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Removal of Cu(II) ions from single component and Cd(II) containing solutions by micellar enhanced ultrafiltration utilizing micellar effects on complex formation

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ABSTRACT

Optimum conditions for the removal of Cu(II) ions from both single-component and Cd(II) containing solutions by ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) were determined. Complexation behaviors of 20 ligands with Cu(II) and Cd(II) ions were investigated in micellar medium of SDS at different pH values to determine the ligands which could provide selective separation. In this respect, the most effective ligand was found to be 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ). In the presence of 6.6×10^{-8} mol L^{-1} TPTZ in the feed solution, SDS concentration required for complete removal of Cu(II) ions from single-component solution was lowered two times compared to conventional MEUF process. Complete removal of Cu(II) ions from Cd(II)-containing solutions could be achieved by LM-MEUF with Cd(II) rejections lower than 10%. It was demonstrated that SDS concentration in the feed solution and thereby in the filtrate can be lowered in substantial amounts, and metallic ions of similar properties can be separated simply by a LM-MEUF process.

Keywords: Selective separation; Ligand-modified MEUF; Removal of Cu(II) ions; Cd(II) ions; TPTZ

1. Introduction

Environmental damage caused by pollutants in wastewater streams is well established. Cu(II) and Cd (II) ions are toxic heavy metal ions found in many industrial wastewaters and in analytical samples. Heavy metal ions have been included in the EPA priority pollutant list since they are hazardous to man's health and aquatic biota. As a result, their removal from waters has received much attention in recent decades and new techniques have been developed for this purpose. Wastewater fluxes require a method able to treat large amounts of polluted water in which the pollutants are mostly extremely diluted. Recently, several surfactant-based separation processes have been developed, which have superiorities in simplicity and low cost compared to the former methods. Of these, micellar-enhanced ultrafiltration (MEUF) which was introduced in the 1980s is the most preferred technique [1]. MEUF is effective in removing pollutants from effluents of industrial processes, and applied also in analytical science as a separation, pre-concentration, and recovery method for the target ions and organics [2–7].

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Surfactant monomers form colloidal aggregates called micelles at concentrations higher than the critical micellization concentration (CMC) of the surfactant. MEUF process is based on adsorption of small target ions or solubilization of organics by surfactant micelles [8]. Micellar-bound ions or organics are removed by an ultrafiltration process carried out with membranes capable of retaining micelles [9–11]. Thus, the solute as well as the micelles are rejected from the downstream fluid (permeate), while the concentrations of the solute and surfactant in the feed (retentate) are increased.

Removal efficiency of MEUF depends on the characteristics and concentrations of targeted ions and surfactants, solution pH, ionic strength, surfactant to metal ion mole ratio, and parameters related to membrane operation such as pressure, filtration flow rate, stirring speed, membrane pore size, and material. Choice of surfactants depends on the type of the ions to be removed, so anionic surfactants are used for removing heavy metal cations and cationic surfactants are used to remove anions [8,12–17]. MEUF is substantially effective in separating Cu(II) ions and retentions between 90 and >99% have been reported for MEUF process with SDS [12,15,18–25]. Recently, Juang et al. have reported Cu(II) removal higher than 90% at optimum SDS/Cu(II) mole ratio and pH conditions [26].

MEUF has a drawback such that it cannot provide a high selectivity in removing metallic ions from solutions. MEUF can be only moderately effective in selective removal of metal ions, even if they have dissimilar properties such as Cu(II) and Ca(II) ions [27]. On the other hand, selective separation of ions in the medium can be effectively achieved by use of a ligand which undergoes selective complexation with the target ions. The complex is solubilized by surfactant micelles and retained in the retentate during MEUF, enhancing the metal rejection. This process is called “ligand-modified MEUF” (LM-MEUF).

The efficiency of LM-MEUF process depends on the ligand to metal ion mole ratio, the nature of the ligand, and on the pH of the sample solution since complex formation is pH dependent [28–33]. The working pH is generally between 3 and 7, so it can be achieved easily with wastewaters. A limited number of LM-MEUF studies have been employed for removal of copper [32,34] and removal efficiency of about 97% was achieved with cationic cetylpyridinium chloride. Ref. [32] is the only LM-MEUF study in which SDS is used, reporting that use of SDS as the surfactant imposes a negative effect on Cu(II) removal.

