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Use of Ligand-Modified Micellar-Enhanced Ultrafiltration in the Selective Removal of Metal Ions from Water

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Abstract

Ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) is a membrane-based separation technique which can selectively remove specific ions from an aqueous solution containing several ions of like charge. In LM-MEUF, surfactant and amphiphilic ligand are added to the contaminated water. The surfactant forms aggregates called micelles, and the ligand is selected to complex the ion of interest and to solubilize strongly in the micelles. The result is micelles containing a high fraction of the ligand and the target ion. If the surfactant is chosen to have the same charge as the target ion, other ions in solution with this same charge will not associate with the micelles, making the retention of ions by the micelles very selective. The solution is then passed through an ultrafiltration membrane with pore sizes small enough to block the passage of micelles. In this study, divalent copper is the target ion in a solution also containing divalent calcium. A cationic surfactant is used with *N*-*n*-dodecyl-iminodiacetic acid as the copper-specific ligand. Rejections of copper of up to 99.2% are observed, with no rejection of calcium, showing that LM-MEUF has almost perfect selectively, as well as high capacity in this case.

INTRODUCTION

Micellar-enhanced ultrafiltration (MEUF) is a separation technique which involves adding surfactant to a polluted water stream. The surfactant forms roughly spherical aggregates called micelles which contain about 50 to 100 molecules (*1*). The interior of the micelle contains the hydrocarbon

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chain of the surfactant and forms a hydrophobic environment. Organic pollutants in the water dissolve or solubilize in micelles primarily through hydrophobic association and interactions with the surfactant head groups (*2*). If an anionic surfactant is used, the micelle has a high negative electrical potential on the surface where the charged hydrophilic groups are located. Any multivalent heavy metals present will tend to adsorb or bind preferentially on the micelle surface due to electrostatic attraction. If a cationic surfactant is used, multivalent anionic species in solution will bind to the micelle instead. The solution is then treated in an ultrafiltration device with membrane pore sizes small enough to block the passage of micelles. Previous studies have demonstrated the ability of MEUF to remove nonionic organics with rejections up to 99.8% and high fluxes (*3–11*). Generally, the more hydrophobic the organic solute, the higher the degree of solubilization and subsequent rejection in MEUF (*9, 10*). The use of MEUF to remove divalent cations using an anionic surfactant or divalent anions using a cationic surfactant is also quite effective, with rejections as high as 99.8% and good fluxes (*10–15*). MEUF can also remove both organics and divalent cations simultaneously without the removal of one type of pollutant affecting the removal of the other [*15*].

Any divalent cation is removed with approximately the same rejection as any other in MEUF (*16*), since the binding to the micelle is not very sensitive to factors other than charge. In many applications, there will be only one or a few types of ions in solution which need to be removed. Wastewaters containing a toxic heavy metal cation with other relatively innocuous cations are often produced in industries such as metal plating plants. Another example is abandoned metal mines which can fill with acid mine water, polluting nearby drinking water aquifers. For instance, in Northeastern Oklahoma, abandoned zinc mine water contains substantial zinc concentrations, but much higher calcium concentrations. In order to discharge the water to the environment, only the zinc needs to be removed. If this water were treated by traditional MEUF, much effort would be wasted removing calcium from such a stream in order to remove the zinc.

In ligand-modified micellar-enhanced ultrafiltration (LM-MEUF), a ligand is added to the polluted solution in addition to the surfactant prior to ultrafiltration. The ligand is designed to complex the target ion of interest and to solubilize effectively in the micelles. If the surfactant has the same charge as the target ion, the selectivity for the target ion is expected to be very high since other co-ions will not bind to the micelle. A schematic diagram of LM-MEUF is shown in Fig. 1.

In this paper, LM-MEUF using a cationic surfactant is shown to be effective in removing copper preferentially from a solution containing both copper and calcium.

