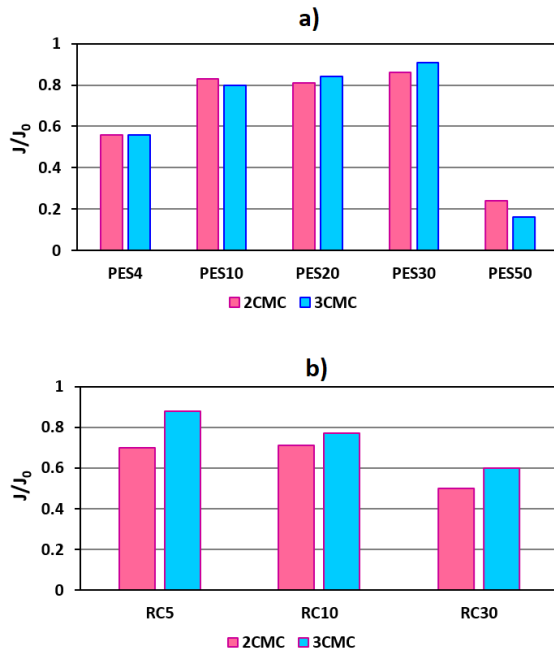
a)

b)

Fig.5. Relative flux (J/J_0) versus membrane cut-off and CTAB dosage for the PES (a) and RC (b) membranes: C_i = 28 mg N- NO_3^-/dm^3 (single-component solution); ΔP = 0.15 MPa
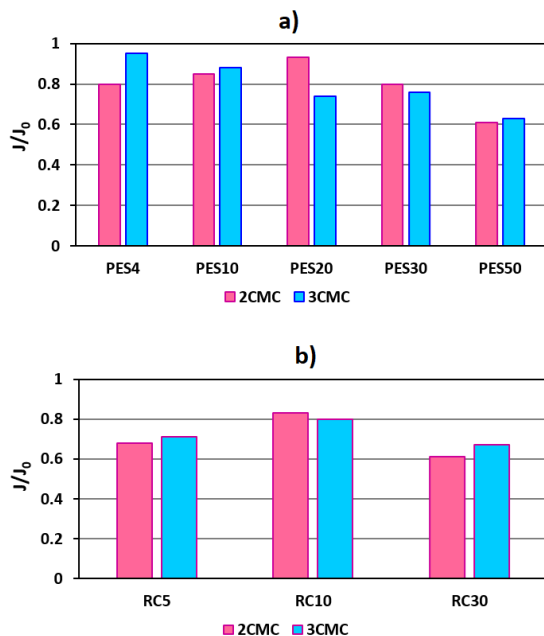
a)

b)

Fig.6. Relative flux (J/J_0) versus membrane cut-off and CTAB dosage for the PES (a) and RC (b) membranes: C_i = 15 mg P- PO_4^{3-}/dm^3 (single-component solution); ΔP = 0.15 MPa

a)

b)

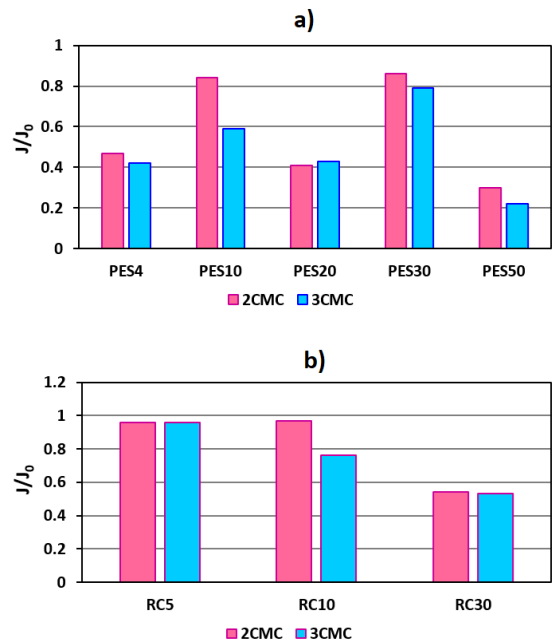**Fig.7**. Relative flux (J/J_0) versus membrane cut-off and CTAB dosage for the PES (a) and RC (b) membranes: C_i = 28 mg N- NO_3^-/dm^3 + 15 mg P- PO_4^{3-}/dm^3 (two-component solution); ΔP = 0.15 MPa

3.4. Permeate pollution with surfactant

It is obvious that the separation efficiency of a given pollutant is the key parameter in the MEUF process, however, the surfactant rejection is also very important. The recommended surfactant dosages should enable the formation of micelles, which are then retained by UF membranes. However, many practical applications of the MEUF process have revealed the presence of surfactant in the permeate. It was proved that not all surfactant monomers are transformed into micelles, even if the CMC is applied. Therefore, due to the presence of surfactant monomers in the feed, the UF permeate can be contaminated by surfactant.

The degree of permeate pollution with CTAB in the course of nitrate and phosphate removal was evaluated by determining TC. The comparison of the TC content in the feed solution and the MEUF permeate enabled the assessment of the scale of the permeate pollution problem. The TC concentration in the permeate for the chosen MEUF experiments is given in Table 4. The percentage passage of the CTAB from the feed to the permeate is also given (values in brackets). According to the data given in Table 4, it can be stated that the used surfactant contaminated the permeate to varying degrees, depending on the feed composition, membrane type, and membrane MWCO. The percentage of CTAB passing from the feed to the permeate ranged from 12.9 to 26% for the PES membranes, and from 19.3 to 36.2% for the RC membranes.