Selective removal of Cu(II) ions from Ca(II) ions which have dissimilar properties can be effectively achieved by LM-MEUF [30,31,35–37]. On the other hand, 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. Therefore, the main objective of this research was to explore the feasibility of LM-MEUF as a method for selective removal of Cu(II) ions from aqueous solutions containing Cd(II) ions. 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. On the other hand, surfactant micelles exert a “medium effect” which is a combination of cage, pre-orientation, charge, polarity, and microviscosity effects. As a result of this effect, micellar-bound reactants reside in microenvironments with quite different properties from those of the bulk phase [8]. As a consequence, ionization equilibria of the substrates interacting with micelles are changed by the “medium effect” of micelles and thereby, the stability constants as well as the stoichiometry of their complexes are changed [8,38]. Thus, it can be expected that micellar medium can differentiate 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 SDS micellar medium to determine the ligands which potentially could provide selective removal of Cu(II) ions. Effects of these ligands on Cu(II) removal from both single-component and Cd(II)-containing solutions were investigated. MEUF experiments for separation of Cu(II) ions were carried out in the absence and presence of these ligands, in an effort to minimize the SDS concentration in the feed solution, and thereby in the filtrate.

2. Materials and methods

2.1. Chemicals

All the reagents used in this study were of analytical purity and were used without further purification. Anionic surface active agent—sodium dodecyl sulfate (SDS, Merck, Germany) was used as the surfactant. Cu $(NO_3)_2·3H_2O$ (Merck, Germany) and $Cd(NO_3)_2·4H_2O$ (Merck, Germany) salts were used as sources of Cu(II) and Cd(II) ions, respectively.

The complexing agents used in the experiments were 3-hydroxy-4-[2-sulpho-4-(4-sulphophenylazo)phenylazo] -2,7-naphthelene disulphonic acid sodium salt (Ponceau S, PS; Merck, Germany); 1-phenylazo-2-naphthol-6,8-disulphonic acid sodium salt (Orange G, OG; Merck, Germany); 4-amino-5-hydroxy-3-[(4-nitrophenyl)azo]-6-(phenylazo)-2,7-naphthalene disulphonic acid disodium salt (Naphthol Blue Black, Amido Black 10 B,

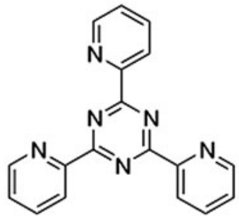

Fig. 1. Structural formula of TPTZ (2,4,5-Tri(2-pyridyl)-1,3,5-triazine).

AB10B; Merck, Germany); 4-(4-nitrophenylazo)-resorcinol (44NPR; Merck, Germany); diphenylthiocarbazone (Dithizone, DZ; Merck, Germany); 4-[4-(dimethylamino) phenylazo]benzene sulphonic acid sodium salt (Methyl Orange, MO; Hopkin and Williams, UK); 2-hydroxy-1-(1-hydroxy-2-naphthylazo)-6-nitronaphthalene-4-sulphonic acid sodium salt (Eriochrome Black T, ECST; Merck, Germany); 1-(2-pyridylazo)-2-naphthol (PAN, 12P2N; Merck, Germany); 5,5´-indigo disulphonic acid sodium salt (Indigo Carmine, INCAR; Merck, Germany); 2,4,6-tri (2-pyridyl)-1,3,5-triazine (TPTZ (Fig. 1); Merck, Germany); 3,5,6-triphenyl-2,3,5,6-tetraaza[2.1.1.]bicyclo-1-hexene (Nitron, NTR; Merck, Germany); 2,9-dimethyl-1,10-phenanthroline (Neocuproine, NEOC; Sigma, USA); 2-hydroxy-1-(2-hydroxy-1-naphthylazo)napthalene-4-sulphonic acid sodium salt (Calcon, CAL; Merck, Germany); 2-hydroxy-1-(2-hydroxy-4-sülfo-1-naphthylazo)naphtelene-3-carboxylic acid (Calconcarboxylic Acid, CALCA; Merck, Germany); disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)diazenylphenyl]phenyl]diazenyl-naphthalene-1-sulfonate (Congo Red, COR; Merck, Germany); 5-(3-nitrophenylazo)-2-hydroxy benzoic acid sodium salt (Alizarin Yellow, AY; Merck, Germany); 1-[4-(phenylazo)phenylazo]-2-naphthol (Sudan III, SIII; Fluka, Germany); 2-[(4-dimethylamino)phenylazo]benzoic acid (Methyl Red, MR; Merck, Germany); 4-([2,4-dihidroxyphenyl]azo)benzene sulphonic acid sodium salt (Tropaeolin O, Acid Orange 6, TROP; Schering Kahlbaum, Germany); and 2-Carboxy-2´-hydroxy-5´-sulfoformazyl-benzene monosodium salt (Zincon, ZNCN; Merck, Germany).

Deionized water was used throughout the study.

2.2. Apparatus and procedures

Dead-end ultrafiltration experiments were carried out using a batch-stirred UF cell (Amicon 8050 stirred cell, Millipore, USA; Fig. 2). Organic regenerated cellulose ultrafiltration membranes (Millipore, USA) with molecular weight cut-off 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 bar 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 ultrafiltration rate.

The first 5 mL of filtrate was discharged and the subsequent 20 mL of permeate was collected and analyzed. Permeate and feed concentrations of ions were measured by an ionmeter (Orion 720A Plus) combined with Orion 9629BN Cu(II) and Orion 9648BN Cd(II) selective electrodes. 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). FAAS measurements were carried out in triplicate.

The optical absorption spectra were taken with a UNICAM UV2-100 spectrophotometer. In these experiments, the concentrations of SDS, Cu(II), Cd(II), and ligand solutions were kept as 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} SDS solution since they were mostly insoluble in water. SDS concentration in filtrates was determined by surface tension measurements. Surface tension measurements were made by a Traube stalagmometer. A Sartorious 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, the 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 backflushed with 20 mL deionized water at a pressure of 4 bars. The membrane permeability was checked to ensure that the permeability remains constant between successive usages. Following UF experiments performed at pH 7, pH of deionized water to be used in the first stage of cleaning process was brought to 4.5, so that any hydroxide residue on the membrane could be dissolved.

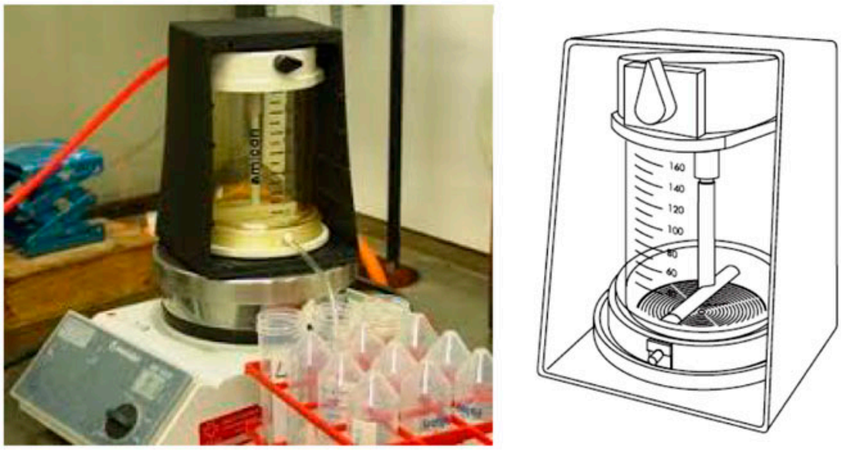

Fig. 2. UF cell used in the experiments.

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*:

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

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

3. Results and discussion

3.1. Determination of CMC values of SDS

CMC values of SDS were determined under different conditions since the MEUF experiments were to be carried out in the presence of SDS in concentrations higher than its CMC. Metallic ions with net charges favor the formation of micelles by decreasing the repulsions between the negatively charged head groups. Therefore, CMC values were also determined in the presence of Cu(II) and Cd(II) ions. CMC values of SDS 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 5.9×10^{-3}, 1.8×10^{-3}, and 2.2×10^{-3} mol L^{-1}, respectively.

3.2. Determination of the optimum SDS concentration for Cu(II) removal by MEUF

Dependence of Cu(II) removal efficiency on SDS concentration was investigated at the first stage of MEUF experiments. The [SDS]—*R*% graph plotted with the results of these experiments is given in Fig. 3. It can be concluded from the evaluation of Fig. 3 that complete removal of Cu(II) can be achieved in the presence of ~2.0×10^{-2} mol L^{-1} SDS. This is a concentration ~3.4 times higher than the CMC of SDS in water.

3.3. Determination of ligands for selective separation of Cu(II) and Cd(II) ions

Optical absorption spectra of SDS, Cu(II), Cd(II), and ligand solutions; binary solutions of SDS with ligands and Cu(II) and Cd(II) ions; and ternary solutions composed of SDS, ligand, and Cu(II) or Cd(II) ions were recorded at pH values 1, 3, 5, 7, and 9 to determine the ligands that could be used in LM-MEUF process for selective separation of Cu(II)

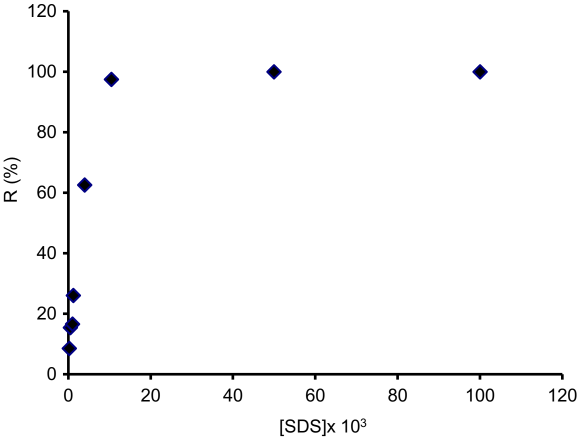

Fig. 3. Dependence of Cu(II) removal efficiency of MEUF on SDS concentration at pH 5.

Table 1
The ligands which exhibit different affinities for Cu(II) and Cd(II) ions in SDS micellar medium, and the pH values at which spectral disparities are observed

Ligand	pH
MO	5, 7
44NPR	5, 7
MR	5, 7
CALCA	1, 3, 5, 7, 9
CAL	3, 5, 7, 9
AB10B	5, 7, 9
OG	5, 7, 9
PS	5, 7, 9
INCAR	5, 7
12P2N	1, 3, 5, 7, 9
ECST	5, 7, 9
ZNCN	1, 3, 5, 7, 9
TPTZ	3, 5, 7

Table 2
Ligand effect on Cu(II) removal by MEUF performed at pH 5

Ligand (1.00×10^{-3} mol L^{-1})	$(Cu(II))_p$ concn. (mg L^{-1})	R (%)
TPTZ	–	100.00
INCAR	6.53	79.45
44NPR	7.49	76.42
CAL	–	100.00
AB10B	2.84	91.06
OG	6.58	79.28
PS	6.09	80.84
CALCA	–	100.00
MO	7.24	77.21
ZNCN	–	100.00
12P2N	–	100.00

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

and Cd(II) ions. Thus, 323 spectra were obtained using 20 azo compounds as ligands. The ligands which exhibit different complexation behaviors with Cu(II) and Cd(II) ions were determined by the inspection of these spectra in a comparative way. These ligands and the pH values at which they exhibit different affinities to Cu(II) and Cd(II) ions are given in Table 1. The results reveal that all the ligands in Table 1 interact differently with Cu(II) and Cd(II) ions in micellar media at pH 5 and 7. Of these values, 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. pH 7 was not preferred to exclude the formation of metallic hydroxides.

3.4. Comparison of the efficiencies of ligands in removal of Cu(II) ions by LM-MEUF

Among the ligands in Table 1, 11 ligands which interact with Cu(II) ions but not with Cd(II) ions were chosen to be used in LM-MEUF experiments for selective removal of Cu(II) ions. Their effects on Cu(II) removal were investigated in the presence of 5.0×10^{-3} mol L^{-1} SDS. 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 removal of Cu (II) ions are TPTZ, CAL, CALCA, ZNCN, and 12P2N.

Based on the results in Table 2, effects of these 5 ligands on separation of Cu(II) ions were investigated in more detail to determine the concentrations of these ligands required for complete separation of Cu(II) ions. In these experiments, the SDS and Cu(II) concentrations were kept as 5.0×10^{-3} and 5.0×10^{-4} mol L^{-1}, respectively. The results obtained from these experiments are presented in Table 3.

The results in Table 3 reveal that among these 5 ligands, the most effective ligand in removal of Cu(II) ions is TPTZ.

TPTZ molecules are supposed to reside in the micellar interior since its hydrophobic character is dominated (Fig. 1). On the other hand, it is expected to be located near to the micellar interface, to some extent, such that it can still be solvated by water since it has six nitrogen atoms in its structure. Thus, it can gain a configuration imposed by pre-orientation effect of micelles that facilitates its complexation with Cu(II) ions electrostatically attracted to the micellar surface [8].

The effect of TPTZ on Cu(II) removal was further investigated in more detail to determine the minimum SDS and TPTZ concentrations for complete removal of Cu(II) ions, by altering the concentrations of both TPTZ and SDS. The results of these LM-MEUF studies are given in Table 4.

The results in Table 4 display the inverse proportionality between the SDS and ligand concentrations. It can be concluded from the results in Table 4 that the minimum SDS concentration required for complete removal of Cu(II) ions by LM-MEUF decreases with increase in the ligand concentration. 6.6×10^{-8} mol L^{-1} TPTZ provides complete removal of 5.0×10^{-4} mol L^{-1} Cu(II) ions in the presence of 1.0×10^{-2} mol L^{-1} SDS, i.e. in the presence of SDS in two times lower concentration than that required for complete removal of Cu(II) ions by conventional MEUF (Fig. 3). The existence of 1.0×10^{-4} mol L^{-1} TPTZ in the feed solution enables complete removal

Table 3
Effect of ligand concentration on Cu(II) removal by LM-MEUF performed at pH 5

Ligand and concn. (mol L^{-1})	$(\mathrm{Cu(II)})_p$ concn. (mg L^{-1})	R (%)	Ligand and concn. (mol L^{-1})	$(\mathrm{Cu(II)})_p$ concn. (mg L^{-1})	R (%)
TPTZ 3.33×10^{-5}	1.21	96.19	ZNCN 3.33×10^{-5}	8.97	71.76
TPTZ 6.66×10^{-5}	0.59	98.14	ZNCN 1.66×10^{-4}	4.15	86.93
TPTZ 1.66×10^{-4}	–	100.00	ZNCN 3.33×10^{-4}	3.95	87.56
CAL 3.33×10^{-5}	6.32	80.11	ZNCN 6.66×10^{-4}	–	100.00
CAL 1.66×10^{-4}	2.64	91.69	12P2N 3.33×10^{-5}	6.48	79.60
CAL 3.33×10^{-4}	–	100.00	12P2N 6.66×10^{-4}	5.86	81.55
CALCA 3.33×10^{-5}	6.22	80.42	12P2N 1.66×10^{-4}	5.22	83.57
CALCA 1.66×10^{-4}	4.96	84.38	12P2N 3.33×10^{-4}	2.93	90.77
CALCA 3.33×10^{-4}	4.76	85.02	12P2N 6.66×10^{-4}	1.29	95.73
CALCA 6.66×10^{-4}	–	100.00	12P2N 9.99×10^{-4}	–	100.00

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

Table 4
Dependence of the concentration of TPTZ required for complete removal of Cu(II) by MEUF on SDS concentration, at pH 5

$[\mathrm{SDS}]_o \times 10^3$	$[\mathrm{Cu(II)}]_o \times 10^4$	[TPTZ]	$(\mathrm{Cu(II)})_p$ concn. (mg L^{-1})	R (%)
7.00	5.00	3.33×10^{-5}	1.59	94.99
7.00	5.00	6.66×10^{-5}	0.47	98.52
7.00	5.00	1.00×10^{-4}	–	100.00
8.00	5.00	3.33×10^{-5}	–	100.00
8.00	5.00	1.66×10^{-5}	–	100.00
8.00	5.00	1.25×10^{-5}	0.31	99.02
8.00	5.00	8.33×10^{-6}	0.83	97.38
9.00	5.00	4.17×10^{-6}	–	100.00
9.00	5.00	2.08×10^{-6}	–	100.00
9.00	5.00	1.04×10^{-6}	–	100.00
9.00	5.00	5.17×10^{-7}	–	100.00
9.00	5.00	2.66×10^{-7}	–	100.00
9.00	5.00	1.66×10^{-7}	0.85	97.32
9.00	5.00	1.33×10^{-7}	2.22	93.00
10.00	5.00	8.33×10^{-8}	–	100.00
10.00	5.00	6.66×10^{-8}	–	100.00
10.00	5.00	5.00×10^{-8}	0.52	98.36

Note: Subscripts o and p denote "feed solution" and "permeate", respectively.

of Cu(II) ions in the presence of SDS in a lower concentration (7.0×10^{-3} mol L^{-1}). It can be predicted from these results that [SDS] in the feed solution can be lowered to a concentration close to CMC by increasing the concentration of TPTZ without any concern of increased TPTZ concentration in the permeate since Cu complex of TPTZ has a structure of $[\mathrm{Cu(TPTZ)_2}]^{2+}$ and TPTZ has a very low solubility in water [39,40]. Undissolved TPTZ and TPTZ solubilized by micelles will be retained by the membrane.

