

Removal of metal ions from aqueous solutions by micellar enhanced ultrafiltration (MEUF)

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The results of preliminary research on the possibility of removing of chromium(III) and copper(II) ions from micellar solutions in MEUF were described. The effectiveness of metal ions removal in the classical UF and MEUF was compared. It was confirmed that in the classical UF the retention of metal ions is small, independent of the concentration of the feed solution. The cross-flow micellar enhanced ultrafiltration experiments showed the usefulness of this method for the separation of metal ions from micellar solutions. The retention of metal ions in MEUF process is almost total in the case of the solutions of low concentration. However, for more concentrated solutions the retention is much smaller.

Keywords: removal of metal ions, micellar enhanced ultrafiltration, MEUF.

INTRODUCTION

The pollution of industrial sewages by the heavy metals causes serious problems for the environment¹. Some of them are dangerous to health or to the environment (e.g. Hg, Cd, As, Pb, Cr), some may cause corrosion (e.g. Zn, Pb), some are harmful in other ways (e.g. Arsenic may pollute catalysts). The choice of the method for industrial sewage treatment depends on the number of factors, among which the most important are: the content of individual form of a given chemical element in sewage, its concentration, presence of different impurities, final required concentration, costs of the process as well as the standards for wastewater². There are a lot of methods of sewage treatment, for example: solvent extraction, distillation, adsorption and also membrane techniques: electro dialysis, dialysis, microfiltration, nanofiltration or reverse osmosis.

Lately the growth of interest in unconventional extraction systems, more friendly for the ecosystem according to the *green chemistry*, has been observed. The reason for searching an alternative to solvent extraction as a method of metal ion removal are high operating costs of the process (caused by the loss of an organic phase, therein extractant) and first of all the ecological aspects³. The unconventional methods of metal ion separation permit to eliminate the large volume of the organic phase from the process, which makes up the essential ecological threat, particularly in the case of the mixer-settler systems. Among unconventional solutions the use of ionic liquids in the extraction systems (as solvent or extractant), the use of micellar solutions in the ultrafiltration or the micellar extraction process⁴ could be mentioned.

In recent years the use of unconventional separation techniques for the treatment of the sewage mentioned above has been researched. A lot of works present the utilization of micellar enhanced ultrafiltration (MEUF). MEUF is the hybrid process – combination of classical ultrafiltration and solubilization of selected compounds from aqueous solution by surfactants^{5–7}.

The ultrafiltration from micellar solutions is a promising method of the treatment of the aqueous solutions

polluted by heavy metal ions¹, the small organic compounds, and also the inorganic impurities⁸.

Membrane techniques are a younger field of the separation process than solvent extraction. From the economical point of view the solvent extraction is a cheaper technique comparing the cost of installation building as well as the costs of its exploitation, or the energy requirement. However, including the efficiency of the process the micellar enhanced ultrafiltration (MEUF) is more effective than solvent extraction techniques. Sometimes the retention of the separated substances could achieve almost 100%. Moreover, the purified sewage (permeate) by the micellar ultrafiltration has the highest qualitative standards, the technology has no waste products. Thus this technique is consistent with environmental standards and *green chemistry* rules⁹.

In the micellar ultrafiltration process the solution of surfactants with the concentration above the critical micellar concentration (CMC) is added to the solution of a separated substance, where the molecules/the ions of the removed substances are solubilized in the micelles. The diameter of the micelles is usually larger than the diameter of membrane pores and due to the ultrafiltration process the solubilized compounds stay in retentate, while permeate contains nonsolubilized molecules of the separated compounds as well as the small amount of the monomeric form of the surfactant¹⁰. The elimination of the organic solvent from the separated system is the primary advantage of the MEUF method. The replacement of the hydrocarbon solvents by the surfactants is profitable from the ecological point of view providing that the surfactant shows the smaller toxicity than the solvent, it permeates in small amounts to the permeate flux, and having penetrated there it is neutralized, for example by precipitation or relatively fast and full biodegradation, without creating toxic metabolites.

The type and structure of the applied surfactants have fundamental importance in the micellar enhanced ultrafiltration process. It influences the size of the micelles and their abilities to solubilize the removed substances/ions, possibility of precipitation, tendency to block the membranes as well as the quantity of the surfactant in the permeate flux.

In MEUF process ionic surfactants (anionic or cationic) or nonionic surfactants could be applied¹¹. The cationic surfactants are seldom used, because of the tendencies to adsorb on the membrane surface, which causes the increase of the mass transport resistance during the MEUF process¹². Among anionic surfactants sodium dodecyl sulfate (SDS) is widely applied because of an effective removal of the heavy metal ions, such as: chromium¹⁰, cadmium^{13, 14}, cobalt¹⁵, nickel¹⁶ as well as zinc¹⁷.

The aim of this preliminary work is to show the usefulness of micellar enhanced ultrafiltration techniques as the method of the removal of Cu(II) and Cr(III) ions from aqueous solutions.

EXPERIMENTAL PART

In the initial stage of the research the separation of ions of Cu(II) from the solutions of copper sulphate(II) ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and Cr(III) from nitrate solutions of chromium(III) ($\text{Cr}(\text{NO}_3)_3$) with the classical technique of ultrafiltration was carried out. Then the same procedure was repeated in micellar systems with the addition of anionic surfactant – sodium dodecyl sulfate (SDS). The concentration of the surfactant was equal to 5 CMC. The critical micelle concentration (CMC) of SDS in deionized water was equal to 2.39 g/L.

The ultrafiltration experiments were carried out in the SEPA CF Membrane Cell produced by OSMONICS, USA (Fig. 1) using membranes made of polyvinylidene fluoride (PVDF). The effective surface area of the membrane was 0.0155 m². The molecular weight cut-off of PVDF

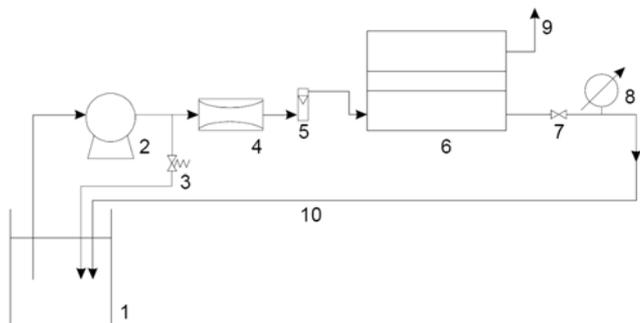
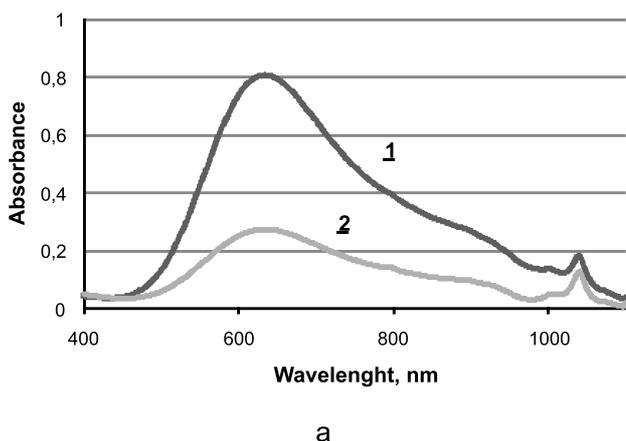


Figure 1. The scheme of the experimental setup: (1) feed vessel, (2) pump, (3) overflow valve, (4) vibration damper, (5) rotameter, (6) membrane module OSMONICS, (7) valve, (8) manometer, (9) permeate flux, (10) retentate flux



membrane was 15 000 – 25 000. The membranes were used repeatedly. Prior to ultrafiltration, the membranes were conditioned in deionized water for 24 hours. The fluid was forced through the membrane at a transmembrane pressure of 0.2 MPa. The inlet reservoir was initially filled with a 1000 ml of feed solution and the process was stopped when 500 ml was taken as a permeate.

The concentration of the surfactant in the permeate as well as the CMC of surfactant were determined by the conductometric method¹⁸. The metal concentration in the permeate was determined by UV spectroscopy (Fig. 2) using a UV VIS SPECORD 40, Analytic Jena, Germany¹⁹.

In the experiments with or without the addition of surfactants, the separation efficiency is defined by the following equation, where c_p represents the concentration of metal ion in the permeate and c_N is an initial concentration of metal ion in the feed solution:

$$R(\%) = 1 - \frac{c_p}{c_N} \cdot 100$$

RESULTS

Characterization of the membrane

In the first stage of the research the basic parameters describing the membrane were estimated and the obtained data are summarized in Table 1. Hydrodynamic permeability coefficient (L_p) obtained during the water filtration (derived from the linear relationship between permeate flux and transmembrane pressure) was compared to the value of L_p obtained for solution of SDS. More than threefold higher values of hydrodynamic permeability coefficients were determined during the filtration of deionized water, because there was no additional filtration resistance. The obtained results demonstrate strong interaction between surfactant molecules and the surface of the PVDF membrane, which causes significant filtration resistance.

Table 1. The values of the hydrodynamic permeability coefficient (L_p)

Feed	$L_p \cdot 10^{10}$ [m ³ /m ² sPa]
Water	6.95
SDS solution	2.00

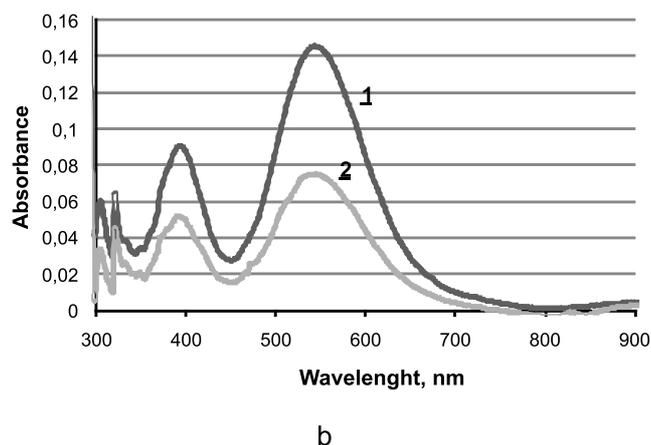


Figure 2. UV/VIS absorption spectra of a) Cu(II) and b) Cr(III), line 1 – permeate without SDS, line 2 – permeate with addition of SDS

Determination of metal concentration

Initially, the metal concentration was determined using atomic absorption spectrophotometry (Varian SPECTRAA800). However, the addition of the surfactant to the system constituted a serious limitation of this method. During the analysis the flame disappeared. Therefore other methods were searched. It was found that spectral analysis of UV/VIS has no such restrictions. Addition of surfactants did not cause a shift in absorbance maximum (Fig. 2).

Determination of surfactant

One of the disadvantages of the micellar enhanced ultrafiltration is, as it was mentioned above, penetration of the surfactant through the membranes to permeate fluxes. Since pollution due to the presence of the surfactant in the permeate can present an environmental problem, the retention of the surfactant, in the absence of any metal ion in the filtrated solution was investigated.

For this purpose the filtration of the surfactant solution was performed. Figure 3 presents typical filtration results of 5 CMC SDS solution through a polyvinylidene fluoride membrane. Significant changes in the surfactant concentration were observed during the first 30 min of the separation process. However, during the whole time of the experiment (3 hours) the concentration of SDS in the permeate flux was below its CMC. Thus the applied ultrafiltration membranes allow permeation of the surfactant monomers only, but simultaneously reject micelles almost completely. A similar relationship was observed by other authors²⁰.

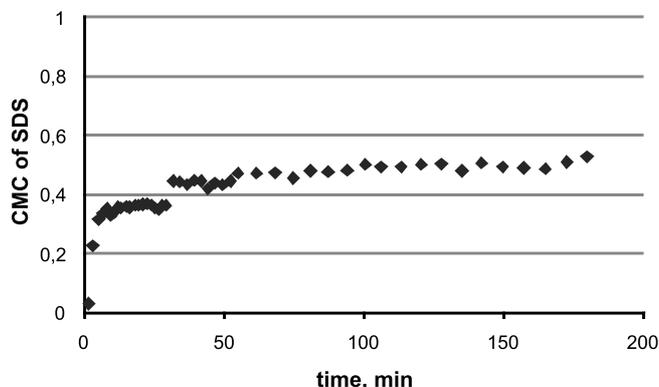


Figure 3. Concentration of SDS in the permeate (CMC of SDS) as a function of time

Ultrafiltration of metal ions in the absence of surfactant (classical UF process)

Figure 4 shows the results of metal separation using classical ultrafiltration. It is noted that the rejections of Cu(II) and Cr(III) are small and do not reach 25%. Higher retention is observed when the dilute solution of metal ions is investigated. Thus, as it could be expected, the efficiency of the classical ultrafiltration process is unsatisfactory. Similar results were observed by Ennigrou et al.²¹ in the process of Cd(II) ion separation. Cited authors observed also a low value of the retention (near 11%).

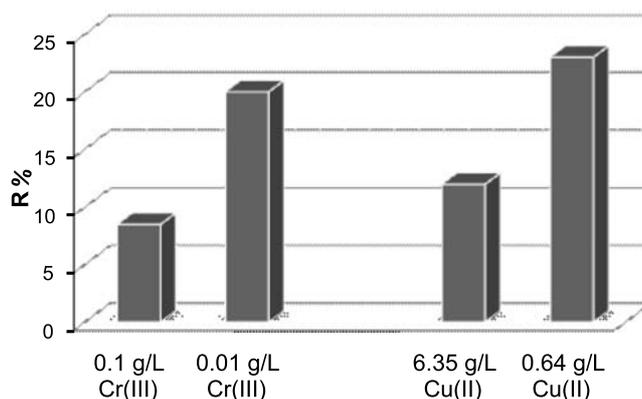


Figure 4. Separation of metal ions of different concentration in a classical ultrafiltration process

Ultrafiltration of metal ions with addition of surfactant (MEUF process)

The applicability of micellar enhanced ultrafiltration method to metal ions separation was examined by the use of sodium dodecyl sulfate. Figure 5 shows the results of metal ions separation using the MEUF. It is to be noted that the rejection of Cr(III) and Cu(II) is significantly higher in comparison with the classical ultrafiltration process presented in Figure 4.

The results presented in Figure 5 show high effectiveness of the proposed method for the removal of chromium(III) and copper(II) from aqueous solutions. It is particularly noticeable in the case of the solutions with low concentrations of metal ions, where there was almost total retention of copper and chromium on ultrafiltration membrane, as evidenced by the high degree of retention of metal ions, within the range 90 – 95%. In the case of high concentrations of copper sulphate(II) in the feed (6.35 g/L), despite large amount of surfactant present in the system (5 CMC) the results of copper(II) ion separation are unsatisfactory. In this case, the retention of Cu(II) amounted to around 14%.

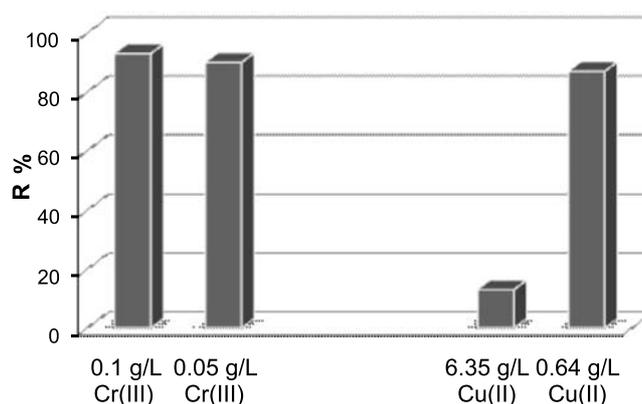


Figure 5. Separation of metal ions of different concentration in the micellar enhanced ultrafiltration process

CONCLUSIONS

The cross-flow micellar ultrafiltration preliminary experiments showed the usefulness of this method for the separation of Cr(III) and Cu(II) ions from micellar solutions.

It was confirmed that the effectiveness of chromium(III) and copper(II) ion separation in the classical ultrafiltration was not satisfactory.

The micellar-enhanced ultrafiltration of metal ions has proved to be a promising new technique for the concentration of these ions in an aqueous waste stream under controlled operating conditions. Moreover, the MEUF process could be adopted for obtaining pure water from the aqueous solution containing metal ions.

The improved percentage removal of chromium and copper at lower concentration is a valuable practical aspect of MEUF. While some metal clean-up techniques, such as precipitation by pH adjustment, exhibit a decrease in efficiency as the metal becomes more dilute, MEUF exhibits an increase in efficiency.

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