Generally, the quality of the permeate with regard to the TC content was less differentiated for the PES membranes than for the RC membranes. The cut-off of the PES membranes and the CTAB dosage had a rather minor impact on the TC content in the permeate, especially when salt mixtures were treated by MEUF. This observation suggests that the PES membranes reject most of the CTAB micelles and that only single surfactant monomers can migrate to the permeate. In the case of the single phosphate salt solution, the amount of CTAB in the permeate was slightly higher than in the case of the salt mixtures. The effect of the composition of the solution on the TC content in the permeate can be explained by taking into account the data given in Table 3. According to this table, the single phosphate salt does not affect the CMC value, whereas the presence of both phosphate and nitrate salts lowers the CMC value significantly. Thus, in the case of a salt mixture, more micelles should be present in the feed than in the case of single phosphate salt, and, in consequence, better CTAB rejection will be observed. The membranes made of regenerated cellulose (RC) are characterized by a larger pore size and higher flux than that of the PES membranes (see subsection 3.1), and therefore more monomers/micelles can be transported to the MEUF permeate. What is more, the TC content in the permeate increased with an increasing MWCO of the RC membranes.

Table 4
TC content in the permeate in relation to the feed composition and membrane used in the MEUF with CTAB

Feed composition[a]	Initial TC in the feed, mg C/dm³	TC in the permeate, mg C/dm³ (percentage of CTAB transported from the feed to the permeate)[b]				
		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)
		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)

[a] 15P – 15 mg P- PO_4^{3-}/dm³; 28N – 28 mg N- NO_3^-/dm³
[b] calculated in relation to the initial TC in the feed solution

It can generally be stated that in the course of MEUF nitrate and phosphate removal, permeate contamination with CTAB surfactant is significant. Although the removal efficiency of nitrate ions is enough to even meet the recommended WHO standards for drinking water (< 10 mg NO_3^-/dm³), the permeate cannot be used as potable water due to the elevated TC content. A decrease in the TC content in permeate can be accomplished by adding an electrolyte to the treated solution. Gzara et al. [27] found that an increase in the NaCl concentration from 1 to 500 mM/dm³ brought about a decrease in the surfactant concentration (CPC) in the permeate from 1 to 0.15 mM/dm³. However, the use of surfactants characterized by low CMC values can be seen to be the most beneficial.

4. Conclusions

The performance of MEUF with the use of CTAB surfactant with regard to nitrate and phosphate removal was evaluated. The obtained results showed that an increasing ionic strength of the surfactant solution resulted in a decrease in the CMC value. When the concentration of the nitrate and phosphate in the two-component solution amounted to 15 mg P-PO_4^{3-}/dm³ and 28 mg N- NO_3^-/dm³, a 2-fold reduction in the CMC value of the CTAB was observed. The decrease in the CMC value under the presence of mineral salts was caused by a diminishing electrostatic repulsion between the polar head groups. It was also proved that MEUF performed at low CTAB dosages (2 and 3CMC) enabled a high removal of nitrate from single-component salt solutions. The nitrate rejection coefficients amounted to 84.3÷93% and 73.8÷91.1% for the PES and RC membranes, respectively. The membrane cut-off (in the range of 4÷50 kDa) had a minor impact on nitrate rejection in the case of the PES membranes, whereas for the RC membranes an increase in the cut-off value (from 5 to 10 and 30 kDa) brought about a slight improvement in nitrate rejection. When phosphate removal by MEUF from a single-component salt solution was considered, rather poor separation results were obtained. The phosphate rejection coefficients ranged from 37 to 55% (PES membranes) and from 15 to 47% (RC membranes). The simultaneous removal of nutrients by MEUF with CTAB revealed a deterioration in phosphate ion rejection by up to 50% in comparison to the separation efficiency for single-component salt solutions. On the other hand, the worsening in nitrate rejection was insignificant (by 5-10%), irrespective of the membrane type and cut-off value. The adverse effect of nitrate ions on phosphate ion removal was due to the greater affinity of the nitrate ions than phosphate ions towards CTAB micelles. Secondary contamination of the permeate (measured as an increase in TC) was observed. This undesirable worsening of the permeate quality was caused by CTAB monomers passing through the UF membranes. The percentage of CTAB passing from the feed to the permeate ranged from 12.9 to 26% for the PES membranes, and from 19.3 to 36.2% for the RC membranes. The vulnerability of the PES and RC membranes to fouling in the course of the MEUF process varied significantly – the relative flux fluctuated from 0.16 to 0.95, depending on the membrane applied and the composition of the treated solution.

Abbreviations

CMC	Critical micelle concentration
CPC	Cetylpyridinium chloride
CTAB	Cetyltrimethylammonium bromide
MWCO	Molecular weight cut-off
MEUF	Micellar enhanced ultrafiltration
PES	Polyethersulfone
RC	Regenerated cellulose
TC	Total carbon

CRediT authorship contribution statement

K. Majewska-Nowak: Conceptualization, Supervision, Writing – review & editing.
J. Górna: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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