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# REMOVAL OF INORGANIC NITROGEN AND PHOSPHOROUS COMPOUNDS FROM TWO-COMPONENT AQUEOUS SOLUTIONS BY MICELLAR ENHANCED ULTRAFILTRATION

The micellar enhanced ultrafiltration of model aqueous solutions containing inorganic nitrogen and phosphorous compounds was studied. In the experiments, cellulose membranes of 5, 10 and 30 kDa molecular weight cut-off and cetyltrimethylammonium bromide (CTAB) as a cationic surfactant were used. The concentration of CTAB amounted to 2 and 3*CMC* (critical micelle concentration). The influence of surfactant concentration, membrane cut-off and operating pressure on permeate flux, as well as on nitrate and phosphate separation was evaluated. The results showed that the presence of both nitrates and phosphates caused deterioration of the retention coefficient in comparison to separation efficiency achieved for one-component solutions.

## 1. INTRODUCTION

Nitrogen and phosphorus are essential elements for all living plants and animals. Nitrogen is one of the basic components of proteins and nucleic acids that make up the living parts of cells. Phosphorus, like nitrogen, is extremely important for the development and life of living organisms. This is an essential element for production of an ATP molecule, which is the lifeblood of every cell. Furthermore, phosphorus is an element which constitutes 0.08% of the Earth's crust. It is also an essential component of DNA and RNA of living cells. Nitrogen and phosphorous compounds can also enter the environment through anthropogenic activity. Phosphates are the main contaminants that accelerate eutrophication process in surface water. The main source of phosphorus in the water environment is run-off of fertilizers as well as wastewater

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discharging. It is necessary to minimize phosphorus concentration in the treated domestic and industrial wastewater [1]. Nitrogen compounds present in surface waters may be of organic or inorganic origin. Inorganic nitrogen compounds can be derived from surface runoff including nitrogen fertilizers, industrial wastewater and precipitation. Currently used methods for removing nitrogen and phosphorous compounds are expensive and time-consuming. Attempts to use micellar enhanced ultrafiltration for the removal of these pollutants are an interesting alternative to conventional methods.

The search for low-pressure membrane process allowing separation of either organic impurities of low molecular weight or ionic inorganic components led to the development of a process named micellar enhanced ultrafiltration (MEUF). MEUF is a hybrid process of the classic ultrafiltration technique with the ability of surfactants to create micelles. The advantage of the micellar enhanced ultrafiltration process is the possibility of obtaining rather high permeate fluxes (typical of ultrafiltration) and very good selectivity (typical of reverse osmosis) using low transmembrane pressures. During the MEUF process, mineral and organic substances of small size are dissolved in micelles, and ionic impurities, having an opposite charge to the charge of the surfactant used, are bonded to the surface of the micelles. The resulting complexes are generally larger in size than the diameter of ultrafiltration membrane pores and are retained by the membrane [2–4].

A prerequisite for carrying out the MEUF is the use of a surfactant dose in excess in relation to the critical micelle concentration (*CMC*). *CMC* is the lowest concentration at which the surfactant has the ability to create micelles. The created micelles can interact electrostatically with pollutants of ionic type [5]. The MEUF process using cationic surfactants is mostly used for wastewater treatment. Cationic surfactants can be applied in removal of anionic pollutants. Worldwide studies are being conducted for the MEUF removal of anionic dyes [6] and heavy metals [7]. Beak et al. [8] studied the MEUF process with the use of cetylpyridinium chloride (CPC) for nitrate and phosphate removal. The research showed the influence of surfactant molar ratios on the rejection of nitrates and phosphates.

The objective of the study was to evaluate the removal efficiency of inorganic nitrogen and phosphorous compounds from two-component aqueous solutions by micellar enhanced ultrafiltration (MEUF) using cetyltrimethylammonium bromide (CTAB).

## 2. EXPERIMENTAL

In the experiments, commercially available asymmetric ultrafiltration membranes made of regenerated cellulose (RC) were used. Membranes were characterized by various molecular weight cut-off (MWCO) – 5, 10 and 30 kDa.