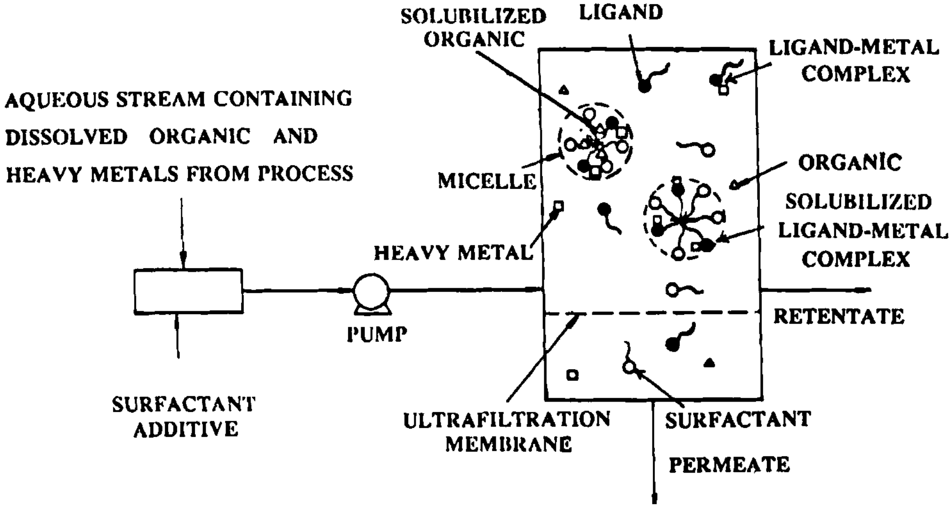

FIG. 1. Schematic of the ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) process.

EXPERIMENTAL

Methods

Ultrafiltration was studied by using Spectrum 400 mL stirred cells at 25°C and 414 kPa (60 psig). Spectrum cellulose acetate membranes with a molecular weight cut-off of 5000 were used. A feed solution of 300 mL was used to initiate a run. The run was terminated when 200 mL had passed through the membrane as permeate. The separation of copper or calcium was determined by measuring the concentration of both ions in the permeate. For each run, this permeate concentration is reported at the point in the run where 100 mL permeate have passed through (the mid-point). The retentate (solution not passing through the membrane) composition at any point in the run is calculated from a material balance and a knowledge of permeate concentrations. Therefore, concentrations at one condition are produced from a run. The copper and calcium concentrations were measured using a Varian SpectrAA-20 atomic absorption spectrophotometer.

MATERIALS

Copper chloride dihydrate and calcium chloride dihydrate were used as received (Fisher Certified ACS grade). *N*-Hexadecylpyridinium chloride monohydrate (cetylpyridinium chloride or CPC) from Hexcel Chemical Co. was used as received. This CPC is pharmaceutical grade and its purity was confirmed by surface tension and HPLC analysis. Water was purified by double ion exchange and carbon filtering.

The ligand, *N*-*n*-dodecyl-iminodiacetic acid, was synthesized by condensation of 2 moles chloroacetic acid with 1 mole *n*-dodecylamine in 90:10 ethanol–water (*17*). The ligand was purified by recrystallization from 95:5 ethanol–water. Melting point, NMR, IR, and MS data were in excellent agreement with the literature values (*17*).

RESULTS AND DISCUSSION

The experimental results for all runs made are given in Table 1. Surfactant rejections of more than 99% have been demonstrated for the surfactant/membrane combination used in this study with surfactant retentate concentrations similar to those used here (*5*). The ligand has a large hydrophobic tail. When it is uncomplexed with the metal, it is a monovalent anion. When it is complexed, it is neutral in charge. Therefore, by design, it should be nearly 100% bound to the cationic surfactant micelles (and hence nearly 100% rejected by the membrane) under conditions of all experiments reported here. Therefore, complete rejection of both the surfactant and the ligand is assumed in calculating the retentate ligand concentrations shown in Table 1.

TABLE 1
Ultrafiltration Run Results (all concentrations in m*M*)

Retentate				Permeate		Rejection of Cu^{2+} (%)[a]
[Surfactant]	[Ligand]	$[Cu^{2+}]$	$[Ca^{2+}]$	$[Cu^{2+}]$	$[Ca^{2+}]$	
157.0	0.785	0.734	0.728	0.040	1.57	94.6
235.0	0.785	0.777	0.512	0.017	1.88	97.8
314.0	0.785	0.769	0.268	0.006	2.27	99.2
157.0	0	0.428	0.998	0.645	1.14	—
157.0	0.314	0.636	1.010	0.292	1.20	54.1
157.0	1.57	0.770	1.128	0.017	0.917	97.8
157.0	0.785	0	0.721	0	1.48	—
157.0	0.785	0.306	0.683	0.008	1.59	97.4
157.0	0.785	0.677	0	0.069	0	89.8
157.0	0.785	0.742	0.179	0.048	0.225	93.5
157.0	0.785	0.759	0.405	0.042	0.678	94.5

[a] Rejection (%) = 100(1 − [permeate]/[retentate]).