3.5. Optimization of the ligand and SDS concentrations for selective separation

3.5.1. Optimum ligand and SDS concentrations for selective removal of Cu(II) ions at pH 5

Following the determination of the optimum concentrations of SDS and ligands for LM-MEUF of single-component Cu(II) solutions, another sets of experiments were performed at pH 5 to determine the optimum ligand and SDS concentrations for selective removal of Cu(II) ions from Cd(II)-containing solutions. In these studies, effects of 13 ligands which were observed to have different affinities to Cu(II) and Cd(II) ions (Table 1) in micellar medium were investigated. The results of these studies are given in Table 5.

The results in Table 5 reveal that TPTZ, CAL, and ZINCON are the most effective ligands in the selective removal of Cu(II). Based on these results, further LM-MEUF experiments were carried out using these ligands to determine both the SDS and the dependent ligand concentrations required for complete removal of Cu(II) ions. The results of these experiments are given in Table 6.

With the inspection of the results in Table 6 in a comparative way, it can be concluded that increase in both ligand and SDS concentrations improves the rejection of Cu(II) ions, but increases the rejection of Cd(II) ions, i.e. impose a negative effect on selective separation. The other conclusions that can be drawn from the data in Table 6 are that the necessary SDS concentrations for complete removal of 5.00×10^{-4} mol L^{-1} Cu(II) ions in the presence of

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

(1.00×10^{-3} mol L^{-1}) Ligand	$(Cu(II))_p$ concn. (mg L^{-1})	$(Cd(II))_p$ concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	0.03	50.67	99.91	9.84
INCAR	13.03	46.20	58.98	17.79
44NPR	11.80	50.10	62.85	10.85
CAL	0.08	52.70	99.74	6.22
AB10B	10.07	53.50	68.30	4.80
OG	13.26	46.80	58.26	16.72
PS	13.86	44.80	56.37	20.28
CALCA	0.75	47.10	97.64	16.19
MO	10.83	50.50	65.91	10.14
ZNCN	2.13	51.30	93.29	9.55
12P2N	0.38	36.80	98.80	34.52
ECST	3.01	51.00	90.52	9.25
MR	10.97	48.60	65.47	13.52

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

Table 6
Dependence of the required concentrations of TPTZ, CAL, and ZNCN to achieve complete removal of Cu(II) ions from Cd(II)-containing solution, on SDS concentration

	$[SDS]_o \times 10^3$	[Ligand]	$(Cu(II))_p$ concn. (mg L^{-1})	$(Cd(II))_p$ concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	5.00	2.66×10^{-3}	0.0010	52.10	99.99	7.29
	5.00	3.33×10^{-3}	–	50.86	100.00	9.50
	10.00	1.00×10^{-3}	0.0079	49.90	99.98	11.20
	13.30	1.00×10^{-3}	–	48.76	100.00	13.24
CAL	5.00	1.66×10^{-3}	0.045	48.60	99.86	13.52
	5.00	2.66×10^{-3}	0.020	47.46	99.93	15.55
	5.00	3.33×10^{-3}	–	45.23	100.00	19.51
	10.00	1.00×10^{-3}	0.042	46.97	99.87	16.07
	13.30	1.00×10^{-3}	–	46.25	100.00	17.70
ZNCN	5.00	2.66×10^{-5}	0.1320	50.20	99.58	10.67
	5.00	3.33×10^{-3}	0.0620	49.06	99.80	12.70
	5.00	5.00×10^{-3}	0.0051	48.66	99.98	13.52
	5.00	6.66×10^{-3}	–	47.43	100.00	15.60
	10.00	1.00×10^{-3}	0.4500	48.90	98.58	12.98
	13.30	1.00×10^{-3}	0.1300	48.30	99.59	14.06
	16.62	1.00×10^{-3}	–	47.56	100.00	15.37

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

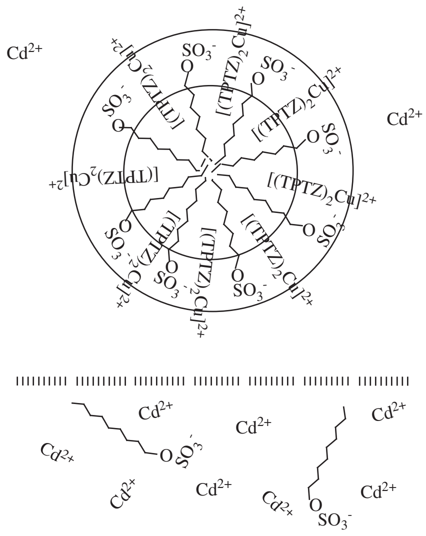

Fig. 4. Schematic representation of the mechanism of LM-MEUF process in which Cu(II) ions are separated from Cd(II) ions via selective complexation with TPTZ and subsequent solubilization of the complex by surfactant micelles.

1.0×10^{-3} mol L^{-1} TPTZ, CAL, and ZINCON are 1.3×10^{-2}, 1.3×10^{-2}, and 1.6×10^{-2} mol L^{-1}, respectively. These SDS concentrations are all lower than the minimum SDS concentration required for complete removal of 5.00×10^{-4} mol L^{-1} Cu(II) ions from single-component solutions by MEUF (Fig. 3).

The rejection coefficients reveal that the least Cd(II) rejection occurs in the presence of TPTZ. In fact, Cd (II) rejection in such a small extent may be attributed mostly to the adsorption of Cd(II) ions by the membrane itself since TPTZ were found not to undergo complexation with Cd(II) ions at pH 5. Cd(II) rejections are somewhat higher in the presence of ZNCN and the highest Cd(II) rejection is observed in the presence of CAL, i.e. the selectivity decreases in the order TPTZ > ZNCN > CAL, implying that the most effective ligand in selective separation of Cu(II) ions is TPTZ. On the other hand, CAL provides complete removal of Cu(II) ions at lower concentrations than that of ZNCN.

It can be concluded from the results in Table 6 that the required concentration of TPTZ for complete removal of Cu(II) ions and the selectivity increases as the concentration of SDS decreases. This result reveals that the same considerations for Cu(II) separation from single-component solutions in the presence of TPTZ is also valid for selective separation of Cu(II) ions, i.e. [SDS] in the feed solution can be lowered to a concentration close to CMC by increasing the concentration of TPTZ. The mechanism of selective separation of Cu(II) ions from Cd(II) ions by LM-MEUF, which is based on complexation of Cu(II) ions with TPTZ and subsequent stabilization of the complex by surfactant micelles, has been schematized in Fig. 4.

That TPTZ undergoes complexation with Cu(II) ions but not with Cd(II) ions, in micellar media, has been reported for the first time.

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

The effects of the ligands which were found to have different affinities to Cu(II) and Cd(II) ions in micellar media at pH 3 (Table 1), on selective removal of Cu(II) ions were investigated in another set of LM-MEUF experiments performed at pH 3. The conditions and the results of these LM-MEUF experiments are given in Table 7. By the comparison of the data in Tables 5 and 7, it can be concluded 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 decrease in rejection of both Cu(II) and Cd(II) ions.

3.5.3. 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 ligands which exhibit different complexation behaviors with Cu(II) and Cd(II) ions at this

Table 7
Ligand effect on Cu(II)–Cd(II) selective separation by LM-MEUF performed in the presence of SDS, at pH 3

Ligand (1.00×10^{-3} mol L^{-1})	$(Cu(II))_p$ concn. (mg L^{-1})	$(Cd(II))_p$ concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	28.60	39.56	9.97	29.61
12P2N	25.70	38.45	19.10	31.58
CALCA	27.75	40.15	30.89	28.55
CAL	21.80	48.40	31.38	44.16
ZNCN	24.40	36.70	23.19	34.69

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

Table 8
Ligand effect on Cu(II)–Cd(II) selective separation by LM-MEUF performed in the presence of SDS, at pH 7