MEUF experiments were carried out at room temperature in a stirred AMICON 8400 cell (Fig. 1). The total volume of the UF cell amounted to 350 $cm^3$ and the diameter of the membranes being tested was 76 mm. Model aqueous solutions of the biogenic compounds and surfactant were continuously mixed with use of magnetic stirrer. The UF process was run at the transmembrane pressure (TMP) of: 0.10, 0.15 and 0.20 MPa.

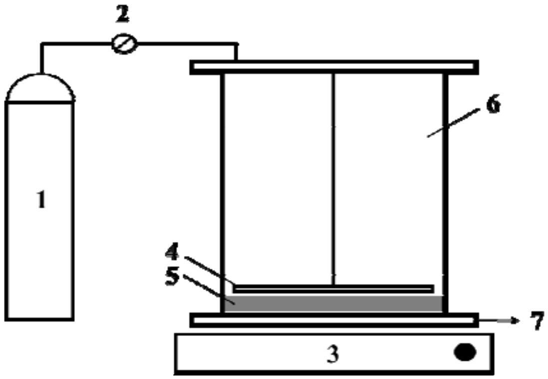


Fig. 1. Scheme of the Amicon 8400 ultrafiltration cell:
1 – gas cylinder, 2 – pressure gauge, 3 – magnetic stirrer,
4 – stirrer bar, 5 – membrane, 6 – feed, 7 – permeate/filtrate

The experiments were carried out for one- and two-component aqueous model solutions. The solutions contained potassium dihydrogen phosphate ($KH_2PO_4$) and sodium nitrate ($NaNO_3$). The concentrations of nitrates and phosphates in the tested solutions were equal to 28 mg $NO_3^-$-N/$dm^3$ and 15 mg $PO_4^{3-}$-P/$dm^3$, respectively. In the experiments, surface active agent of cationic type (cetyltrimethylammonium bromide, CTAB) was applied. The concentration of CTAB amounted to 2*CMC* and 3*CMC*. The *CMC* of CTAB surfactant in pure water corresponds to 335.30 mg/$dm^3$ (Table 1).

Table 1

Characteristic and concentration of CTAB [9]

| Surfactant | *CMC* [mM] | *CMC* [mg/dm³] | *MW* [Da] | 2*CMC* [mg/dm³] | 3*CMC* [mg/dm³] |
|---|---|---|---|---|---|
| Cetyltrimethylammonium bromide, CTAB | 0.92 | 335.30 | 364.46 | 670.60 | 1005.9 |

During the study, the retention coefficients of nitrates and phosphates as well as permeate volume fluxes were evaluated. Concentrations of nitrates and phosphates in aqueous solutions were determined by the spectrophotometric method. To determine the nitrate content, a spectrophotometer HACH type DR/2000 (HACH method 8171) was used, while phosphate concentration was determined by the PN-EN ISO

6878:2006 method with the use of the spectrophotometer WTW type MPM 3000. Concentration of both pollutants was analyzed in model solutions before and after the MEUF. The pollutant retention coefficient, $R$, was calculated from the formula:

$$R = \frac{C_R - C_P}{C_R} \times 100, \ \%$$

where $C_R$ and $C_P$ are the concentrations of nitrates or phosphates in the retentate and permeate, respectively (mg/dm$^3$).

In the course of experiments, the permeate volume flux was determined. The permeability of distilled water, $J_0$, was also measured. The experiments were conducted under steady conditions of flow.

The permeate volume flux, $J$, was calculated according to the equation:

$$J = \frac{V}{At}, \qquad [\mathrm{m}^3/(\mathrm{m}^3 \cdot \mathrm{day})],$$

where $V$ denotes the permeate volume, m$^3$, obtained in a certain time $t$, day. The membrane had an effective area ($A$) of 0.045 m$^2$.

## 3. RESULTS AND DISCUSSION

Surfactants have the ability to aggregate and form micelles. Micellization occurs when the concentration of the surfactant exceeds the critical micelle concentration (*CMC*). Satisfactory results of the MEUF process are dependent on the proper choice of the surfactant and its concentration. Studies were conducted using CTAB solutions of concentration equal to 2*CMC* and 3*CMC*.