In order to observe trends more easily, the effect of retentate concentration of ligand, copper, surfactant, and calcium on permeate copper and calcium concentrations are shown in Figs. 2–5. However, it should be noted that the other retentate concentrations being held "constant" while the variable of interest is changing are not exactly constant, and average values for that concentration are shown in Figs. 2–5. For example, in Figure 2, the retentate calcium concentration varies from 0.728 to 1.108 m*M* for the data show, so an average value of 0.966 m*M* is shown in the plot. The reason that it was impossible to vary only one variable at a time is that while the variables at the beginning of a batch run could be defined, the value of those variables at the midpoint of the run, where data are reported, is affected by the separation efficiency. The exact values of these variables are shown in Table 1 at the midpoint.

As shown in Table 1, when no ligand is added to the solution, the concentration of both copper and calcium is higher in the permeate than in the retentate. This is due to the ion-expulsion effect and is the basis for a separation technique called ion-expulsion ultrafiltration (*18*). The posi-

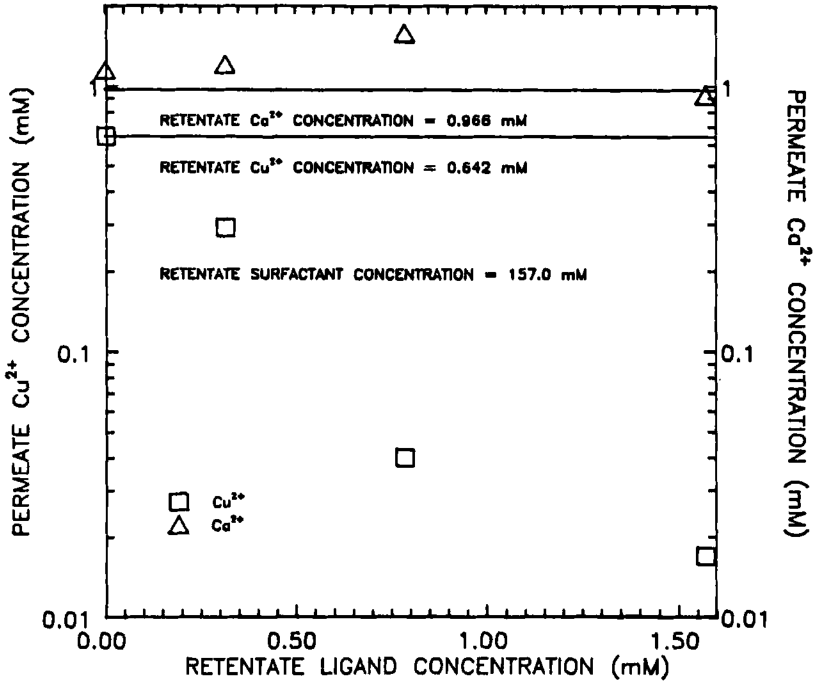

FIG. 2. Effect of retentate ligand concentration on separation.

tively charged micelle rejects the positively charged copper and calcium (negative adsorption of the cations occur on the cationic micelle). As seen in Figs. 2–5, the ion-expulsion effect causes calcium to be present in the permeate at higher concentrations than in the retentate, ***even in the presence of the ligand.*** Figure 4 shows that the calcium concentration in the permeate increases as the surfactant concentration in the retentate increases, reflecting an increased ion-expulsion effect.

Figure 2 shows that an increase in ligand concentration in the retentate causes a decrease in permeate copper concentration (or an increase in rejection of the copper). At an added ligand concentration of 1.57 m*M*, the rejection of copper is 97.8%, indicating the extremely high removal efficiency even when the surfactant has the same charge as the target ion. Also, the calcium shows a net concentration (rather than removal) during the ultrafiltration, further enhancing the selectivity of removal. Therefore, LM-MEUF has both a high separation factor and high selectivity.

