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## SURFACTANT ENHANCED ULTRAFILTRATION FOR THE REMOVAL OF INORGANIC PHOSPHOROUS COMPOUNDS FROM AQUEOUS SOLUTIONS

The usability of the micellar enhanced ultrafiltration (MEUF) for removal of phosphates from aqueous solutions has been evaluated. The process was performed with the use of polyethersulfone membranes under various transmembrane pressures (0.1, 0.15, and 0.2 MPa). Phosphorous solutions containing 15 mg of  $\text{PO}_4^{3-}/\text{dm}^3$  and two cationic surfactants: octadecylamine acetate (ODA) and hexadecylpyridium chloride (CPC) were used in the tests. The concentration of ODA and CPC amounted to 2 and 3 CMC (Critical Micelle Concentration) as well as 2, 3 and 6 CMC, respectively. The results of the study showed that the surfactant type and its concentration influenced the process efficiency. The phosphate removal with the use of ODA was approximately 95%, whereas application of CPC gave unsatisfactory results.

### 1. INTRODUCTION

Phosphorus circulates constantly in the local and global environment. As a biogenic element, it is important for life and growth of living organisms. Anthropogenic phosphorus enters the water environment mainly due to run-off of fertilizers and wastewater discharging. Phosphates are the main contaminants that accelerate eutrophication process in surface water. To avoid uncontrolled growth of algae in surface waters there is a need to minimize phosphorous concentration in the treated domestic and industrial wastewater. A number of effective and reliable techniques can be applied. The phosphorous is removed from wastewater phase mostly into sludge phase. However, there are some techniques where phosphorous can be removed in the form of inorganic phosphate salt. This salt can be useful in some industrial applications [1].

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The most efficient methods of phosphorous removal are quite expensive. On the other hand, the cheapest ones are not very efficient. Therefore, surfactant enhanced ultrafiltration is being investigated. This is a new pressure membrane method that enables removal of low-molecular-weight contaminants (mainly inorganic) from water or wastewater.

Micellar enhanced ultrafiltration (MEUF) is a surfactant-based separation technology allowing removal of dissolved contaminants by the ultrafiltration technique. It is characterized by high separation coefficients (similarly as in the case of reverse osmosis) and high permeate volume fluxes under low transmembrane pressures (as in the case of ultrafiltration, UF). The former MEUF feature is gained due to the use of surfactants facilitating removal of small pollutants by entrapping them into micelles. Surfactant micelles are large enough to be rejected by UF membranes. The latter characteristics arises from the use of UF membranes which can operate under low transmembrane pressure providing a relatively high permeate flux. Pollutant molecules and surfactant micelles create complexes which do not pass through UF membranes, concentrating in the retentate, while the permeate is practically pure water. Only small amounts of surfactant monomers and unfixed pollutant molecules can pass through the membrane into permeate [2–6].

Cationic surfactants have a tendency to form micelles with positive surface electrical charge at concentrations higher than the so-called critical micelle concentration (CMC). The created micelles can interact electrostatically with pollutants of anionic type [7]. MEUF performed with the use of cationic surfactants can be applied in removal of anionic pollutants, for example anionic heavy metals [8], dyes [9] or phosphates [10]. The MEUF process using cationic surfactants is mostly used for wastewater treatment.

The most powerful and often used surfactant in wastewater treatment is hexadecylpyridium chloride (CPC). With the help of this surfactant it is possible to remove anionic contaminants, e.g. anionic dyes from textile effluents. Purkait et al. [9] studied the MEUF process with the use of CPC towards eosin dye removal and proved that it was possible to eliminate this dye from aqueous solution in 74%. Other researchers, Ahmad et al. [11] report 99% removal of reactive dyes using CPC as a cationic surfactant in the MEUF process. These results confirm the suitability of CPC, as well as the MEUF method in diminishing of anionic dye concentration in industrial effluents. What more, hexadecylpyridium chloride (CPC) surfactant can be used to separate other hazardous pollutants from wastewaters. Luo et al. demonstrated [12] that the removal of phenol using CPC was higher than with the use of other cationic surfactants. This was due to structural similarity of phenol and CPC molecules – both substances have aromatic rings in their molecules. The removal efficiency of phenol was 93.8% (in the case of CPC), whereas in the MEUF process involving other cationic surfactants such as hexadecyltrimethylammonium bromide (CTAB) or octadecyl trimethyl ammonium bromide (OTAB), the results obtained were slightly worse – the

separation coefficient amounted to 85.9% and 92.4%, respectively. These findings supported the importance of surfactant selection on the basis of its structural properties as well as the knowledge of the molecular structure and ionic charge of separated contaminants. Camarillo et al. [10] applied octadecylamine acetate (ODA) and CPC to remove phosphate ions from treated domestic wastewaters. They found that the concentration of both surfactants should be increased over 1 CMC to obtain the phosphate rejection coefficient of about 95%. However, the loss of permeate flux was equal to 30% in both cases. Majewska-Nowak [13] obtained almost 100% retention of anionic dyes in UF process enhanced by CTAB.

It can be anticipated that MEUF process could be one of the alternative techniques of water or wastewater treatment due to promising high rejection of contaminants. The prime factor in enhancing the process efficiency is the knowledge of surfactant properties and appropriate surfactant selection for a given pollutant [14].

The objective of the study was to evaluate the removal efficiency of inorganic phosphorous compounds from aqueous solutions by the surfactant enhanced ultrafiltration (MEUF) using two cationic surfactants.

## 2. EXPERIMENTAL

In the experiments, commercially available asymmetric ultrafiltration membranes made of hydrophilic polyethersulfone (PESH) were used. Membranes were characterized by various molecular weight cut-off – 4, 30, 50 kDa (Table 1).

Table 1

Characteristics of Microdyn Nadir<sup>®</sup> membranes [15]

| Membrane | MWCO [kDa] | Membrane material | Water flux <sup>1</sup> [dm <sup>3</sup> /(m <sup>2</sup> ·h)] |
|----------|------------|-------------------|--|
| UH004    | 4          | PESH              | >20  |
| UH030    | 30         |                   | >100   |
| UH050    | 50         |                   | >250   |

<sup>1</sup>Measured under 0.3 MPa.

In the experiments, aqueous model solutions containing potassium dihydrogen phosphate (KH<sub>2</sub>PO<sub>4</sub>) were used. The concentration of phosphates in the tested solutions was 15 mg PO<sub>4</sub><sup>3-</sup>/dm<sup>3</sup>. Two surface active agents of cationic type: hexadecylpyridium chloride (CPC) and octadecylamine acetate (ODA) were applied in the experiments. The concentration of CPC was equal to 2, 3, and 6 CMC (Critical Micelle Concentration), whereas ODA concentration amounted to 2 and 3 CMC. The CMC of CPC surfactant

in pure water corresponds to  $322.2 \text{ mg/dm}^3$ , whereas the value of CMC for ODA surfactant is equal to  $296.6 \text{ mg/dm}^3$  (Table 2).

Table 2

Characteristics and concentration of cationic surfactants used in the experiments [10]

| Surfactant                       | CMC<br>[mM] | $M_w$<br>—[g/mol] | 2CMC                  | 3CMC  | 6CMC   |
|----------------------------------|-------------|-------------------|-----------------------|-------|--------|
|                                  |             |                   | [mg/dm <sup>3</sup> ] |       |        |
| Hexadecylpyridium chloride (CPC) | 0.90        | 358.01            | 644.4                 | 966.6 | 1933.2 |
| Octadecylamine acetate (ODA)     | 0.90        | 329.05            | 593.2                 | 889.8 | —      |

In the MEUF process of phosphate removal from aqueous solutions the Amicon 8400 ultrafiltration cell was used (Fig. 1). The total volume of the UF cell amounted to  $350 \text{ cm}^3$  and the diameter of the membranes being tested was 76 mm. The aqueous solution containing phosphates and surfactant were continuously mixed with a magnetic stirrer. The UF process was run under the transmembrane pressure (TMP) ranging from 0.1 to 0.2 MPa.

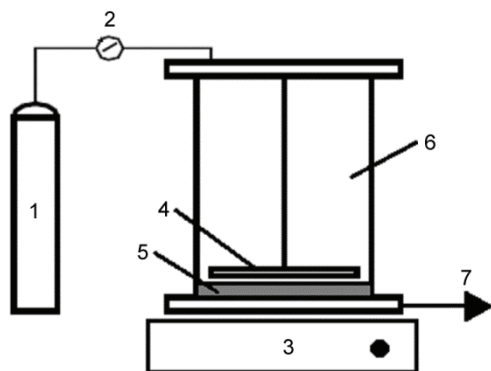


Fig. 1. Schematic representation of Amicon 8400 ultrafiltration cell: 1 – gas cylinder, 2 – pressure gauge, 3 – magnetic stirrer, 4 – stirrer bar, 5 – membrane, 6 – feed, 7 – permeate/filtrate

In the course of experiments, the permeate volume flux and phosphate retention coefficient were determined. The distilled water permeability,  $J_0$  was also measured. The experiments for phosphate model solutions were conducted under conditions of steady flow.

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

$$J = \frac{V}{At} \quad [\text{m}^3/(\text{m}^2 \cdot \text{d})]$$

where  $V$  denotes the permeate volume,  $\text{m}^3$ , obtained during a certain time  $t$ , day. The surface area of the membrane  $A$  was equal to  $4.52 \times 10^{-3} \text{ m}^2$ .

Phosphate concentration in aqueous solutions was determined by the spectrophotometric method (according to PN-EN ISO 6878:2006). To determine the phosphate content (in the form of orthophosphates) a spectrophotometer WTW type MPM 3000 was used. The phosphate concentration in model solutions was measured before and after the MEUF process. The phosphate retention coefficient  $R$  was calculated from the formula:

$$R = \frac{C_R - C_P}{C_R} \cdot 100 \quad [\%]$$

where  $C_R$  and  $C_P$  are phosphate concentrations in the retentate and permeate, respectively.

### 3. RESULTS AND DISCUSSION

The MEUF efficiency in the removal of phosphates from aqueous solutions has been evaluated using UF membranes varied in MWCO as well as various surfactants. Figure 2 shows the phosphate retention coefficients at various concentrations of CPC (2, 3 and 6 CMC), ODA (2, 3 CMC) under various TMP (0.1, 0.15, 0.2 MPa).

The phosphate retention coefficients for experiments with CPC varied in a great range – from 42 to 79% depending on the surfactant concentration, membrane MWCO and applied pressure. On the contrary, the removal of phosphates in MEUF process with ODA surfactant followed quite a different pattern – the retention coefficients varied in a small range (from 95 to 99%) with variable process parameters.

The removal of phosphates with the use of CPC significantly depends on the surfactant concentration. Upon increasing the CPC concentration in the treated solution, the separation efficiency also increases (Figs. 2a–c). Experiments with ODA demonstrated very good phosphate rejection (above 95%) irrespectively of the surfactant amount added to the feed solution (Figs. 2d–f). The retention coefficients obtained for experiments performed with CPC were below 90%, which does not provide a satisfactory MEUF performance in view of phosphorous compound removal. Camarillo et al. [10] also investigated the MEUF process with the use of CPC and ODA with the aim 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%. However, loss of permeate flux (in relation to water flux) was equal to approximately 30% regardless of the surfactant applied. The investigations reported by Camarillo et al. [10] have been conducted on the treated domestic wastewater from the reclamation station of the University Campus of Toledo. What more, they used ceramic membranes in the MEUF. Application of a real effluents instead of model solutions as well as inorganic membrane material instead of polymer

material could be a key reasons of the differences in the results obtained by Camarillo et al. [10] and those reported in the present paper. Ceramic and polymer membranes can be characterized by different surface charge (negative or positive) depending on the composition and pH of the feed solution. These factors may affect electrostatic interaction between surfactant micelles, membrane and ionic compounds present in treated solution.