Before MEUF process was evaluated, the values of *CMC* for CTAB in distilled water and one- or two-component solutions were verified. The *CMC* value was evaluated based on the electrolytic conductivity measurements at various surfactant concentrations (from 0.05 to 3 g/dm$^3$). The real *CMC* value was obtained at the intersection point of the linear relationships (conductivity vs. CTAB concentration) varying in slope (Fig. 2). The determined *CMC* value was compared with the literature data (Table 1). Camarillo et al. [9] evaluated the *CMC* for CTAB equal to 0.3353 g/dm$^3$ which is almost identical to the value read from the chart – 0.3357 g/dm$^3$ (Fig. 2a).

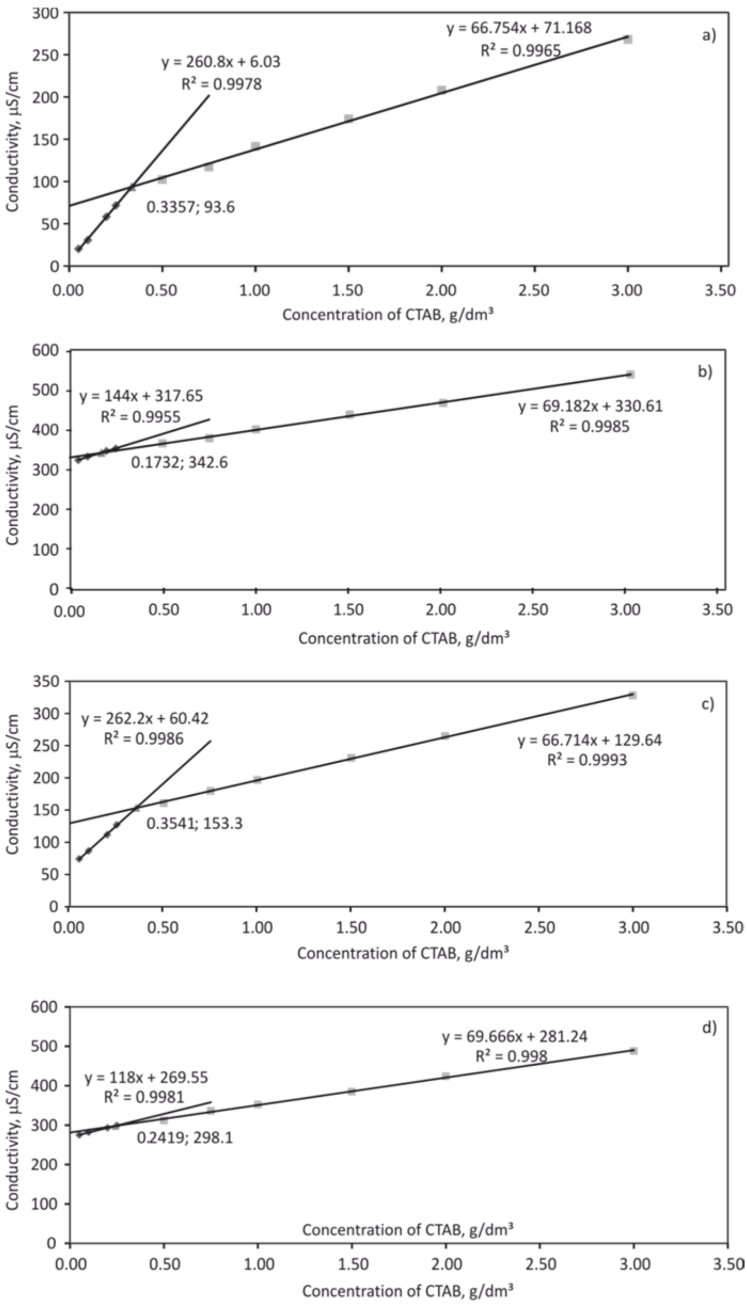


Fig. 2. Electrolytic conductivity vs. CTAB concentration in: a) distilled water, b) two-component aqueous solution – 28 mg $NO_3^-$-N/dm$^3$ and 15 mg $PO_4^{3-}$-P/dm$^3$, c) one-component aqueous solution – 15 mg $PO_4^{3-}$-P/dm$^3$, d) one-component aqueous solution – 28 mg $NO_3^-$-N/dm$^3$