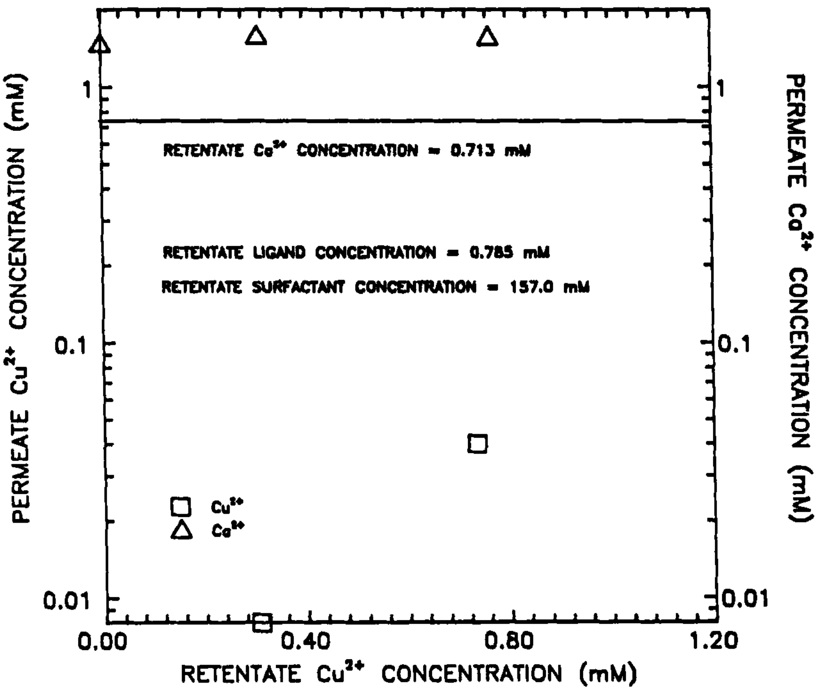

FIG. 3. Effect of retentate copper concentration on separation.

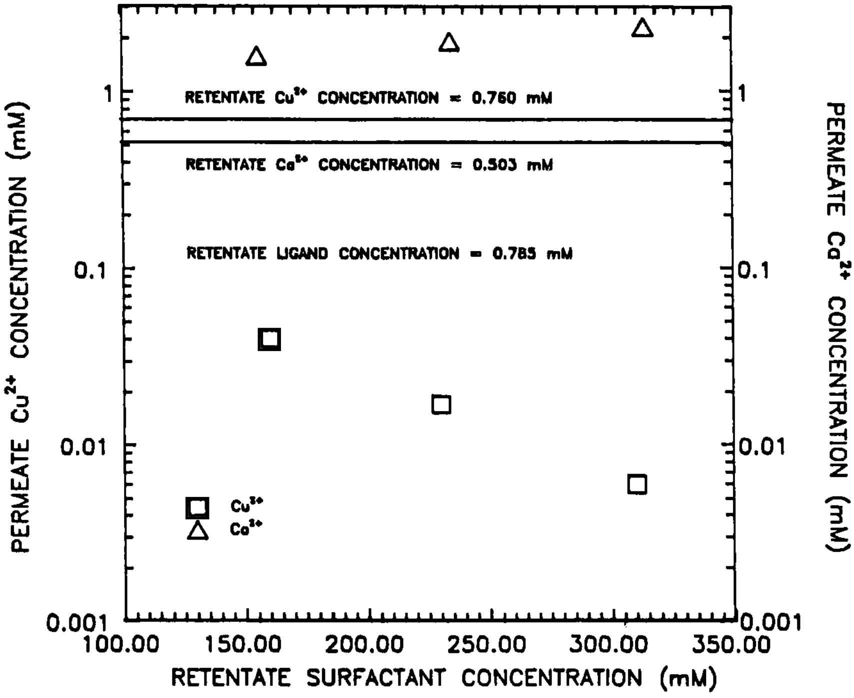

FIG. 4. Effect of retentate surfactant concentration on separation.

Figure 3 shows that the permeate copper concentration increases as the retentate copper concentration increases. As seen in Table 1, the rejection of copper decreases as the retentate copper concentration increases since there is a constant concentration of ligand in the retentate. