Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2018.22317

118 (2018) 143–152
June

Separation of Cu(II) ions from single-component and Cd(II)-containing solutions by LM-MEUF utilizing micellar effects of CTAB and TX100 on complex formation

Deniz Şahin, Senay Taşcıoğlu*

Department of Chemistry, Faculty of Sciences, Gazi University, Ankara 06500, Turkey, Tel. + 90 312 2021109; email: senaytas@gazi.edu.tr (S. Taşcıoğlu), Tel. + 05326019792; email: dennoka1197@yahoo.com (D. Şahin)

Received 26 October 2017; Accepted 5 April 2018

ABSTRACT

Optimum conditions for removal of Cu(II) ions from both single-component and Cd(II)-containing solutions by ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) in the presence of cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX100) micelles were determined. TX100 was not found to be effective in Cu(II) separation by LM-MEUF. The most effective ligand in CTAB micellar media, out of 20 ligands, was found to be 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) in removal of Cu(II) ions from single-component solutions. 99.99% removal of 5.0×10^{-4} mol L^{-1} Cu(II) ions from single-component solutions could be provided in the presence of 5.0×10^{-3} mol L^{-1} CTAB and 1.0×10^{-3} mol L^{-1} TPTZ. Complete removal of 5.0×10^{-4} mol L^{-1} Cu(II) ions from 5.0×10^{-4} mol L^{-1} Cd(II)-containing solutions could be achieved by LM-MEUF with 6.4% Cd(II) rejection in the presence of 1.3×10^{-2} mol L^{-1} CTAB and 2-hydroxy-1-(2-hydroxy-4-sülfo-1-naphthylazo)-naphthalene-3-carboxylic acid. The results demonstrated that metallic ions of quite similar properties can be separated simply by a membrane filtration process and that Cu(II) removal can be provided not only by anionic but also by cationic micelles. The results of this study were discussed in a comparative way with those obtained in a LM-MEUF process performed previously in the presence of sodium dodecyl sulfate (SDS) micelles. The ligands were shown to exert similar effects in the presence of both cationic CTAB and anionic SDS micelles, and a mechanism was proposed for Cu(II) removal by LM-MEUF.

Keywords: Selective separation; Ligand-modified MEUF; Removal of Cu(II); Cd(II); CTAB; TX100; TPTZ; Calconcarboxylic acid

1. Introduction

Environmental damage caused by pollutants in wastewater streams is well established. Heavy metals are included in the EPA priority pollutant list since they are hazardous to man's health and aquatic biota. Cu(II) and Cd(II) ions are toxic heavy metal ions found in many industrial wastewaters.

Various techniques have been developed for removal of heavy metals from wastewaters. Separation methods should enable to treat large amounts of polluted water in which the pollutants are extremely diluted. Several surfactant-based separation processes have been developed which have superiorities in simplicity and low cost compared with the other methods. Of these, micellar-enhanced ultrafiltration (MEUF) which was first applied in the 1980s is the most preferred technique [1]. MEUF is highly effective in removing pollutants from effluents of industrial processes. Besides, it is applied in analytical science as a separation, preconcentration, and recovery method for the target ions and organics [2–7].

Monomers of surfactants exist separately in diluted solutions, but they self-aggregate to form colloidal micelles at concentrations higher than the critical micellization concentration (CMC) of the surfactant [8]. When two self-assembling compounds coexist in the same solution, they form mixed micelles (comicelles). Comicelles are formed with

---

* Corresponding author.

1944-3994/1944-3986

micellar-solubilized amphiphilic substances, such as ligands, drugs, and catalyzers [8–11].

MEUF process is based on adsorption of small target ions or solubilization of organic molecules by surfactant micelles. Micellar-bound ions or organics are removed by an ultrafiltration (UF) process carried out with membranes capable of retaining micelles [12–14]. Thus, the target ions or organics are rejected from permeate, such that the concentrations of solute and surfactant in the feed (retentate) are increased.

Removal efficiency of MEUF depends on the properties and concentrations of target ions and surfactants, solution pH, ionic strength, surfactant to metal ion mole ratio; and on the parameters such as filtration pressure, flow rate, stirring speed, and pore size and material of the membrane. Kind of surfactants depends on the type of the ions to be removed: anionic surfactants are used for removing cations, but cationic surfactants are used to remove anions [8,15–20]. Therefore, cationic cetyltrimethylammonium bromide (CTAB) has not been used before for Cu(II) separation since it is not expected to attract cations.

MEUF is substantially effective in separating Cu(II) ions from single-component solutions. Retentions between 90% and >99% have been reported for MEUF process with sodium dodecyl sulfate (SDS) [21–28]. Recently, Juang et al. [29] have reported Cu(II) removal higher than 90% at optimum SDS/Cu(II) mole ratio and pH conditions. Schwarze et al. [30] achieved *R* values >95% for Cu(II) removal. A review on MEUF prepared by Schwarze has been published recently [31].

On the other hand, MEUF has a drawback that it cannot provide a high selectivity in removing metallic ions from solutions. MEUF can be only moderately effective in selective separation of metal ions even if they have not similar properties such as Cu(II) and Ca(II) ions [32]. On the other hand, selective separation of ions can effectively be provided by the use of a ligand which undergoes selective complexation with one of the target ions. The complex solubilized in micelles is retained during MEUF providing metal ion rejection. This process is called "ligand-modified MEUF" (LM-MEUF).

The efficiency of LM-MEUF process depends on the pH of the sample solution since complex formation is pH-dependent, other factors are the ligand to metal ion mole ratio and the nature of the ligand [33–38]. The working pH is generally between 3 and 7 which can be achieved easily with wastewaters. There is a limited number of LM-MEUF studies performed for removal of copper. Removal efficiency of about 97% was achieved with cationic cetylpyridinium chloride [37,39].

Selective separation of Cu(II) ions from ions with quite dissimilar properties such as Ca(II) and Co(II) can effectively be achieved by LM-MEUF [35,36,40–43]. But there is not any report in the literature on selective separation of Cu(II) and Cd(II) ions which have similar properties, by neither MEUF nor LM-MEUF. Thus, we explored the feasibility of LM-MEUF as a method for selective removal of Cu(II) ions from Cd(II)-containing solutions. Cu(II) and Cd(II) ions are expected to interact with complexing agents in the same way under the same conditions, since they have quite similar chemical and physical properties. But their complexation behaviors can be differentiated in micellar media by virtue of the "medium effect" of surfactant micelles, which is a combination of cage, preorientation, charge, polarity, and microviscosity effects. Thus, micellar-bound reactants reside in microenvironments which have quite different properties from those of the bulk phase [8]. As a consequence, ionization equilibria of the substrates which interact with micelles, and thereby, the stability constants as well as the stoichiometry of their complexes are changed [8,44]. Therefore, it can be expected that micellar medium can differentiate the interactions of Cu(II) and Cd(II) ions with the same ligands. On this basis, complexation behaviors of 20 azo compounds with Cu(II) and Cd(II) ions were investigated in this research to determine the ligands which could provide selective removal of Cu(II) ions in CTAB and triton X-100 (TX100) micellar media. Effects of these ligands on Cu(II) removal from Cd(II)-containing solutions were investigated. MEUF experiments were carried out in the absence and presence of these ligands to show that cationic surfactants can also be used in separation of Cu(II) cations. In a previous research of us, carried out with SDS as the surfactant, we showed that complete removal of Cu(II) ions from Cd(II)-containing solutions could be achieved by LM-MEUF with Cd(II) rejections lower than 10% [45]. The results of this study carried out in CTAB and TX100 micellar media have been discussed in a comparative way with those obtained in the presence of SDS.

2. Materials and methods

2.1. Chemicals

The reagents used in this study were used as purchased, without purification. Cationic surface-active agent CTAB (≥98%, Aldrich, Germany) and nonionic Isooktilfenoksipolietoksietanol (TX-100, analytical grade, Merck, Germany) were used as surfactants. $Cu(NO_3)_2{\cdot}3H_2O$ (≥99.5%, Merck, Germany) and $Cd(NO_3)_2{\cdot}4H_2O$ (98%, Merck, Germany) salts were used as the sources of Cu(II) and Cd(II) ions, respectively.

The complexing agents used in the experiments were 3-hydroxy-4-[2-sulfo-4-(4-sulfophenylazo)phenylazo]-2,7-naphthelene disulfonic acid sodium salt (Ponceau S, PS; ≥80%, Merck, Germany); 1-phenylazo-2-naphthol-6,8-disulfonic acid sodium salt (Orange G, OG; ≥ 80%, Merck, Germany); 4-amino-5-hydroxy-3-[(4-nitrophenyl)azo]-6-(phenylazo)-2,7-naphthalenedisulfonic acid disodium salt (Naphthol Blue Black, Amido Black 10 B, AB10B; ≥80%, Merck, Germany); 4-(4-nitrophenylazo)-resorcinol (44NPR; >96% Merck, Germany); diphenylthiocarbazone (Dithizone, DZ; 98%, Merck, Germany); 4-[4-(dimethylamino)phenylazo] benzene sulfonic acid sodium salt (Methyl Orange, MO; analytical grade, Merck, Germany); 2-hydroxy-1-(1-hydroxy-2-naphthylazo)-6-nitronaphthalene-4-sulfonic acid sodium salt (Eriochrome Black T, ECST; analytical grade, Merck, Germany); 1-(*2-pyridyl*azo)-2-naphthol (PAN, 12P2N; 99%, Merck, Germany); 5,5′-indigodisulfonic acid sodium salt (Indigo Carmine, INCAR; analytical grade, Merck, Germany); 2,4,6-tri(2-pyridy*l)-1,3,5-triazine* (TPTZ (Fig. 1); ≥99%, Merck, Germany); 3,5,6-triphenyl-2,3,5,6-tetraaza[2.1.1.] bicyclo-1-hexene (Nitron, NTR; ≥99%, Merck, Germany);

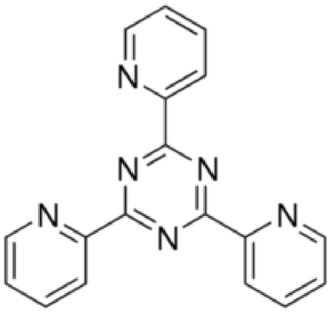

Fig. 1. Structural formula of TPTZ.

2,9-dimethyl-1,10-phenanthroline (Neocuproine, NEOC; ≥98%, Sigma, USA); 2-hydroxy-1-(2-hydroxy-1-naphthylazo) napthalene-4-sulfonic acid sodium salt (Calcon, CAL; analytical grade, Merck, Germany); 2-hydroxy-1-(2-hydroxy-4-sülfo-1-naphthylazo)-naphthalene-3-carboxylic acid (Calconcarboxylic Acid, CALCA (Fig. 2); analytical grade, Merck, Germany); disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)diazenylphenyl]phenyl]diazenyl-naphthalene-1-sulfonate (Congo Red, COR; analytical grade, Merck, Germany); 5-(3-nitrophenylazo)-2-hydroxy benzoic acid sodium salt (Alizarin Yellow, AY; analytical grade, Merck, Germany); 1-[4-(phenylazo) phenylazo]-2-naphthol (Sudan III, SIII; analytical grade, Fluka, Germany); 2-[(4-dimethylamino)phenylazo]benzoic acid (Methyl Red, MR; analytical grade, Merck, Germany); 4-([2,4-dihydroxyphenyl]azo) benzene sulfonic acid sodium salt (Tropaeolin OO, Acid Orange IV, TROP; 65%, Schering-Kahlbaum, Germany); and 2-carboxy-2′-hydroxy-5′-sulfoformazyl-benzene monosodium salt (Zincon, ZNCN; ≥75%, Merck, Germany).

Deionized water was used throughout the study.

2.2. Apparatus and procedures

Dead-end UF experiments were carried out by using a batch-stirred ultrafiltration (UF) cell (Amicon 8050, Millipore, USA, Fig. 3). Organic-regenerated cellulose UF membranes (Millipore, USA) with molecular weight cutoff (MWCO) 5,000 Da were used in MEUF experiments. A fresh membrane was placed on the porous support at the bottom of the UF cell. The cell was initially filled with 30 mL of feed solution, and the applied transmembrane pressure to the solution was adjusted at 4.0 bars by pressurized air. The feed solution was stirred using a magnetic stirrer (Chiltern MS21S) to provide an efficient mixing at a constant speed of 500 rpm. The stirrer speed was measured using a digital tachometer (Optic DT-838). UF processes were carried out at room temperature. The applied values of transmembrane pressure, stirring speed, and membrane porosity were the optimum conditions which were determined in preliminary studies performed to minimize the surfactant concentration in the filtrate and to maximize the UF rate.

The first 5 mL of filtrate was discharged, and the subsequent 20 mL of permeate was collected to be analyzed. Permeate and feed concentrations of ions were measured by an ion meter (Orion 720A Plus) combined with Orion 9629BN Cu(II) and Orion 9648BN Cd(II) selective electrodes.

