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SURFACTANT-AIDED MEMBRANE PROCESS
FOR COPPER ION REMOVAL FROM WATER SOLUTIONS

The usefulness of micellar-enhanced ultrafiltration (MEUF) for copper ion removal was evaluated. The experiments were performed in a semi-pilot installation in a cross-flow regime with the use of ultrafiltration modules (5 kDa and 10 kDa). The first stage of the tests included copper ion removal in the classic UF process. During the next step, anionic surfactant (sodium dodecylbenzenesulfonate, SDBS) was added to the feed solution in a wide range of concentrations. The effect of copper and surfactant concentrations on separation efficiency and permeate flux was evaluated. It was found that MEUF enables high copper ion removal. Depending on surfactant concentration in the feed solution, the average copper concentration in the permeate was in the range from 0.02 to 0.08 mM (feed solution 0.79 mM). Surfactant rejection was strongly dependent on its concentration in the feed; the highest retention was obtained when surfactant was in the form of micelles, i.e., for concentrations exceeding the CMC.

1. INTRODUCTION

Industrial development leads to the production of large amounts of wastewater containing various types of heavy-metal compounds, which have harmful effects on living organisms. Heavy-metal ion removal processes are usually conducted on the premises of the producing facility, due to the danger of toxic impurities escaping into the environment during transport to the wastewater treatment plant.

Industrial wastewater treatment may be realised by the use of various conventional methods such as precipitation, flotation, adsorption, ion exchange, and electrochemical deposition [1]. Heavy metals are valuable compounds; thus, not only their removal is required, but also recovery of useful ingredients. Membrane separation processes are

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treatment techniques which enable this purpose to be fulfilled in contrast to conventional methods. Literature data reports high-pressure driven membrane processes (reverse osmosis and nanofiltration) as suitable methods for divalent ion separation [2, 3]. Micellar enhanced ultrafiltration (MEUF) is often proposed as a method for dissolved-matter removal from water solutions. MEUF is a hybrid process, which connects a pressure-driven membrane process with the ability of surface-active agent's micelles to bind ionic impurities of opposite charge to that of the surfactant. The concentration of surfactant above which micelles are formed is named the critical micelle concentration (CMC). The useful property of the micelles is the fact that their size is generally greater than the pore size of the ultrafiltration membrane; thus, separation of micelles (and bound ions) based on a sieve mechanism may be performed with high efficiency. As a result, a feature of reverse osmosis (high rejection) is combined with lower pressure, typical of ultrafiltration [4].

MEUF has been tested for the removal of organic compounds (phenol [5], organic acids [6], pharmaceuticals [7, 8], dyes [9, 10]) and dissolved ions (heavy [11, 12] and precious metals [13], inorganic ions [14, 15]) from water solutions. Literature data mostly report high separation efficiency of the above-mentioned pollutants; however, most studies ignore the problem of secondary contamination of the treated solutions by surfactant molecules. The second, equally important issue is the need to recover valuable compounds and/or surfactants to reduce the operating costs of the MEUF process.

Huang et al. [16] recovered more than 85% of SDS (sodium dodecyl sulfate) from concentrate obtained during cadmium MEUF in the process of acidification. Also, by means of acidification, Li et al. [17] recovered and reused SDS employed for zinc and cadmium removal. The obtained separation of heavy metals by application of reclaimed SDS was above 80%. These examples prove the possibility of surfactant regeneration from the concentrate and reuse in following processes.

Table 1

Removal of single metals by MEUF process with the use of SDS

Contaminant		Membrane			SDS concentration [CMC]	Metal retention [%]	Ref.
Metal ion	Concentration in the feed [mg/dm^3]	Material	MWCO [kDa]	Filtration regime			
Co^{2+}	10	zirconium oxide	210	cross-flow	0.5	88	[19]
Cr^{3+}	100	cellulose acetate	15		2.5	90	[20]
Mn^{2+}	100	polysulfone	–		1.2	97	[21]
Mn^{2+}	55		10		0.2	>97	[22]
Mo^{6+}	96		30		0.75	90	[23]
Pb^{2+}	50	cellulose	10		0.2–2	>93	[24]
Zn^{2+}	20.2	polyacrylonitrile	300		1	73	[25]

So far, the anionic surfactant most employed for removal of heavy metal cations is sodium dodecyl sulfate (SDS, CMC ca. 2250 mg/dm^3, molecular weight 288.37 Da) [18]. Examples of values of single-ion removal in the MEUF process using SDS are shown in Table 1. The effectiveness of the MEUF is the result of many factors, including ion concentration in solution, surfactant concentration, type of membrane used (cut-off, type of polymer), as well as process parameters (transmembrane pressure, linear velocity for the cross-flow system). Process parameters must be selected individually, and making generalisations in this area is practically impossible. The proposal for design of the MEUF process is shown in Fig. 1.

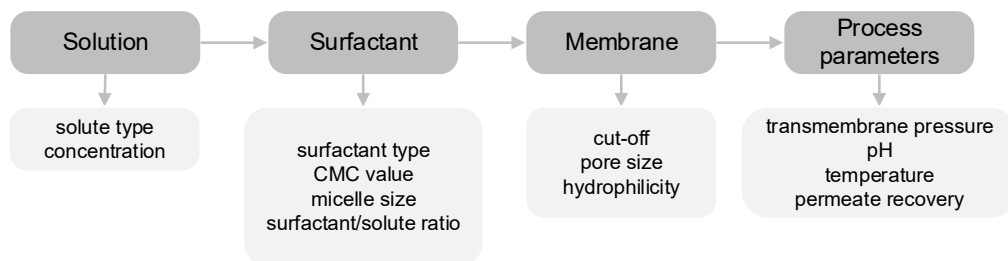| Solution	Surfactant	Membrane	Process parameters
solute type concentration	surfactant type CMC value micelle size surfactant/solute ratio	cut-off pore size hydrophilicity	transmembrane pressure pH temperature permeate recovery

Fig. 1. Design procedure of the MEUF system

Study of the use of other surfactants in order to lower the process costs and to increase system efficiency seems to be crucial. Schwarze et. al. [26] proposed nonaoxyethylene oleylether carboxylic acid (RO90) for divalent cation removal. The results obtained showed the better selectivity of RO90 compared to the commonly used surfactant SDS for the MEUF process, due to a much lower CMC value (ca. 0.014 g/dm^3) and formation of larger aggregates (ca. 8 nm).

In this experimental study, an assessment of copper ion removal by means of MEUF in comparison with classic UF process was made. The leakage of surfactant to the permeate side was evaluated as an important factor limiting the usefulness of the MEUF process. For the experiments, sodium dodecylbenzenesulfonate (SDBS) was chosen, as its characteristics (critical micelle concentration, hydrodynamic radius) suggest a better applicability in the MEUF process than the standard SDS.
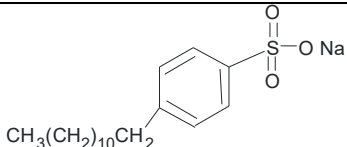
2. EXPERIMENTAL

The first part of the experimental research was ultrafiltration of a copper sulfate solution. Next, in order to enhance the rejection of copper ions, anionic surfactant was added to the feed solution in a wide range of concentrations. Model solutions of 0.08, 0.16, 0.31 and 0.79 mM copper ions were prepared from distilled water (conductivity 2.6 μS/cm) and copper sulfate (CuSO$_4$·5H$_2$O). A bicinchoninate method (DR/2000 spectrophotometer, Hach) was employed to determine the copper content in the samples.

For MEUF experiments, anionic surfactant sodium dodecylbenzenesulfonate was employed (Table 2). The concentration of SDBS in the feed solutions amounted to 0.25, 0.5, 1.0, 3.0 and 5.0 CMC (0.58, 1.15, 2.30, 6.90 and 11.50 mM). A potentiometric titrator 785 DMP Titrino (Metrohm) was used for measurement of surfactant concentration.

Table 2

Surfactant characteristics

Chemical name	sodium dodecylbenzenesulfonate (SDBS)
Type	anionic
Chemical structure	$CH_3(CH_2)_{10}CH_2$ — benzene ring — S (O, O) — O Na
Molecular weight, Da	348.48
CMC, mM	2.30 at 22 °C
Aggregation number	51 [27]
Molecular weight of a micelle, Da	17 748 [27]
Hydrodynamic radius, nm	2.2 [28]
Purity	80%

Due to the size of the micelles being formed by SDSB (ca. 17.7 kDa), two modules (Table 3) with smaller cut-off values were selected for the experiments.

Table 3

Characteristics of the UF module

Parameter	Module type	
	KOCH/ROMICON 1″	Mollsep Fiber FUS0181
Cut-off, kDa	5	10
Polymer	polysulfone	polyethersulfone
Surface charge	negative	negative
Surface area, m²	0.09	0.26
Capillary length, mm	457	280
Number of capillaries	66	382
Inner diameter of capillaries, mm	1.1	0.8
Water volume flux (under 0.05 MPa), dm³/(m²·h)	60	32

Membrane filtration was performed under a pressure of 0.05 MPa. The experiments were conducted in a semi-pilot installation (Fig. 2). Processes were conducted in an open-loop system where the retentate from the membrane was recycled back to the feed tank. The feed solution was pumped to the membrane module by a circulation pump (Grundfos).
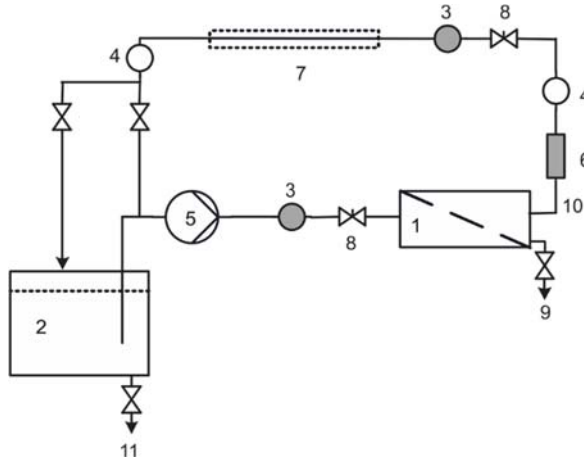
Fig. 2. Schematic diagram of the membrane installation:
1 – membrane module, 2 – feeding tank, 3 – manometer, 4 – thermometer,
5 – pump, 6 – rotameter, 7 – cooler, 8 – pressure regulation valve,
9 – permeate, 10 – retentate, 11 – drain valve

During the experiments, membrane hydraulic capacity and separation properties were assessed. Permeate volume flux J, dm^3/(m^2·h), was calculated by the following equation:

$$J = \frac{V}{tA}$$

where V – volume of the permeate sample collected, dm^3, t – time, h, A – effective membrane surface area, m^2.

To designate the membrane's susceptibility to fouling, the relative flux RF was evaluated:

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

where J_0 – distilled water flux, dm^3/(m^2·h).

The effectiveness of the membrane separation was evaluated as the retention coefficient R:

$$R = \frac{C_f - C_p}{C_f} \times 100\%$$

where C_f – initial compound concentration, mM, C_p – compound concentration in the permeate, mM.

3. RESULTS AND DISCUSSION

3.1. ULTRAFILTRATION

The concentrations of copper ions in the permeate and relative flux obtained over the UF experiments are plotted in Fig. 3. For both modules used, a decrease in separation was observed with the increase in metal ion concentration. In dilute streams of copper ions (0.08 and 0.16 mM), the retention was in the range of 60–79%, and for solutions with a higher concentration of ions (0.31 and 0.79 mM), the retention was reduced to the level of 18–39% and 12–16% for 5 kDa and 10 kDa modules, respectively.
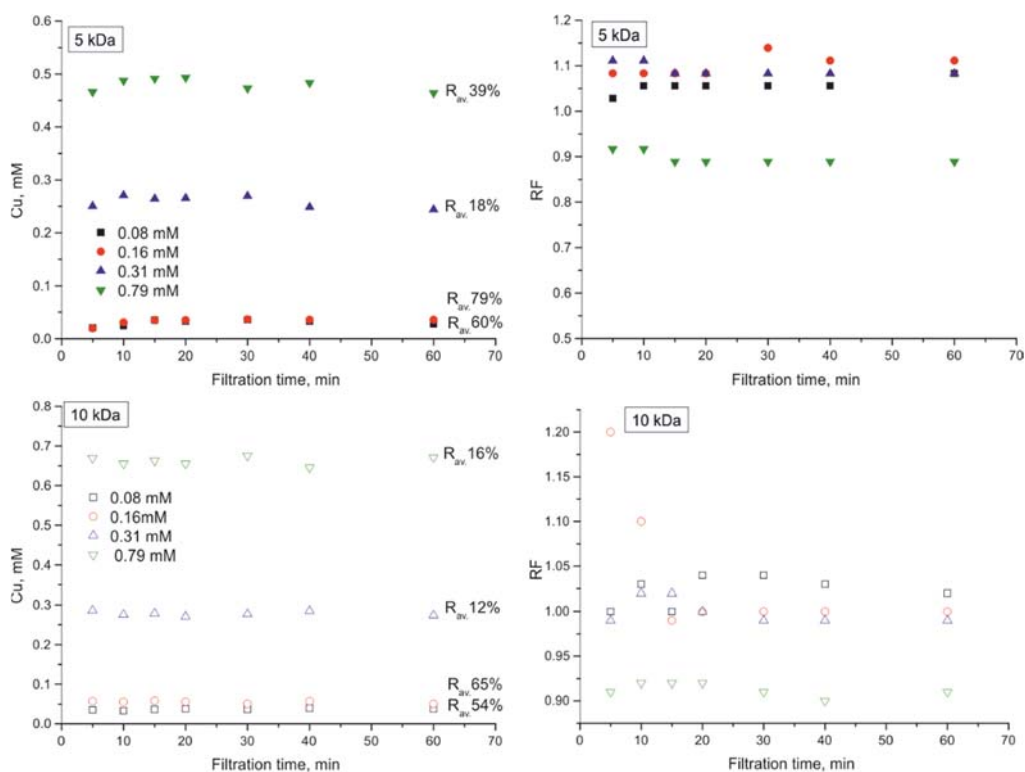

Fig. 3. Copper concentration in the permeate (left) and relative flux *RF* (right)
during the filtration cycle for 5 kDa and 10 kDa modules

Considering the copper radius and the size of UF membrane pores, the achieved separation was probably caused by ion adsorption in the polymer structure, and was not the result of the sieve mechanism of separation. As can be seen, during the 60-min filtration cycle, the modules exhibited stable permeability. For the most concentrated solution (0.79 mM), the decrease in the permeate flux did not exceed 10%.

3.2. SURFACTANT-AIDED MEMBRANE PROCESS

The concentrations of copper ions in averaged permeate samples collected during the 60-min MEUF process are plotted in Fig. 4. As can be seen, the addition of anionic surfactant significantly enhanced membrane selectivity of metal ions. This phenomenon is attributed to electrical adsorption of positively charged copper ions on the negatively charged SDBS micelle surface. Hence, a sieve separation of SDBS aggregates (and trapped copper ions) is possible, since micelle size is substantially greater than membrane pore size.
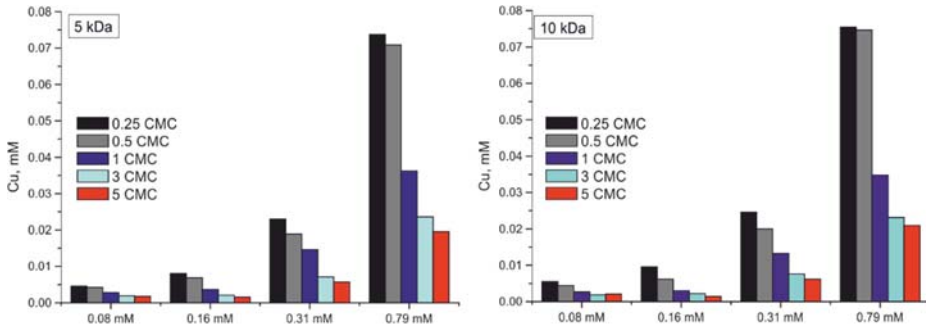

Fig. 4. Concentration of copper in the permeate for 5 kDa and 10 kDa modules

All experiments performed achieved a very high retention of copper ions. Even for the smallest dose of SDBS (0.25 CMC), a surprisingly high separation of metal ions (over 90%) was obtained. This is most likely caused by formation of pre-micelle structures in the concentration polarisation layer. An increase in molar ratio of surfactant to metal ions led to further enhancement in membrane selectivity, due to the larger micelle surface available for electrostatic adsorption. The highest separation of Cu was obtained in tests with SDBS concentration of 5 CMC (98–99% and 97–99% for 5 kDa and 10 kDa, respectively). It seems, however, that the use of such high concentrations of surfactant is not justified, due to the cost of chemicals and an increase in surfactant concentration in the permeate.

Heavy-metal separation obtained during the tests was in accordance with data reported in experiments with SDS. Huang et al. [29] achieved copper ion rejection amounting to 100% by a polyethersulfone membrane with cut-off 10 kDa (feed of 50 mg Cu/dm^3, 1 CMC SDS, pH = 7). Li et al. [30] reported copper removal around 90% in an MEUF process with the use of SDS at a concentration of 1 CMC and a hydrophilic membrane with cut-off 10 kDa; however, when the lower surfactant concentration was applied, the obtained retention coefficients were not satisfactory.

The presence of the surfactants in the treated solutions may negatively affect the pressure-driven membrane process. The first serious limitation of the full-scale application of MEUF is surfactant monomer penetration to the permeate side which may result

in secondary contamination of the process stream, and the necessity for post-treatment steps. Another problem arises from surfactant fouling. In order to evaluate these phenomena and its performance, both SDBS concentration in permeate and flux changes were measured. Figure 5 shows the SDBS retention coefficient and relative flux obtained during the MEUF tests with copper ion concentration in the feed amounting to 0.16 mM. The analysis of data obtained confirmed that the presence of anionic surfactant in the feed affected membrane hydraulic properties.
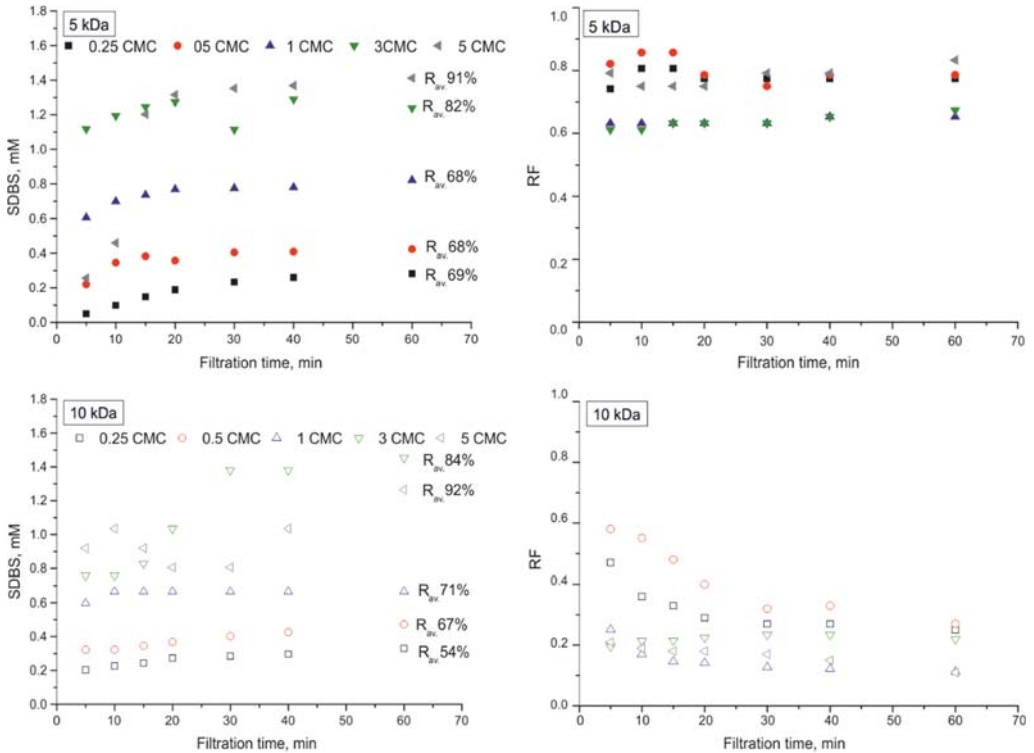

Fig. 5. SDBS retention coefficient R (left) and relative flux RF
during the MEUF (right) for 5 kDa and 10 kDa modules; transmembrane pressure 0.05 MPa,
copper concentration in the feed 0.16 mM

The average value of the permeate flux for 5 kDa and 10 kDa modules amounted to about 78% and 32% of distilled water flux, respectively, during the filtration of a solution containing SDBS in a concentration of 0.25 CMC. Surfactant application at a dose of 3 CMC resulted in slightly lower J/J_0 values, i.e., about 64% and 22% for 5 kDa and 10 kDa modules, respectively. However, the causes of flux changes can be different;

below the CMC value, the main reason for membrane permeability is decrease is monomer adsorption on membrane pores, while in solutions of 3 CMC, the permeability change may be ascribed to a polarisation concentration layer created by micelles near the membrane surface. It should also be mentioned that permeate flux was relatively stable during the MEUF process. According to De and Mondal [31], the phenomenon of membrane pore blocking by SDBS particles is complete in the initial stages of membrane filtration. This phenomenon was much more pronounced for 10 kDa, which was more susceptible to blocking (lower values of relative permeability) by the SDBS molecules due to the larger pore diameter.

Xu et al. [32] reported a twofold decrease of permeate flux compared to distilled water at the initial stage of cadmium treatment process with SDS (100 mg Cd/dm^3, SDS 1 CMC, polysulfone hollow-fibre membrane, cut-off 6 kDa). During the 30-min filtration process, further deterioration of permeability was observed. In the same experimental work, increasing SDS concentration from 1 CMC to 4 CMC resulted in reduced permeate flux from 3.5×10^{-8} to 2.5×10^{-8} m^3/(m$^2 \cdot$s$\cdot$Pa).

It was observed that surfactant concentration in the feed is a crucial parameter in the separation efficiency. When SDBS molecules exist in the form of aggregates, high retention can be achieved. For example, 88–98% and 89–93% of surfactant were removed from the 5 CMC solution using 5 kDa and 10 kDa modules, respectively. Although at the beginning of membrane filtration, modules exhibited a higher selectivity of SDBS, during the process a decrease of retention coefficient was observed in all tests. This fall in rejection may be attributed to the phenomenon of sorption capacity exhaustion of the membrane during filtration, which is particularly pronounced for the solution of 0.25 CMC. With the increase in the concentration of SDBS in the solution, an enhancement in surfactant separation on the modules was observed. Despite the increase in the retention coefficient, permeates more highly contaminated by surfactant were obtained (Table 4).

Table 4

SDBS concentration of MEUF permeates expressed as CMC

Permeate	Feed solution				
	0.25	0.50	1	3	5
After 60 min of filtration	0.12	0.18	0.36	0.54	0.61
Average sample	0.08	0.16	0.32	0.53	0.46

Application of surfactants in doses above the CMC (3 CMC and 5 CMC) resulted in SDBS concentration reaching more than 0.5 CMC at the end of the filtration time (Table 4). Such concentration in treated streams significantly limits MEUF application in full-scale systems due to permeate post-treatment required, which is associated with difficulties in surfactant removal from aqueous solutions.

4. SUMMARY

The experimental research proved that surfactant-aided ultrafiltration exhibited much better copper ion retention compared to classic UF processes. The results obtained for MEUF with SDBS correspond to data reported for processes enhanced by commonly used SDS. Copper rejection in all experiments was very satisfactory and exceeded 90%; however, the highest copper rejection was observed for surfactant dosages above the CMC value. During the MEUF experiments, surfactant monomer penetration to the permeate side was observed. In the course of membrane filtration this phenomenon was intensified. The concentration of surfactant in the feed solution above the CMC resulted in SDBS concentration in the permeate reaching higher than 0.5 CMC at the end of filtration time.

REFERENCES

[1] BARAKAT M.A., *New trends in removing heavy metals from industrial wastewater*, Arab. J. Chem., 2011, 4, 361.
[2] AL-RASHDII B.A.M., JOHNSON D.J., HILAL N., *Removal of heavy metal ions by nanofiltration*, Desalination, 2013, 315, 2.
[3] QDAIS H.A., MOUSSA H., *Removal of heavy metals from wastewater my membrane processes. A comparative study*, Desalination, 2004, 164, 105.
[4] ZAGHBANI N., HAFIANE A., DHAHBI M., *Removal of Erichrome Blue Black R from wastewater using micellar enhanced ultrafiltration*, J. Hazard. Mater., 2009, 168, 1417.
[5] JIN-HUI H., YA-LAN X., GUANG-MING Z., SHAO-HUI G., GENG-XIN X., DONG-MEI Z., XIAO-JIAO T., ZHI-FENG L., *Separation of phenol from various micellar solutions using MEUF*, Sep. Purif. Technol., 2012, 98, 1.
[6] GEANTA R.M., RUIZ M.O., ESCUDERO I., *Micellar-enhanced ultrafiltration for the recovery of lactic acid and citric acid from beet molasses with sodium dodecyl sulphate*, J. Membrane Sci., 2013, 430, 11.
[7] ACERO J.L., BENITEZ J., REAL F.J., TEVA F., *Removal of emerging contaminants from secondary effluents by micellar-enhanced ultrafiltration*, Sep. Purif. Technol., 2017, 181, 123.
[8] EXALL K., BALAKRISHNAN V.K., TOITO J., MCFADYEN R., *Impact of selected wastewater constituents on the removal of sulfonamide antibiotics via ultrafiltration and micellar enhanced ultrafiltration*, Sci. Total Environ., 2013, 461–462, 371.
[9] PURKAIT M.K., DASGUPTA S., DE S., *Micellar enhanced ultrafiltration of eosin dye using hexadecyl pyridinium chloride*, J. Hazard. Mater., 2006, B136, 972.
[10] AHMAD A.L., PUASA S.W., *Reactive dyes decolourization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process*, Chem. Eng. J., 2007, 132, 257.
[11] HUANG J.H., ZENG G.M., ZHOU C.F., LI X., SHI L.J., HE S.B., *Adsorption of surfactant micelles and $Cd^{2+}/Zn2+$ in micellar-enhanced ultrafiltration*, J. Hazard. Mater., 2010, 183, 287.

[12] LIN W., JING L., ZHU Z., CAI Q., ZHANG B., *Removal of heavy metals from mining wastewater by micellar-enhanced ultrafiltration (MEUF): experimental investigation and Monte Carlo-based artificial neural network modeling*, Water Air Soil Pollut., 2017, 228, 205.

[13] AKITA S., YANG L., TAKEUCHI H., *Micellar-enhanced ultrafiltration of gold(III) with nonionic surfactant*, J. Membrane Sci., 1997, 133, 189.

[14] BEOLCHINI F., PAGNANELLI F., DE MICHELIS I., VEGLIÒ F., *Micellar enhanced ultrafiltration for arsenic(V) removal: effect of main operating conditions and dynamic modelling*, Environ. Sci. Technol., 2006, 40, 2746.

[15] KAMBLE S. B., MARATHE K. V., *Membrane characteristics and fouling study in MEUF for the removal of chromate anions from aqueous streams*, Sep. Sci. Technol., 2005, 40, 3051.

[16] HUANG J., QI F., ZENG G., SHI L., LI X., GU Y., SHI Y., *Repeating recovery and reuse of SDS micelles from MEUF retentate containing Cd^{2+} by acidification UF*, Colloid. Surface. A., 2017, 520, 361.

[17] LI X., ZENG G.M., HUANG J.H., ZHANG C., FANG Y.Y., QU Y.H., LUO F., LIN D., LIU H.L., *Recovery and reuse of surfactant SDS from a MEUF retentate containing Cd^{2+} or Zn^{2+} by ultrafiltration*, J. Membrane Sci., 2009, 337, 92.

[18] SAMPER E., RODRIGUEZ M., DE LA RUBIA M.A., PRATS D., *Removal of metal ions at low concentration by micellar-enhanced ultrafiltration (MEUF) using sodium dodecyl sulfate (SDS) and linear alkylbenzene sulfonate (LAS)*, Sep. Purif. Technol., 2009, 65, 337.

[19] TORTORA F., INNOCENZI V., PRISCIANDARO M., VEGLIO F., MAZZIOTTI DI CELSO G., *Heavy metal removal from liquid wastes by using micellar-enhanced ultrafiltration*, Water Air Soil Poll., 2016, 227, 240.

[20] KONOPCZYŃSKA B., DYPKO M., PROCHALSKA K., *Application of MEUF technique for the separation of chromium(III) ions from model aqueous solutions chromium(III) perchlorate*, Proc. ECOpole 2013, 7 (2), 633.

[21] GHAZI M.M., QOMI M.H., *Removal of manganese from an aqueous solution using micellar-enhanced ultrafiltration (MEUF) with SDS surfactants*, AET, 2015, 1, 17.

[22] SANGLE J.S., MARATHE K.V., *Removal of manganese from wastewater by using micellar enhanced ultrafiltration (MEUF)*, IJRDET, 2016, 5, 1.

[23] YOBILISHETTY S.M., MARATHE K.V., *Removal of molybdenum (VI) from effluent waste water streams by cross flow micellar enhanced ultrafiltration (MEUF) using anionic, non-ionic and mixed surfactants*, Indian J. Chem. Techn., 2014, 21, 321.

[24] LI X., HE S., FENG C., ZHU Y., PANG Y., HOU J., LUO K., LIAO X., *Non-competitive and competitive adsorption of Pb^{2+}, Cd^{2+} and Zn^{2+} ions onto SDS in process of micellar-enhanced ultrafiltration*, Sustainability, 2018, 10, 92.

[25] LEE S.H., SHRESTHA S., *Application of micellar enhanced ultrafiltration (MEUF) process for zinc (II) removal in synthetic wastewater: kinetics and two-parameter isotherm models*, Int. Biodeter. Biodegr., 2014, 95, 241.

[26] SCHWARZE M., GROSS M., MORITZ M., BUCHNER G., KAPITZKI L., CHIAPPISI L., GRADZIELSKI M., *Micellar enhanced ultrafiltration (MEUF) of metal cations with oleylethoxycarboxylate*, J. Membrane Sci., 2015, 478, 140.

[27] HUANG J.H., ZHAO Y., ZENG G.M., PENG L., LI X., LIU L.X., LI F., SHI L.X., YUAN F., *Micellar-enhanced ultrafiltration for the solubilization of various phenolic compounds with different surfactants*, Water Sci. Technol., 2015, 72, 623.

[28] JÖNSSON A.S., JÖNSSON B., *The influence of nonionic and ionic surfactants on hydrophobic and hydrophilic ultrafiltration membranes*, J. Membrane Sci., 1991, 56, 49.

[29] HUANG J., YUAN F., ZENG G., LI X., GU Y., SHI L., LIU W., SHI Y., *Influence of pH on heavy metal speciation and removal from wastewater using micellar-enhanced ultrafiltration*, Chemosphere, 2017, 173, 199.

[30] LI C.W., LIU C.K., YEN W.S., *Micellar-enhanced ultrafiltration (MEUF) with mixed surfactants for removing Cu(II) ions*, Chemosphere, 2006, 63, 353.

[31] DE S., MONDAL S., *Micellar Enhanced Ultrafiltration, Fundamentals and Applications*, Taylor and Francis Group, Boca Raton 2012.

[32] XU K., ZENG G.M., HUANG J.H. WU J.Y., FANG Y.Y., HUANG G., LI J., XI B., LIU H., *Removal of Cd^{2+} from synthetic wastewater using micellar-enhanced ultrafiltration with hollow fiber membrane*, Colloid. Surface. A., 2007, 294, 140.