The impact of salt presence in CTAB solution on *CMC* value was also examined (Fig. 2b). The aqueous surfactant solutions contained potassium dihydrogen phosphate ($KH_2PO_4$) and/or sodium nitrate ($NaNO_3$). The concentration of nitrates and phosphates in the tested solutions was equal to 28 mg $NO_3^-$-N/dm$^3$ and 15 mg $PO_4^{3-}$-P/dm$^3$, respectively. In two-component solution, the *CMC* of the surfactant was equal to 0.1732 g/dm$^3$ (Fig. 2b). This value was far lower than that determined for distilled water (Fig. 2a). The presence of potassium dihydrogen phosphate and sodium nitrate caused a decrease in the *CMC* of CTAB almost by 50%. The *CMC* for one--component solutions with CTAB was equal to 0.3541 g/dm$^3$ for potassium dihydrogen phosphate solution (Fig. 2c) and 0.2419 g/dm$^3$ for sodium nitrate solution (Fig. 2d). The presence of the phosphate caused an increase in the *CMC*, and therefore higher doses of surfactant were required. On contrary, the addition of the nitrate caused diminishing of the *CMC* value; it was lower than that for distilled water and significantly lower than that for the phosphate solution.

The phosphate retention coefficient varied in a wide range depending on the surfactant concentration, membrane MWCO and applied pressure. The removal of phosphates from one- and two-component solutions was influenced by the surfactant concentration – upon the increasing CTAB content in the treated solution, the separation efficiency also increased. Figure 3 shows the removal efficiencies of phosphates from one- (Figs. 3a–c) and two-component (Figs. 3d–f) solutions. The phosphate retention coefficients for experiments with two-component solutions were too low (11–34%), while for one-component solutions better removal efficiency was obtained (from 15 to 53%). No evident effect of transmembrane pressure (TMP) on the retention coefficients has been observed.

Beak et al. [8] studied the MEUF process with use of CPC for nitrate and phosphate removal from two-component feed solution. Similarly as in the present study, they used batch-stirred cell (Amicon 8400) and membranes made of regenerated cellulose (with MWCO of 3 and 10 kDa). The obtained results proved the importance of molar ratio of solution components on nitrate and phosphate ion removal. As the CPC:nitrate:phosphate ratio was increased from 1:1:0.06 to 3.18:1:0.06 and to 5.30:1:0.06), the rejection of nitrates increased from 77% to 84%, and to 92%, while phosphate rejection increased from 83% to 87%, and to 95%, respectively [8]. For one-component solution treated by the MEUF, the phosphate rejection sharply increased to 99% when the molar ratio $PO_4$:CPC reached 1:20.

Comparing the process efficiency for both one- and two-component aqueous solutions (Figs. 3 and 4), it can be stated that MEUF process of one-component solution is much more favorable for diminishing phosphorous concentration in water environment. For both types of solution, the process performance was slightly better when CTAB was applied at 3*CMC* than at 2*CMC* (Fig. 3). In most of experiments (83%) performed with the use of CTAB at 3*CMC*, the phosphate retention coefficient was greater than 20%.

According to the results given in Fig. 3, it can be concluded that the 10 kDa membrane was characterized by the best separation properties (irrespectively of the solution type) (Figs. 3b, e), while the worst separation characteristics was obtained for the 30 kDa membrane (Figs. 3c, f). In our previous studies [10], we tested the usability of cationic surfactants for inorganic phosphorous compound removal from water solutions by MEUF. Two cationic surfactants, CTAB and CPC (cetylpyridinium chloride), were compared and it was found that application of CPC resulted in better process efficiency than that obtained with the CTAB usage. Similar research [11] conducted with octadecylamine acetate (ODA) demonstrated very good phosphate rejection (above 95%) irrespectively of the surfactant amount added to the feed solution. The retention coefficients obtained for MEUF with CPC were below 90%, which does not provide a satisfactory performance in view of phosphorous removal [10]. Camarillo et al. [9] also investigated the MEUF process with the use of CPC and ODA in terms of phosphate elimination. They concluded that the concentration of tested surfactants should be increased over 1*CMC* to obtain a satisfactory phosphate rejection coefficient of approximately 95%.

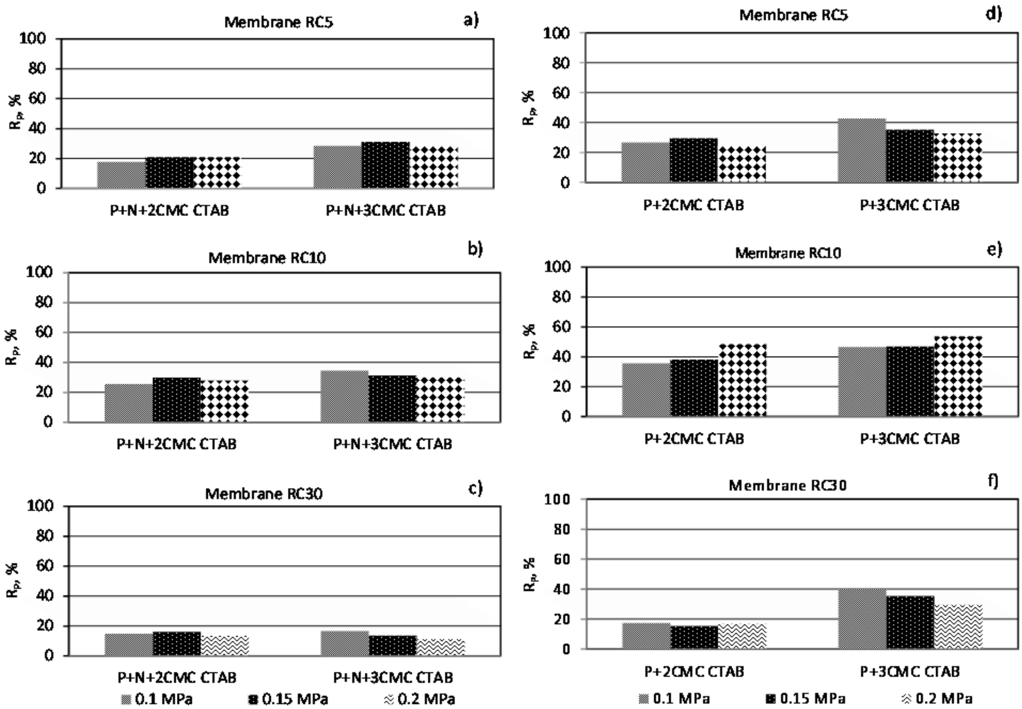


Fig. 3. Phosphate retention coefficient ($R_p$) for membranes made of regenerated cellulose (RC5 – 5 kDa, RC10 – 10 kDa and RC30 – 30 kDa) vs. CTAB concentration in: a), b) and c) two-component solutions; d), e) and f) one-component solutions

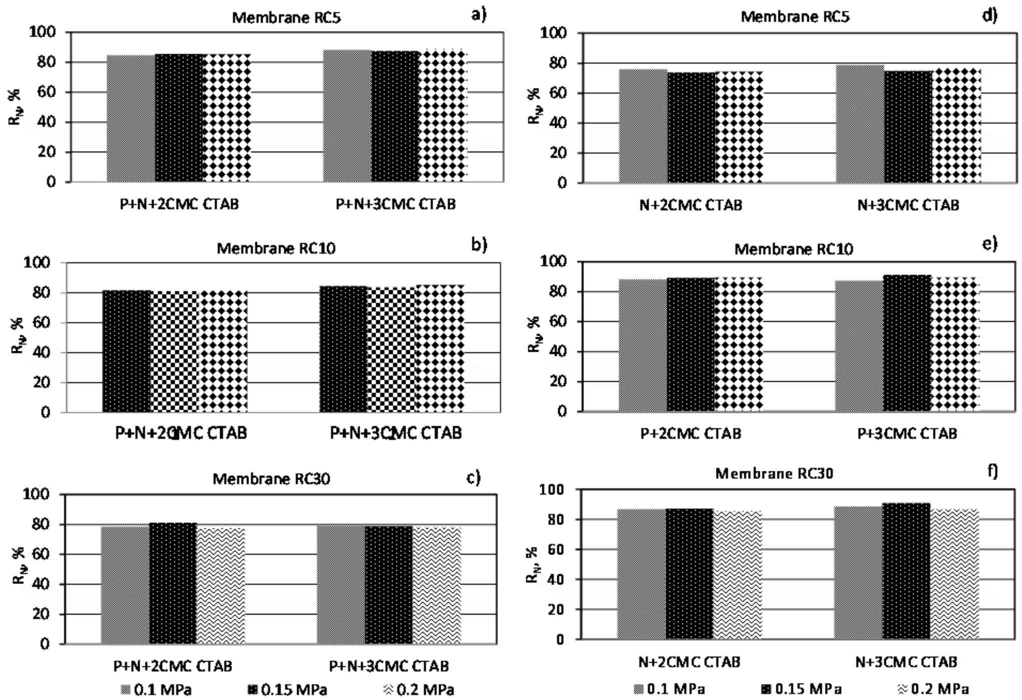


Fig. 4. Nitrate retention coefficient ($R_N$) for membranes made of regenerated cellulose (RC5 – 5 kDa, RC10 – 10 kDa and RC30 – 30 kDa) vs. CTAB concentration in: a), b) and c) two-component solutions; d), e) and f) one-component solutions

Figure 4 shows the nitrate retention coefficients for various concentrations of CTAB (2*CMC* and 3*CMC*) in one- and two-component aqueous solutions. The obtained results demonstrated very good nitrate rejection (from 73 to 91%). In the majority of experiments, the results obtained for CTAB concentration of 3*CMC* were slightly better compared to those for 2*CMC*, irrespectively of the solution type. Nitrate removal varied slightly for applied membranes, without indicating the unambiguous influence of phosphate presence in the two-component solution on nitrate separation efficiency. For RC5 membrane, the $NO_3^-$ rejection was better for two-component than for one-component solution. The worse nitrate rejection was observed for RC30 membrane (Figs. 4c, f). This membrane was also characterized by poor phosphate elimination (Figs. 3c, f). The nitrate retention coefficient for RC10 membrane varied in a great extent – from 81 to 91%. There was also no clear effect of TMP on the retention coefficients. Our previous studies [11] performed with ODA and CTAB for polyethersulfone UF membranes demonstrated very good nitrate rejection. When surfactant concentration amounted to 3*CMC*, the nitrate rejection for experiments with CTAB was equal to 82–85%, while with ODA – 72–83%.

Beak et al. [8] showed that the removal of nitrates sharply increased as the surfactant molar ratio increased. When the molar ratio CPC:nitrate was 6:1, over 90% of nitrates were removed. As was mentioned earlier, similar tendency was observed for two-component solutions (CPC:nitrate:phosphate).

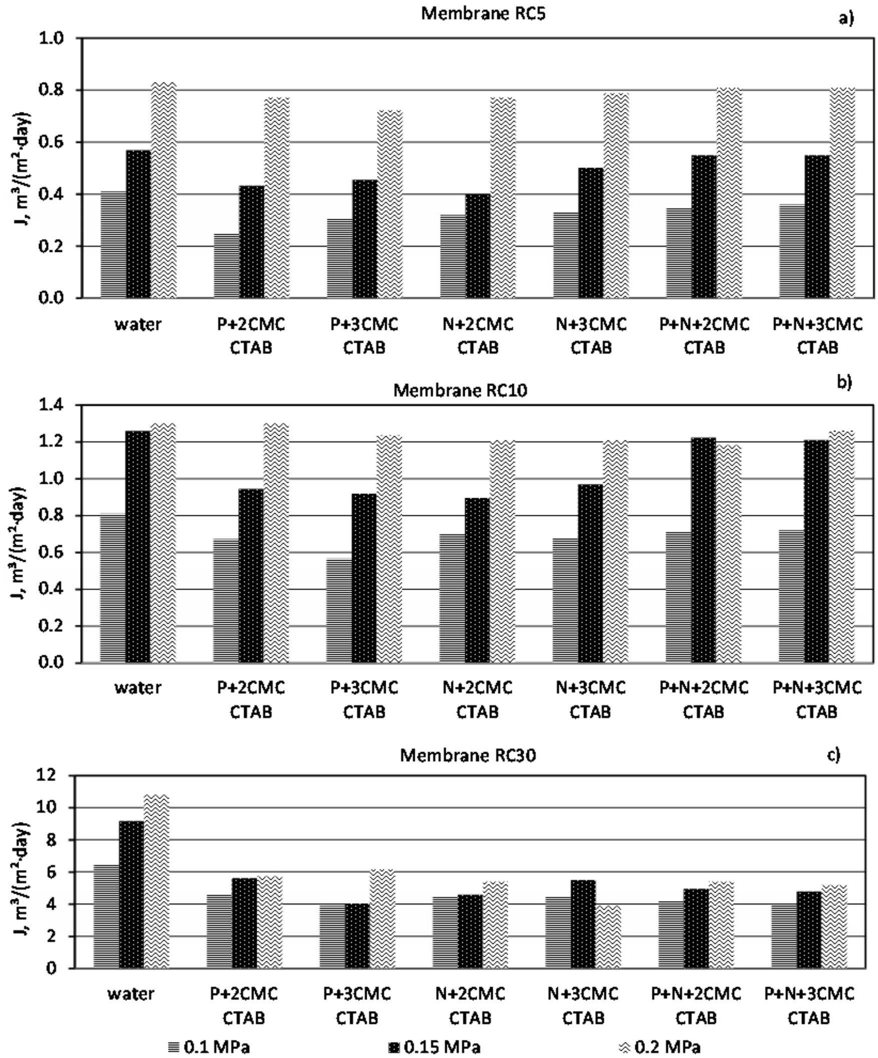


Fig. 5. Volume flux (*J*) for membranes made of regenerated cellulose (RC) vs. CTAB concentration in one- and two-component model aqueous solutions a) MWCO 5 kDa, b) MWCO 10 kDa, and c) MWCO 30 kDa

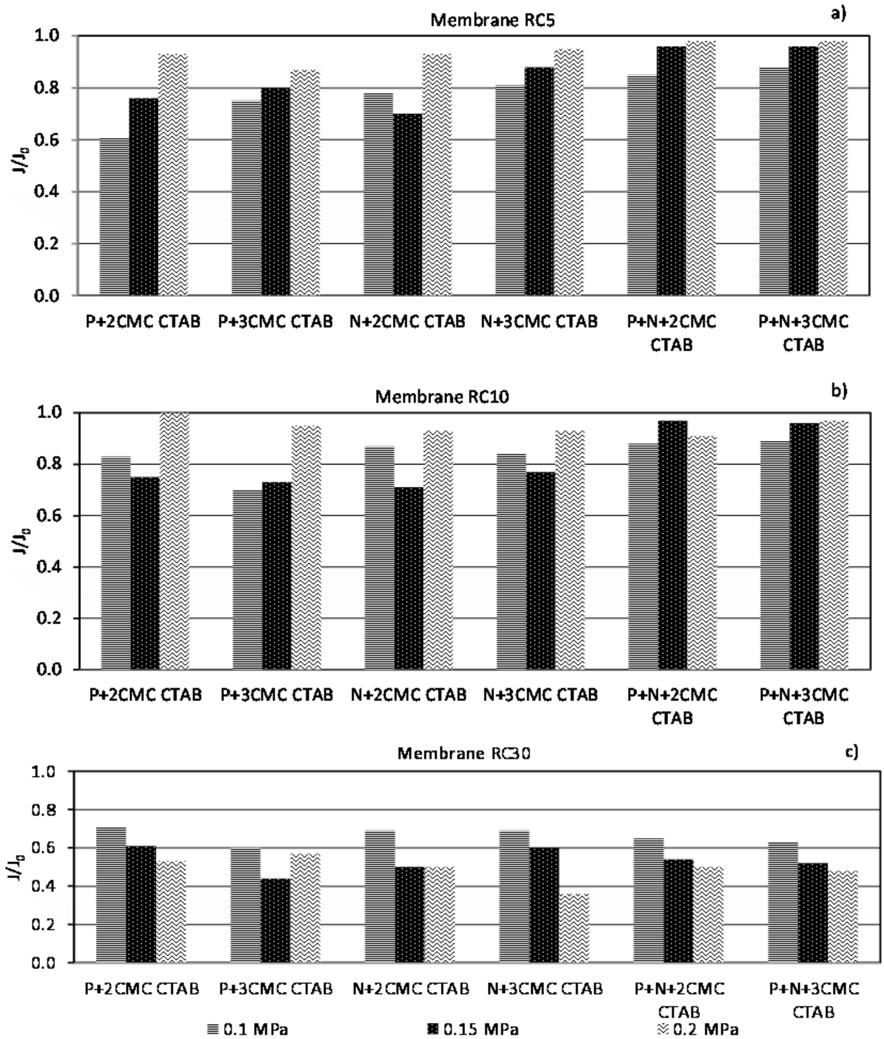


Fig. 6. The membrane relative permeability ($J/J_0$) for membranes made of regenerated cellulose (RC) vs. CTAB concentration in one- and two-component model aqueous solutions: a) MWCO 5 kDa, b) MWCO 10 kDa and c) MWCO 30 kDa

Comparing the process efficiency for one- and two-component aqueous solutions, it is evident that the MEUF process of one-component solution is much more promising for diminishing nitrate and phosphate concentration and that the RC10 membranes are characterized by the best properties towards nitrate and phosphate separation. The MEUF process seems to be suitable for nitrate and phosphate removal from aqueous solution, however the relevant surfactant should be selected for this purpose.

In the course of experiments, the permeate volume flux was also determined. During the experiments, the volume flux of distilled water ($J_0$) was measured for all tested membranes and the following values were obtained (at 0.2 MPa): 0.83; 1.30, and 10.80 $m^3/(m^2 \cdot day)$ for RC5, RC10 and RC30, respectively. Apart from good separation results, the membrane process should be characterized by sensible hydraulic permeability. Thus, the permeate volume flux for all tested membranes in relation to the type and kind of solutions at various TMP was determined (Fig. 5).

The volume flux was strongly dependent on the TMP – the higher the transmembrane pressure the greater the value of volume flux. The observed volume fluxes for two-component solutions for all tested membranes were much higher than for one-component solutions (Fig. 5).

Analyzing the membrane relative permeability ($J/J_0$) (Fig. 6) it can be proved that the least susceptible to fouling is membrane characterized by the quite low MWCO (10 kDa). For both one- and two-component solutions, the membrane relative permeability was the highest for 10 kDa membrane. The MEUF experiments performed with two-component solutions showed less fouling potential of all tested membranes. The relative membrane permeability varied from approximately 0.5 (RC30 membrane) to approximately 0.9 (RC5 and RC10 membrane), however the membranes of the highest MWCO were the most susceptible to pore blocking. Generally, it can be concluded that increasing the concentration of surfactant increases the membrane susceptibility to fouling in the course of MEUF process.

In terms of the removal efficiency of nitrates and phosphates from one- and two-component solutions, better results were obtained for one-compound solutions. However, the membrane relative permeabilities were higher in the MEUF process of two-component solutions. Generally, increasing the concentration of surfactant increases the retention coefficient of pollutants. The concentration of CTAB had no significant effect on the removal of nitrogen compounds, which proves an appropriate selection of the surfactant ($R > 70\%$). The phosphate removal from both one- and two-component solutions is not satisfactory but indicates their potential removal by the MEUF process.

## 4. CONCLUSIONS

- The presence of phosphate and nitrate salts in surfactant solutions caused a decrease in the *CMC* of cetyltrimethylammonium bromide (CTAB) by approximately 50%.
- The surfactant enhanced ultrafiltration (MEUF) is a suitable technique for the removal of inorganic nitrogen compounds, to a lesser extent to the removal of inorganic phosphate compounds from aqueous solutions.

• In the MEUF process performed with the use of regenerated cellulose membranes and a cationic surfactant cetyltrimethylammonium bromide, the nitrate retention coefficient amounted to 73–91%, whereas the phosphate retention coefficient gave less promising results (11–34%).

• Increasing the concentration of CTAB in the treated solution did not improve the nitrate retention significantly but phosphate removal was considerably enhanced.

• The regenerated cellulose membranes of the highest MWCO (30 kDa) were the most susceptible to fouling.

• Comparing the process efficiency for one- and two-component solutions, it can be concluded that MEUF process with one-component solution is much more favorable for diminishing nitrate and phosphate concentration than MEUF process with two-component solutions.

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