Ligand (1.00×10^{-3} mol L^{-1})	$(Cu(II))_p$ concn. (mg L^{-1})	$(Cd(II))_p$ concn. (mg L^{-1})	R_{Cu} (%)	R_{Cd} (%)
TPTZ	21.70	26.20	31.68	53.38
INCAR	26.23	42.53	17.43	24.32
44NPR	25.67	52.26	19.20	7.01
CAL	20.06	33.00	36.85	41.28
AB10B	24.85	49.96	21.78	11.10
OG	23.76	50.83	25.21	9.55
PS	23.53	41.37	25.98	26.38
CALCA	26.96	42.10	15.14	25.08
MO	24.73	49.96	24.06	11.10
ZNCN	24.96	43.66	22.15	22.31
12P2N	21.20	47.17	33.27	16.08
ECST	23.86	41.63	24.89	25.92
MR	23.65	45.43	25.56	19.16
NTR	22.80	33.53	28.23	40.33

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

pH (Table 1) to see their effects on selective separation of Cu(II) ions from Cd(II) ions. The experimental conditions and the results of these LM-MEUF experiments are given in Table 8. By the comparison of the data in Tables 5 and 8, 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 and leads to remarkable decrease in rejection of both Cu(II) and Cd(II) ions.

On the basis of these results, it can be conclusively said that selectivity is affected negatively at both pH 3 and 7, as compared to that at pH 5, such that Cd(II) rejection is enhanced and Cu(II) rejection is inhibited at these pH values (Tables 5, 7, and 8).

4. Conclusions

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

(1) CMC of SDS in water (5.9×10^{-3} mol L^{-1}) decreases to 1.8×10^{-3} and 2.2×10^{-3} mol L^{-1} in the presence of 5.0×10^{-4} mol L^{-1} Cu(II) and 5.0×10^{-4} mol L^{-1} Cd(II), respectively.

(2) 5.0×10^{-4} mol L^{-1} Cu(II) can completely be removed by MEUF performed at pH 5 in the presence of 2.0×10^{-2} mol L^{-1} SDS.

(3) Mode of interaction of ligands with Cu(II) and Cd(II) ions in SDS micellar medium is pH dependent.

(4) The most effective ligand, out of 20 ligands, in removal of Cu(II) ions by LM-MEUF performed at pH 5 can be sequenced in the order TPTZ > CAL > CALCA ≈ ZNCN > 12P2N.

(5) 6.6×10^{-8} mol L^{-1} TPTZ provides complete removal of 5.0×10^{-4} mol L^{-1} Cu(II) ions in the presence of SDS in two times lower concentration than that required for complete removal of Cu(II) ions by conventional MEUF (~2.0×10^{-2} mol L^{-1}). The SDS concentration can be further lowered by increasing the ligand concentration since there is an inverse proportionality between these concentrations.

(6) Metallic ions of similar properties can be separated by LM-MEUF. The optimum pH for selective removal of Cu(II) ions from Cd(II)-containing aqueous solutions by LM-MEUF is 5. Selectivity decreases at pH values 3 and 7. The most effective ligands in terms of selective removal of Cu(II) ions from Cd(II)-containing solutions at pH 5 are TPTZ, ZNCN, and CAL. The selectivity decreases in the order TPTZ > ZNCN > CAL. On the other hand, CAL provides complete removal of Cu(II) ions at lower concentrations than that of ZNCN. TPTZ in a concentration of 3.0×10^{-3} mol L^{-1} can provide complete removal of 5.0×10^{-4} mol L^{-1} Cu(II) ions from solutions containing 5.0×10^{-4} mol L^{-1} Cd(II), with Cd (II) rejections lower than 10%, in the presence of 5.0×10^{-3} mol L^{-1} SDS. The concentration of TPTZ required for complete removal of Cu(II) ions and the selectivity increases as the concentration of SDS decreases, i.e. there is an inverse proportionality between SDS and TPTZ concentrations.

(7) LM-MEUF enables to lower [SDS] in the feed solution, and thereby in the filtrate, in substan-

tial amounts, as compared to conventional MEUF. 6.6×10^{-8} mol L^{-1} TPTZ provides complete removal of 5.0×10^{-4} mol L^{-1} Cu(II) ions in the presence of 1.0×10^{-2} mol L^{-1} SDS, i.e. in the presence of SDS in two times lower (50%) concentration than that required for complete removal of Cu(II) ions by conventional MEUF. The existence of 1.0×10^{-4} and 1.6×10^{-4} mol L^{-1} TPTZ in the feed solution enables complete removal of Cu(II) ions in the presence of 7.0×10^{-3} and 5.0×10^{-3} mol L^{-1} SDS, respectively. It can be predicted from these results that [SDS] in the feed solution can be lowered to a concentration close to CMC by increasing the concentration of TPTZ.

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