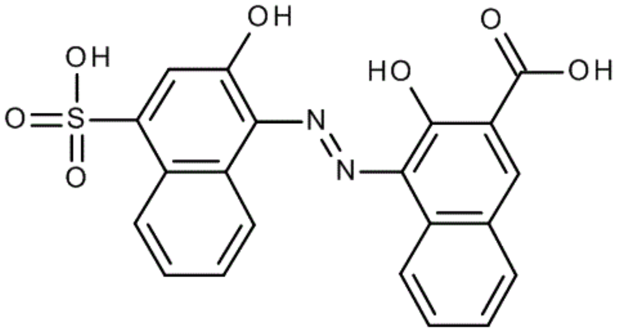

Fig. 2. Structural formula of CALCA.

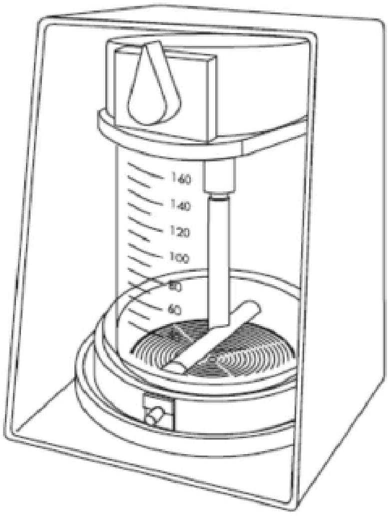

Fig. 3. UF cell used in the experiments.

0.3 mL of ionic strength adjustment solution (Orion) was added to 15 mL of calibration and sample solutions. Four-point calibration was performed before the measurements. Determinations were carried out in triplicate or more, and the mean values were used. *R* values of 100% were also confirmed by atomic absorption spectroscopy (Varian 240FS FAAS). Flame atomic absorption spectroscopy (FAAS) measurements were carried out in triplicate.

The optical absorption spectra were taken by using an UNICAM UV2-100 spectrophotometer with solutions at pHs 1, 3, 5, 7, and 9. In these experiments, the concentrations of CTAB, TX100, Cu(II), Cd(II), and ligand solutions were kept as 2.5×10^{-3}, 2.5×10^{-3}, 2.44×10^{-4}, 2.44×10^{-4} mol L^{-1}, and 2.5×10^{-5} kg L^{-1}, respectively.

The ligands were dissolved in 1.0×10^{-1} mol L^{-1} CTAB and TX100 solutions since they were mostly insoluble in water. A Sartorius 1608-MP8-1 analytical balance with 0.1 mg sensitivity was used for weighing.

In preliminary studies, membranes were used repeatedly in successive experiments: After each run, UF cell was rinsed and filled with 50 mL deionized water. Continuous stirring was applied for 30 min to remove surfactant layer from the membrane surface and disperse the surfactant molecules. Then, membranes were back-flushed with 20 mL deionized water at a pressure of 4 bars. The permeability of the membranes was checked to ensure that it remains constant between successive usages. Following UF experiments performed at pH = 7, pH of the deionized water to be used in the first stage of the cleaning process was brought to 4.5 so that any hydroxide residue on membranes could be removed.

The filtration efficiency in removing the target ion from the feed solution was evaluated through the ion rejection which was measured by the rejection coefficient *R*:

$$R(\%) = \left(1 - \frac{C_p}{C_0}\right) \times 100$$

C_0 and C_p are the initial concentrations of the target ion in feed solution and in permeate, respectively.

3. Results and discussion

3.1. Studies performed in the presence of CTAB micelles

3.1.1. Determination of CMC values of CTAB

CMC values of CTAB and TX100 were determined under different conditions, since the MEUF experiments were to be carried out in the presence of surfactants in concentrations higher than their CMC. CMC values were also determined in the presence of Cu(II) and Cd(II) ions. CMC values of CTAB in water, in 5.0×10^{-4} mol L^{-1} Cu(II) solution and in 5.0×10^{-4} mol L^{-1} Cd(II) solution, were determined to be 9.1×10^{-4}, 2.6×10^{-4}, and 2.7×10^{-4} mol L^{-1}, respectively.

3.1.2. Determination of ligands to be used in LM-MEUF for selective separation of Cu(II) and Cd(II) ions

Optical absorption spectra of CTAB, Cu(II), Cd(II), and ligand solutions; binary solutions of CTAB with ligands and with Cu(II) and Cd(II) ions; and ternary solutions composed of CTAB, ligand, and Cu(II) or Cd(II) ions were recorded at pHs 1, 3, 5, 7, and 9 to determine the ligands that could be used in LM-MEUF process for selective separation of Cu(II) and Cd(II) ions. Thus, the ligands which exhibit different complexation behaviors with Cu(II) and Cd(II) ions were determined by the inspection of 323 spectra in a comparative way. 20 azo compounds were used as ligands. TPTZ, 12P2N, CAL, CALCA, DZ, ECST, INCAR, NEOC, NTR, and ZNCN displayed dissimilar peaks in absorption spectra taken in CTAB micellar media in the presence of Cu(II) and Cd(II) ions at pH = 5 and 7. pH = 5 was chosen as the working pH for LM-MEUF studies, since this pH is mostly the pH of industrial effluents or can be achieved easily. However, the experiments were also performed at pHs 3 and 7. pH = 9 was not preferred because of the high possibility of metal hydroxide formation.

3.1.3. Investigation of the feasibility of removal of Cu(II) cations from single-component solutions by cationic CTAB micelles

In practice, metallic ions are separated by MEUF using anionic surfactants which can bind the reversely charged target ions by electrostatic forces. Nevertheless, feasibility of Cu(II) removal by CTAB micelles was investigated at the first stage of LM-MEUF experiments with the consideration that positively charged CTAB micelles, which are not expected to interact with Cu(II) ions, can interact with its complexes. TPTZ, 12P2N, CAL, CALCA, DZ, ECST, INCAR, NEOC, NTR, and ZNCN were used as ligands, since their interactions with Cu(II) and Cd(II) ions were differentiated in CTAB micellar medium at pH 5. Effects of these ligands on removal of Cu(II) ions from single-component solutions were investigated. The results of these studies and the experimental conditions are given in Table 1. The results show that these ligands are all highly effective in removal of Cu(II) ions in the presence of CTAB. Positively charged CTAB micelles cannot electrostatically attract Cu(II) cations. Therefore, high retention coefficients in this table provide evidence of interaction between CTAB micelles and Cu(II)–ligand complexes. This can be rationalized by the solubilization of Cu(II)–ligand complexes in the interior of CTAB micelles by hydrophobic interactions [8], since hydrophobic characters of these ligands are dominated. The most effective ligand TPTZ is expected to locate near to micellar interface since it bears six nitrogen atoms in its structure (Fig. 1) [8]. Doubly charged Cu(II) complex of TPTZ, $[Cu(TPTZ)_2]^{2+}$, must have been neutralized by Br-counterions of CTAB such that it can be solubilized in CTAB micelles.

The results in Table 1 reveal that TPTZ can be suggested to be used for Cu(II) separation from single-component solutions, as it was also suggested to be used for this purpose depending on the results of the studies performed in the presence of SDS [45]. TPTZ solubilized by micelles and undissolved TPTZ will be retained by the membrane since TPTZ has a very low solubility in water [46,47]. The second and the third alternatives of TPTZ are CAL and CALCA, respectively.

Interestingly, when the results in Table 1 and those in Table 2 in Ref. [45] are inspected in a comparable way, it can be seen that the sequence of the ligands (TPTZ, CAL, CALCA, ZNCN, 12P2N, etc.) in terms of their functionality

Table 1
Ligand effect on Cu(II) removal by LM-MEUF performed in the presence of CTAB at pH = 5

Ligand 1.0×10^{-3} mol L^{-1}	$(Cu(II))_p$ Concn. (mg L^{-1})	R_{Cu} (%)
TPTZ	0.0004	99.99
12P2N	0.2170	99.61
CALCA	0.0737	99.76
CAL	0.0158	99.95
DZ	0.8980	97.17
ECST	0.1661	99.47
INCAR	0.1390	99.56
NEOC	1.9141	93.97
NTR	0.2380	99.25
ZNCN	0.0116	99.63

Feed concentrations of CTAB and Cu(II) are 5.00×10^{-3} and 5.00×10^{-4} mol L^{-1}, respectively. Subscript *p* denotes "permeate."

Table 2
Ligand effect on Cu(II)–Cd(II) separation by LM-MEUF performed in the presence of CTAB at pH = 5

Ligand 1.0×10^{-3} mol L^{-1}	$(Cu(II))_p$ Concn. (mg L^{-1})	$(Cd(II))_p$ Concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	0.0093	55.45	99.97	1.34
12P2N	0.1670	54.75	99.47	2.58
CALCA	0.1160	54.35	99.63	3.29
CAL	0.0368	51.35	99.89	8.63
DZ	0.1143	50.39	99.64	10.34
ECST	0.0427	44.34	99.86	21.10
INCAR	0.1266	46.40	99.60	17.43
NEOC	0.5116	54.33	98.38	3.38
NTR	0.3813	53.10	98.79	5.51
ZNCN	0.0578	52.45	99.82	6.67

Feed concentrations of CTAB, Cu(II), and Cd(II) are 5.00×10^{-3}, 5.00×10^{-4}, and 5.00×10^{-4} mol L^{-1}, respectively. Subscript p denotes "permeate."

in Cu(II) separation is the same in the presence of both anionic SDS and cationic CTAB micelles with very close efficiencies regardless of the electrical charge of micelles. This reveals that the interactions between complex molecules and micelles are not electrostatic but mainly hydrophobic in character. Complexation reaction does not occur at micellar surfaces; that is, the micelles does not function as attractants for metallic ions but solubilize the formed Cu(II)–ligand complex. As a result, Cu(II) ions are retained in the retentate.

3.1.4. Effects of ligands in selectively removal of Cu(II) ions from Cd(II)-containing solutions

10 ligands which were found to interact with Cu(II) ions but not with Cd(II) ions in CTAB micellar medium were chosen to be used in LM-MEUF experiments for selective removal of Cu(II) ions from Cd(II)-containing solutions. The experimental conditions and the results of these studies are given in Table 2. With the inspection of the results in Table 2, it can be seen that the most effective ligands in selective removal of Cu(II) ions are TPTZ, 12P2N, and CALCA.

On the basis of the results in Table 2, effects of these three ligands on separation of Cu(II) ions were further investigated in more detail. In these experiments, the effect of alterations in ligand concentration in the presence of 5.0×10^{-3} mol L^{-1} CTAB and the effect of alterations in CTAB concentration in the presence of 1.0×10^{-3} mol L^{-1} ligand were investigated to determine the optimum CTAB and ligand concentrations for complete separation of Cu(II) ions. The results obtained from these experiments are presented in Table 3.

It can be concluded from the results in Table 3 that increasing the ligand concentration under fixed concentration of CTAB and increasing the CTAB concentration under fixed concentration of ligand lead to increase in R values of both Cu(II) and Cd(II) ions. The increases in R values of Cd(II) ions are larger than those observed in R values of Cu(II) ions. This exerts a negative effect on Cu(II)–Cd(II) separation. Negative effect of increments in ligand concentration is more pronounced compared with that of the increments in CTAB concentration.

Complete separation of Cu(II) ions from Cd(II) ions can be provided by 6.66×10^{-3} mol L^{-1} 12P2N and CALCA or by 3.33×10^{-3} mol L^{-1} TPTZ in the presence of 5.00×10^{-3} mol L^{-1} CTAB. On the other hand, the necessary CTAB concentrations for 12P2N, CALCA, and TPTZ are 1.66×10^{-2} , 1.33×10^{-2}, and 1.16×10^{-2} mol L^{-1} in the presence of 1.00×10^{-3} mol L^{-1} ligand. These results reveal that the most effective ligand in Cu(II) separation is TPTZ. On the other hand, the least R_{Cd} value is observed in the presence of CALCA (6.40). Cd(II) rejection in such a small extent may be attributed mainly to the adsorption of Cd(II) ions by the membrane itself, since CALCA was found not to undergo complexation with Cd(II) ions at pH 5 and CTAB micelles cannot bind positively charged Cd(II) ions. At complete Cu(II) separation conditions, the R_{Cd} value is somewhat higher in the presence of 12P2N (7.65) and the R_{Cd} value in the presence of TPTZ is 12.88. Thus, CALCA seems to be the most effective ligand in selective separation of Cu(II) and Cd(II) ions by LM-MEUF performed in the presence of CTAB.

3.1.5. Studies performed at pH 3 for selective removal of Cu(II) ions by LM-MEUF

Another set of LM-MEUF experiments was performed at pH = 3 using the ligands which their effects on selective separation of Cu(II) ions were investigated at pH = 5. The conditions and the results of these LM-MEUF experiments are given in Table 4. It can be concluded by the comparison of the data in Tables 2 and 4 that lowering the pH of the feed solution from 5 to 3 imposes a negative effect on selective removal of Cu(II) ions and leads to remarkable decreases in rejection of both Cu(II) and Cd(II) ions.

3.1.6. Studies performed at pH 7 for selective removal of Cu(II) ions by LM-MEUF

LM-MEUF experiments were also carried out at pH = 7 using the same ligands as in the experiments carried out at pHs 5 and 3 to see their effects on selective separation of Cu(II) ions from Cd(II) ions at this pH. The experimental conditions and the results of these LM-MEUF experiments are given in Table 5.

By the comparison of the data in Tables 2 and 5, it can be concluded that increasing the pH of the feed solution from 5 to 7 imposes a negative effect on selective separation of Cu(II) ions. It leads to remarkable decreases in rejection of Cu(II) and increases in the rejection of Cd(II) ions.

When the results in Tables 2, 4, and 5 are inspected in a comparative way, it can be seen that shifting pH from 5 to 3 or 7 results in increases in R_{Cd} values and in decreases in R_{Cu} values, in different amounts depending on the ligand, such that complexation of both ions is not favored and selective separation cannot be provided. Cu(II) ions can be associated with micelles only via their complexes since positively charged CTAB micelles cannot bind Cu(II) cations. Therefore, the results reveal that complex formation of

Table 3
Dependence of the required concentrations of TPTZ, CALCA, and 12P2N to achieve complete removal of Cu(II) ions from Cd(II)-containing solution, on CTAB concentration

	$[\text{CTAB}]_0 \times 10^3$	$[\text{Ligand}] \times 10^3$	$(\text{Cu(II)})_p$ Concn. (mg L^{-1})	$(\text{Cd(II)})_p$ Concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	5.00	1.66	0.0063	48.76	99.98	13.23
	5.00	2.66	0.0011	45.56	99.99	18.93
	5.00	3.33	–	44.66	100.00	20.52
	10.00	1.00	0.0002	50.16	99.98	10.74
	11.66	1.00	–	48.96	100.00	12.88
	13.30	1.00	–	46.73	100.00	16.85
CALCA	5.00	3.00	0.0973	50.63	99.69	9.91
	5.00	5.00	0.0330	49.23	99.89	12.41
	5.00	6.66	–	48.93	100.00	12.93
	10.00	1.00	0.0993	54.00	99.68	3.91
	13.30	1.00	–	52.56	100.00	6.40
	16.62	1.00	–	50.63	100.00	9.91
12P2N	5.00	3.00	0.0406	52.16	99.87	7.18
	5.00	5.00	0.0216	50.60	99.90	9.96
	5.00	6.66	–	49.17	100.00	12.52
	10.00	1.00	0.0656	54.63	99.79	2.79
	13.30	1.00	0.0300	53.53	99.91	4.75
	16.62	1.00	–	51.90	100.00	7.65

Feed concentrations of Cu(II) and Cd(II): 5.00×10^{-4} mol L^{-1}; working pH: 5. Subscripts 0 and p denote "feed solution" and "permeate," respectively.

Table 4
Ligand effect on Cu(II)–Cd(II) selective separation by LM-MEUF performed in the presence of CTAB at pH = 3

Ligand 1.0×10^{-3} mol L^{-1}	$(\text{Cu(II)})_p$ Concn. (mg L^{-1})	$(\text{Cd(II)})_p$ Concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	24.43	44.70	23.10	20.46
12P2N	25.53	37.00	19.69	34.16
CALCA	23.76	45.90	25.21	18.32
CAL	24.40	41.55	23.19	26.06
DZ	24.00	44.11	24.45	21.51
ECST	22.10	44.95	30.43	20.01
INCAR	22.10	44.95	30.43	20.01
NEOC	25.25	51.10	20.52	9.07
NTR	24.80	50.50	21.93	1.42
ZNCN	23.53	44.85	25.93	20.19

Feed concentrations of CTAB, Cu(II), and Cd(II) are 5.00×10^{-3}, 5.00×10^{-4}, and 5.00×10^{-4} mol L^{-1}, respectively. Subscript p denotes "permeate."

Table 5
Ligand effect on Cu(II)–Cd(II) selective separation by LM-MEUF performed in the presence of CTAB at pH = 7

Ligand 1.0×10^{-3} mol L^{-1}	$(\text{Cu(II)})_p$ Concn. (mg L^{-1})	$(\text{Cd(II)})_p$ Concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	18.03	46.00	43.24	18.16
12P2N	22.86	40.00	28.04	28.82
CALCA	24.63	47.67	22.47	15.18
CAL	20.63	38.76	35.06	31.03
DZ	22.43	39.67	29.39	29.41
ECST	22.30	36.00	29.80	35.94
INCAR	21.27	41.93	33.05	24.14
NEOC	22.00	50.00	30.75	10.80
NTR	21.30	50.00	32.95	11.03
ZNCN	20.60	46.16	35.16	17.86

Feed concentrations of CTAB, Cu(II), and Cd(II) are 5.00×10^{-3}, 5.00×10^{-4}, and 5.00×10^{-4} mol L^{-1}, respectively. Subscript p denotes "permeate."

Cu(II) ions with these ligands is most favored at pH 5 and that micellar effects which differentiate the complexation behaviors of Cu(II) and Cd(II) ions with the same ligands weaken at pHs 3 and 7.

That R values at pH 7 are higher than those at pH 3, except for a few ligands, may be caused by the initiation of metal hydroxide formation at pH 7.

3.2. Studies performed in the presence of TX100 micelles

3.2.1. CMC values of TX100

CMC values of TX100 in water, in 5.0×10^{-4} mol L^{-1} Cu(II) solution and in 5.0×10^{-4} mol L^{-1} Cd(II) solution, were determined to be 3.6×10^{-4}, 4.4×10^{-5}, and 5.7×10^{-5} mol L^{-1}, respectively.

3.2.2. Determination of ligands to be used in selective separation of Cu(II) and Cd(II) ions at pH 5

The ligands which exhibit different interactions with Cu(II) and Cd(II) ions in TX100 micellar media (12P2N, AB10B, CALCA, CAL, INCAR, ZNCN) were determined by inspection of optical absorption spectra obtained with studies carried out as described in Section 3.1.1.

3.2.3. Investigation of the feasibility of removal of Cu(II) cations by nonionic TX100 micelles

Effects of 12P2N, AB10B, CALCA, CAL, INCAR, and ZNCN on removal of Cu(II) ions from single-component solutions were investigated. The results of these studies are given in Table 6. The results in this table show that these ligands are not effective in removal of Cu(II) ions from TX100 micellar media. The highest *R* value is obtained in the presence of CAL, but it is lower than those obtained with SDS (100%) [45] and CTAB (99.95%, Table 1). The same is valid for the other ligands. Low retention coefficients in Table 6 indicate weak interactions between TX100 micelles and Cu(II)–ligand complexes. This can be attributed to the nonionic character of TX100 micelles which can interact with Cu(II) complex by only hydrophobic forces. That the *R* values attained in both anionic SDS and cationic CTAB micellar media are higher than those obtained in the presence of TX100 micelles can be attributed to the presence of additional interactions besides hydrophobic interactions in case of ionic micelles. Higher *R* values provide evidence for the charge effects of SDS and CTAB micelles which promote Cu(II) separation [8]. Charge effect can induce interactions between HOMO and LUMO sites of the molecular orbitals of complex molecules and CTAB and SDS micelles, respectively. As a result, solubilization of Cu(II) complex takes place more efficiently.

3.2.4. Determination of the efficiencies of ligands in selective removal of Cu(II) ions

Effects of 12P2N, AB10B, CALCA, CAL, INCAR, and ZNCN on selective separation of Cu(II) ions from Cd(II) ions were investigated in TX100 micellar media under the working conditions described in Section 3.1.4. The results of these studies are given in Table 7.

It can be seen from the results in Tables 6 and 7 that the existence of Cd(II) ions in the medium decreases the *R* values of Cu(II) ions drastically causing a negative effect on Cu(II) removal.

It can be concluded by the comparison of the results of the studies carried out in the presence of SDS (Table 5 in Ref. [45]), CTAB (Table 2), and TX100 (Table 7) that TX100 cannot be suggested to be used in Cu(II) separation from Cd(II)-containing solutions. On the other hand, the reason why CTAB is more effective in Cu(II) separation compared with SDS may be the repellant effect of positively charged CTAB micelles on Cd(II) ions.

3.2.5. Studies performed at pH 3 for selective removal of Cu(II) ions in TX100 micellar media

Effects of 12P2N, AB10B, CALCA, CAL, INCAR, and ZNCN on selective separation of Cu(II) ions from Cd(II) ions were investigated in TX100 micellar media under the working conditions described in Section 3.1.5. The results are presented in Table 8.

Table 6
Ligand effect on Cu(II) removal by LM-MEUF performed in the presence of TX100 at pH = 5

Ligand 1.0×10^{-3} mol L^{-1}	$(Cu(II))_p$ Concn. (mg L^{-1})	R_{Cu} (%)
12P2N	21.60	32.01
AB10B	23.10	27.28
CALCA	12.03	62.13
CAL	3.22	89.86
INCAR	28.96	8.99
ZNCN	5.92	81.14

Feed concentrations of TX100 and Cu(II) are 5.00×10^{-3} and 5.00×10^{-4} mol L^{-1}, respectively. Subscript *p* denotes "permeate."

Table 7
Ligand effect on Cu(II)–Cd(II) separation by LM-MEUF performed in the presence of TX100 at pH = 5

Ligand 1.0×10^{-3} mol L^{-1}	$(Cu(II))_p$ Concn. (mg L^{-1})	$(Cd(II))_p$ Concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
12P2N	29.27	53.00	7.80	5.69
AB10B	30.40	54.35	4.31	3.29
CALCA	19.45	52.95	38.77	5.78
CAL	25.70	51.60	19.10	8.18
INCAR	28.50	52.35	10.28	6.85
ZNCN	10.56	50.85	66.76	9.51

Feed concentrations of TX100, Cu(II), and Cd(II) are 5.00×10^{-3}, 5.00×10^{-4}, and 5.00×10^{-4} mol L^{-1}, respectively. Subscript *p* denotes "permeate."

Table 8
Ligand effect on Cu(II)–Cd(II) selective separation by LM-MEUF performed in the presence of TX100 at pH = 3

Ligand 1.0×10^{-3} mol L^{-1}	$(Cu(II))_p$ Concn. (mg L^{-1})	$(Cd(II))_p$ Concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
12P2N	31.20	39.50	2.11	29.71
AB10B	30.70	49.50	3.36	11.92
CALCA	28.70	26.90	9.67	52.13
CAL	29.36	49.50	7.77	11.91
INCAR	29.90	28.50	5.89	49.28
ZNCN	27.40	19.00	13.75	66.19

Feed concentrations of TX100, Cu(II), and Cd(II) are 5.00×10^{-3}, 5.00×10^{-4}, and 5.00×10^{-4} mol L^{-1}, respectively. Subscript *p* denotes "permeate."

Table 9
Ligand effect on Cu(II)–Cd(II) selective separation by LM-MEUF performed in the presence of TX100 at pH = 7

Ligand 1.0×10^{-3} mol L^{-1}	$(\text{Cu(II)})_p$ Concn. (mg L^{-1})	$(\text{Cd(II)})_p$ Concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
12P2N	23.50	49.53	26.03	11.86
AB10B	23.86	25.86	24.89	53.98
CALCA	23.63	22.67	25.62	59.66
CAL	21.26	42.76	33.08	23.91
INCAR	24.83	46.76	21.84	16.79
ZNCN	24.07	47.53	24.23	10.09

Feed concentrations of TX100, Cu(II), and Cd(II) are 5.00×10^{-3}, 5.00×10^{-4}, and 5.00×10^{-4} mol L^{-1}, respectively. Subscript *p* denotes "permeate."

The results in Table 8 reveal that selective separation of Cu(II) cannot be attained at pH 3. Contrary to the aim of the study, *R* values for Cd(II) ions are all higher than those for Cu(II) ions.

3.2.6. Studies performed at pH 7 for selective removal of Cu(II) ions in TX100 micellar media

Effects of 12P2N, AB10B, CALCA, CAL, INCAR, and ZNCN on selective separation of Cu(II) ions from Cd(II) ions were investigated in TX100 micellar media also at pH 7. The experimental conditions and the results of these LM-MEUF experiments are given in Table 9.

The results in Table 9 reveal that increasing the pH of the medium from 5 to 7 imposes a negative effect on selective removal of Cu(II) ions. R_{Cd} values become even higher in the presence of some ligands (AB10B, CALCA) than *R* values of Cu(II) ions.

It can be concluded from the results in Tables 7–9 that selective separation cannot be provided by TX100 micelles neither at pH 5 nor at pHs 3 and 7. The extent of the pH effect on *R* values depends on the kind of the ligand. *R* values for Cu(II) removal from single-component solution at pH 5 are also not favored in the presence of TX100 micelles (Table 6) as compared with the *R* values in the presence of CTAB (Table 1). Depending on the results in Tables 6–9, it can be conclusively said that TX100 cannot be suggested for Cu(II) separation by LM-MEUF.

4. Conclusions

The main conclusions drawn from the results of this study are as follows:

- Metallic ions of similar properties can simply be separated by LM-MEUF process.
- Metallic cations can be removed by MEUF not only in the presence of anionic micelles but also in the presence of positively charged micelles.
- The sequence of efficiency of ligands in Cu(II) removal from single-component solution is the same in the presence of both anionic SDS and cationic CTAB micelles with very close efficiencies regardless of the electrical charge of micelles. This reveals that interaction between Cu(II) complex and micelles is not electrostatic but mainly hydrophobic in character, that is., micelles do not function as attractants for metallic ions. That is, complexation reaction does not occur at micellar surface, between the micellar-solubilized ligand and reactive ions attracted by micelles, but micelles solubilize the Cu(II)–ligand complex such that Cu(II) ions are retained inside the micelles.
- [CTAB] in the feed solution can be lowered by increasing the concentration of ligand to provide complete separation. On the other hand, increasing the ligand concentration under fixed concentration of CTAB or increasing the CTAB concentration under fixed concentration of ligand beyond the limits leads to increases in both R_{Cd} and R_{Cu} values. The observed increments in R_{Cd} values are larger than those observed in R_{Cu} values, that is, selectivity is negatively affected. Negative effect of increments in ligand concentration on Cu(II)–Cd(II) separation is more pronounced compared with that caused by the increments in CTAB concentration.
- The optimum pH for selective removal of Cu(II) ions from Cd(II)-containing solutions by LM-MEUF is 5. Selectivity is affected negatively at pHs 3 and 7 in the presence of both CTAB and TX100 micelles, such that Cd(II) rejection is enhanced and Cu(II) rejection is inhibited.
- TX100 cannot be suggested to be used in Cu(II) removal from both single- and Cd(II)-containing solutions by LM-MEUF.
- By comparing the results of this study with those obtained in a previous LM-MEUF study performed by us in the presence of SDS, it can be conclusively said that the most effective ligand, out of 20 ligands tested, in terms of separation of Cu(II) ions from single-component solutions is TPTZ in both SDS and CTAB micellar media. On the other hand, the most effective ligands in terms of selective Cu(II)–Cd(II) separation are TPTZ and CALCA in SDS and CTAB micellar media, respectively. Since a smaller R_{Cd} value is achieved with CALCA–CTAB system under the same complete Cu(II) removal conditions compared with that achieved with TPTZ-SDS system, use of CALCA and CTAB can be suggested for selective separation.
- The results obtained in the presence of anionic, cationic, and nonionic micelles provided evidences for the mechanism of Cu(II) removal by LM-MEUF: not ligand but Cu(II)-ligand complex is solubilized by micelles. Interaction between complex molecules and micelles is mainly hydrophobic, but there occurs also electrostatic interaction between HOMO and LUMO sites of the molecular orbitals of complex molecules and CTAB and SDS micelles, respectively. This interaction increases the *R* values and renders them independent of micellar charge.

Acknowledgment

The financial support of the Gazi University Scientific Research Fund is gratefully acknowledged.

References

[1] J.F. Scamehorn, R.T. Ellington, S.D. Christian, B.W. Penney, R.O. Dunn, S.N. Bhat, Removal of multivalent metal cations from water using micellar-enhanced ultrafiltration, AIChE Symp. Ser., 82 (1986) 48–58.

[2] S.K. Singh, M. Kraemer, D. Trébouet, Studies on treatment of a thermo-mechanical process effluent from paper industry using ultrafiltration for water reuse, Desal. Wat. Treat., 49 (2012) 208–217.

[3] M. Afifi, H.A. Golestani, S. Sharifi, S. Kiani, Wastewater treatment of raisins processing factory using micellar-enhanced ultrafiltration, Desal. Wat. Treat., 52 (2014) 57–64.

[4] S. Kertész, J. Landaburu-Aguirre, V. García, E. Pongrácz, C. Hodúr, R.L. Keiski, A statistical experimental design for the separation of zinc from aqueous solutions containing sodium chloride and *n*-butanol by Micellar-enhanced ultrafiltration, Desal. Wat. Treat., 9 (2009) 221–228.

[5] Y.-H. Qu, G.-M. Zeng, J.-H. Huang, K. Xu, Y.-Y. Fang, X. Li, H.-L. Liu, Recovery of surfactant SDS and Cd^{2+} from permeate in MEUF using a continuous foam fractionator, J. Hazard. Mater., 155 (2008) 32–38.

[6] S. Sharifi, H.A. Golestani, M. Afifi, S. Kiani, Treatment of edible oil processing wastewater using micellar-enhanced ultrafiltration process, Desal. Wat. Treat., 52 (2014) 2412–2418.

[7] W. Zhang, G. Huang, J. Wei, Study on solubilization capability of various Gemini micelles in micellar-enhanced ultrafiltration of phenol-contaminated waters, Desal. Wat. Treat., 54 (2015) 672–682.

[8] S. Taşcıoğlu, Micellar solutions as reaction media, Tetrahedron, 52 (1996) 11113–11152.

[9] D. Kumar, M.A. Rub, Effect of sodium taurocholate on aggregation behavior of amphiphilic drug solution, Tenside Surfactants Deterg., 52 (2015) 464–472.

[10] M.A. Rub, N. Azum, A.M. Asiri, Binary mixtures of sodium salt of ibuprofen and selected bile salts: interface, micellar, thermodynamic, and spectroscopic study, J. Chem. Eng. Data, 62 (2017) 3216–3228.

[11] D. Kumar, M.A. Rub, Effect of anionic surfactant and temperature on micellization behavior of promethazine hydrochloride drug in absence and presence of urea, J. Mol. Liq., 238 (2017) 389–396.

[12] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: a review, J. Environ. Manage., 92 (2011) 407–418.

[13] R. Bade, S.H. Lee, A review of studies on micellar enhanced ultrafiltration for heavy metals removal from wastewater, J. Water Sustainability, 1 (2011) 85–102.

[14] A.A. Mungray, S.V. Kulkarni, A.K. Mungray, Removal of heavy metals from wastewater using micellar enhanced ultrafiltration technique: a review, Cent. Eur. J. Chem., 10 (2012) 27–46.

[15] A. Hafiane, I. Issıd, D. Lemordant, Counterion binding on micelles: an ultrafiltration study, J. Colloid Interface Sci., 142 (1991) 167–178.

[16] W. Lee, S. Lee, Micellar enhanced ultrafiltration (MEUF) and activated carbon fibre (ACF) hybrid processes for nickel removal from an aqueous solution, Desal. Wat. Treat., 47 (2012) 198–204.

[17] M.K. Aroua, F.M. Zuki, N.M. Sulaiman, Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration, J. Hazard. Mater., 147 (2007) 752–758.

[18] A. Choudhury, S. Sengupta, C. Bhattacharjee, S. Datt, Effects of co-solutes on Cr(VI) removal by micellar enhanced ultrafiltration (MEUF) process, Desal. Wat. Treat., 44 (2012) 67–74.

[19] Ü. Daniş, B. Keskinler, Chromate removal from wastewater using micellar enhanced crossflow filtration: effect of transmembrane pressure and crossflow velocity, Desalination, 249 (2009) 1356–1364.

[20] R. Camarillo, I. Asencio, J. Rincón, Micellar Enhanced Ultrafiltration for phosphorus removal in domestic wastewater, Desal. Wat. Treat., 6 (2009) 211–216.

[21] J.F. Scamehorn, J.H. Harwell, Surfactant-Based Treatment of Aqueous Process Streams, D.T. Wasan, M.F. Ginn, D.O. Shah, Eds., Surfactants in Chemical/Process Engineering, Marcel Dekker, New York, 1988, pp. 77–97.

[22] M. Ismael, C. Tondre, Extraction and back-extraction of metal ions in micellar systems using ultrafiltration: thermodynamic and kinetic aspects, J. Colloid Interface Sci., 160 (1993) 252–257.

[23] J.F. Scamehorn, S.D. Christian, D.A. El-Sayed, H. Uchiyama, Removal of divalent metal cations and their mixtures from aqueous streams using micellar-enhanced ultrafiltration, Sep. Sci. Technol., 29 (1994) 809–830.

[24] Y.-C. Huang, B. Batchelor, Crossflow surfactant-based ultrafiltration of heavy metals from waste streams, Sep. Sci. Technol., 29 (1994) 1979–1998.

[25] S. Ahmadi, Y.C. Huang, B. Batchelor, S.S. Köseoğlu, Binding of heavy metals to derivatives of cholesterol and sodium dodecyl sulfate, J. Environ. Eng., 121 (1995) 645–652.

[26] R.-S. Juang, Y.-Y. Xu, C.-L. Chen, Separation and removal of metal ions from dilute solutions using micellar-enhanced ultrafiltration, J. Membr. Sci., 218 (2003) 257–267.

[27] R. Bade, S.H. Lee, Micellar enhanced ultrafiltration and activated carbon fibre hybrid processes for copper removal from wastewater, Korean J. Chem. Eng., 24 (2007) 239–245.

[28] H. Kim, K. Baek, B.-K. Kim, H.-J. Shin, J.-W. Yang, Removal characteristics of metal cations and their mixtures using micellar enhanced ultrafiltration, Korean J. Chem. Eng., 25 (2008) 253–258.

[29] R.-S. Juang, S.-H. Lin, L.-C. Peng, Flux decline analysis in micellar-enhanced ultrafiltration of synthetic waste solutions for metal removal, Chem. Eng. J., 161 (2010) 19–26.

[30] M. Schwarze, M. Groβ, G. Buchner, L. Kapitzki, L. Chiappisi, M. Gradzielski, Micellar enhanced ultrafiltration (MEUF) of metal cations with oleylethoxycarboxylate, J. Membr. Sci., 478 (2015) 140–147.

[31] M. Schwarze, Micellar-enhanced ultrafiltration (MEUF) — state of the art, Environ. Sci. Water Res. Technol., 3 (2017) 598–624.

[32] C. Das, S. DasGupta, S. De, Prediction of permeate flux and counterion binding during cross-flow micellar-enhanced ultrafiltration, Colloid Surf. A, 318 (2008) 125–133.

[33] C. Tondre, S.-G. Son, M. Hebrant, Micellar extraction: removal of copper(II) by micelle-solubilized complexing agents of varying HLB using ultrafiltration, Langmuir, 9 (1993) 950–955.

[34] E. Pramauro, A.B. Prevot, V. Zelano, W.L. Hinze, G. Viscardi, P. Savarino, Preconcentration and selective metal ion separation using chelating micelles, Talanta, 41 (1994) 1261–1267.

[35] B.R. Fillipi, J.F. Scamehorn, W. Taylor, S.D. Christian, Selective removal of copper from an aqueous solution using ligand-modified micellar-enhanced ultrafiltration using an alkyl-β-diketone ligand, Sep. Sci. Technol., 32 (1997) 2401–2424.

[36] B.R. Fillipi, J.F. Scamehorn, S.D. Christian, R.W. Taylor, A comparative economic analysis of copper removal from water by ligand-modified micellar enhanced ultrafiltration and by conventional solvent extraction, J. Membr. Sci., 145 (1998) 27–44.

[37] C.-K. Liu, C.-W. Li, C.-Y. Lin, Micellar-enhanced ultrafiltration process (MEUF) for removing copper from synthetic wastewater containing ligands, Chemosphere, 57 (2004) 629–634.

[38] C.S. Kedari, S.S. Pandit, K.J. Parikh, S.C. Tripathi, P.M. Gandhi, Extraction of plutonium (IV) from aqueous nitrate solutions into ligand modified micellar phase (LMMP) of Tergitol 15-S-9 with tri-octylphosphine oxide and separation by ultrafiltration, Desal. Wat. Treat., 52 (2014) 446–451.

[39] J. Jung, J.-S. Yang, S.-H. Kim, J.-W. Yang, Feasibility of micellar-enhanced ultrafiltration (MEUF) for the heavy metal removal in soil washing effluent, Desalination, 222 (2008) 202–211.

[40] J. Klepac, L.D. Simmons, R.W. Taylor, J.F. Scamehorn, S.D. Christian, Use of ligand-modified micellar-enhanced ultrafiltration in selective removal of metal ions from water, Sep. Sci. Technol., 26 (1991) 165–173.

[41] U.R. Dharmawardana, S.D. Christian, R.W. Taylor, J.F. Scamehorn, An equilibrium model for ligand-modified micellar enhanced ultrafiltration using a water-insoluble ligand, Langmuir, 8 (1992) 414–419.

[42] S.B. Shadizadeh, R.W. Taylor, J.F. Scamehorn, A.L. Schovanec, S.D. Christian, Use of ligand-modified micellar-enhanced

ultrafiltration to selectively remove copper from water, ACS Symp. Ser., 716 (1999) 280–293.

[43] S.M. Manchalwar, V.A. Anthati, K.V. Marathe, Simulation of micellar enhanced ultrafiltration by multiple solute model, J. Hazard. Mater., 184 (2010) 485–492.

[44] R. Adıgüzel, S. Taşcıoğlu, Micelle nano-reactors as mediators of water-insoluble ligand complexation with Cu(II) ions in aqueous medium, Chem. Pap., 67 (2013) 456–463.

[45] D. Şahin, S. Taşcıoğlu, Removal of Cu(II) ions from single component and Cd(II) containing solutions by micellar enhanced ultrafiltration utilizing micellar effects on complex formation, Desal. Wat. Treat., 57 (2016) 11143–11153.

[46] C. Mesmin, J.-O. Liljenzin, Determination of $H_2TPTZ_2^{2+}$ stability constant by TPTZ solubility in nitric acid, Solvent Extr. Ion Exch., 21 (2003) 783–795.

[47] K. Abdi, H. Hadadzadeh, M. Salimi, J. Simpson, A.D. Khalaji, A mononuclear copper(II) complex based on the polypyridyl ligand 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz), $[Cu(tptz)_2]^{2+}$: X-ray crystal structure, DNA binding and in vitro cell cytotoxicity, Polyhedron, 44 (2012) 101–112.