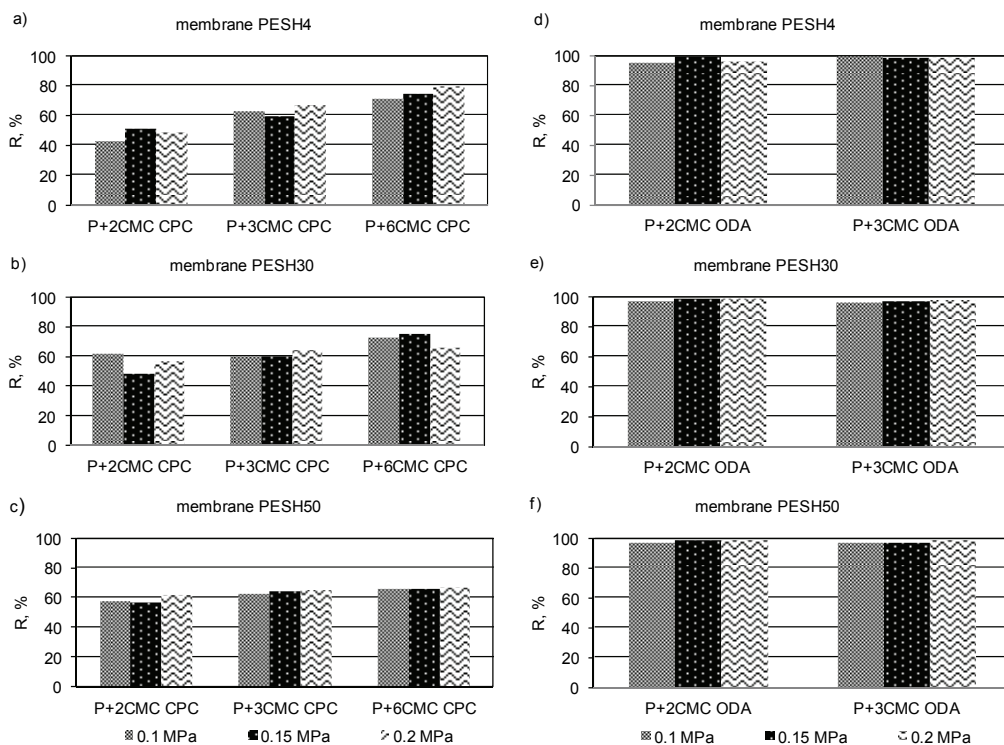


Fig. 2. Phosphate retention coefficient ( $R$ ) for membranes made of hydrophilic polyethersulfone (PESH) versus CPC and ODA concentration in model aqueous solutions:

a) and d) MWCO 4 kDa; b) and e) MWCO 30 kDa; c) and f) MWCO 50 kDa

Comparing the process efficiency for both cationic surfactants it can be stated that the MEUF process with the use of ODA is much more favorable for diminishing phosphorous concentration in water environment than the MEUF process with CPC. The phosphate rejection coefficient amounted to approximately 96% and only 43% for ODA and CPC, respectively at 2 CMC and TMP 0.1 MPa for membranes of MWCO 4 kDa (Fig. 2). The process performance when ODA was applied at 2 CMC was quite satisfactory, whereas the best results (i.e. phosphate rejection of 79%) in the case of CPC were achieved for very high surfactant concentration – 6 CMC (for membrane of MWCO 4 kDa under 0.2 MPa). A slight tendency of rejection improvement with the

increasing TMP, especially for low MWCO membrane, was observed when CPC was used. Basically, the MEUF process with ODA resulted in very high phosphate separation regardless of the transmembrane pressure applied. An insignificant trend of increasing rejection coefficient with the increase of TMP for PESH30 and PESH50 membranes was observed (Figs. 2e, f). The increase in membrane MWCO caused a slight improvement in the phosphate retention coefficient when CPC was applied in the concentration of 2 CMC, whereas for the highest surfactant concentration (6 CMC) the opposite relationship was observed – the higher the membrane MWCO the worse phosphate separation was. The MEUF process with ODA showed satisfactory phosphate retention regardless of the membrane cut-off.

Taking into account the results obtained, it can be concluded that the MEUF process can be suitable for phosphate removal from aqueous solution, however the relevant surfactant should be selected for this purpose.

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 surfactant concentration under various TMP was determined (Fig. 3).

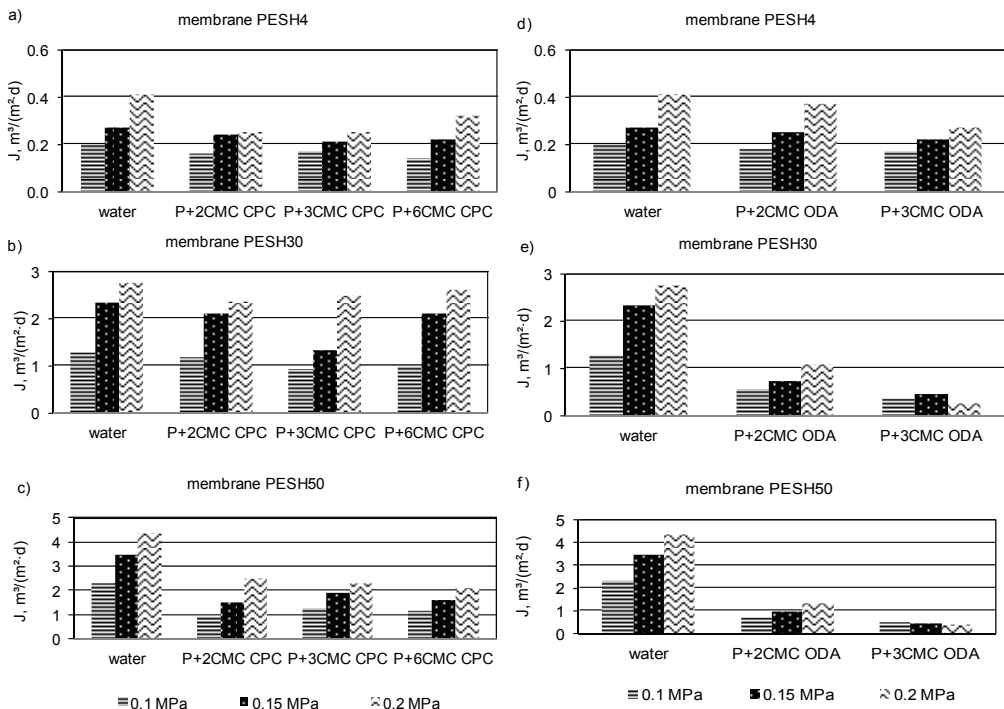


Fig. 3. Volume flux ( $J$ ) for membranes made of hydrophilic polyethersulfone (PESH) versus CPC and ODA concentration in model aqueous solutions: a) and d) MWCO 4 kDa; b) and e) MWCO 30 kDa; c) and f) MWCO 50 kDa

The permeate permeability investigations were carried out by measuring the volume flux of distilled water  $J_0$  for all tested membranes and the following values were obtained (under 0.2 MPa): 0.41, 2.75, and 4.34  $\text{m}^3/(\text{m}^2 \cdot \text{d})$  for PESH4, PESH30, and PESH50, respectively. The volume flux was strongly dependent on the TMP. The higher the transmembrane pressure the greater volume flux was. The observed volume fluxes for solutions containing ODA (Figs. 3d–f) were much lower than for solutions containing CPC (Figs. 3a–c). The PESH membranes in the course of MEUF were subjected to fouling, especially for experiments with ODA and membranes of high MWCO (30 and 50 kDa). The permeate flux for PESH30 and PESH50 membranes determined at ODA concentration equal to 3 CMC constituted only 10% of water flux (Fig. 3d, e). Analyzing the membrane relative permeability ( $J/J_0$ ) it can be proved that the least susceptible to fouling is membrane characterized by the low MWCO (4 kDa). The relative permeability for PESH50 membrane was lower than 0.25 for both ODA concentration and all applied TMP. The MEUF experiments performed with CPC solutions showed lower fouling potential of all tested membranes – the relative membrane permeability varied from approximately 0.5 (PESH50 membrane) to approximately 0.9 (PESH4 membrane).

Previous studies [16] conducted on cellulose UF membranes using hexadecyltrimethylammonium bromide (CTAB) showed less susceptibility of membranes to fouling. However, the separation efficiency of phosphorous compounds was much poorer than that reported in this paper for MEUF with ODA.

Membranes of the highest MWCO were the most susceptible to pore blocking, especially when solutions containing ODA were tested. This may be attributed to the difference in micelle size of various surfactants. The micelles are composed of 50–200 monomers. Their shape and size is affected by geometric and energetic parameters. On the other hand, the micelle size is influenced by an average aggregation number that corresponds to the average number of surfactant molecules in a micelle. The aggregation number depends on many factors such as surfactant concentration, length of the hydrocarbon chain of the surfactant, type of the counter ions associated with the surfactant molecules, and many other parameters [17].

Generally, it can be concluded that increasing the concentration of surfactant increases the membrane susceptibility to fouling in the course of the MEUF process. The usage of surfactants in high concentrations (above 3–4 CMC) should not be recommended. It does not improve significantly the effectiveness of phosphate removal and, what more, has a disadvantageous effect on the membrane relative permeability.

#### 4. CONCLUSIONS

The surfactant enhanced ultrafiltration (MEUF) is a suitable technique for removal of inorganic phosphorous compounds from aqueous solutions provided that an appropriate surfactant is selected.



In the MEUF process performed with the use of hydrophilic polyethersulfone membranes and a cationic surfactant – octadecylamine acetate (ODA), the phosphate retention coefficient amounted to 95–99%, whereas application of hexadecylpyridium chloride (CPC) arrived at a less promising results (42–79% retention of phosphates).

Increasing the concentration of ODA surfactant in the treated solution did not improve significantly the phosphate retention.

Hydrophilic polyethersulfone membranes of the highest MWCO (50 kDa) were the most susceptible to fouling, especially when solutions containing ODA were tested.

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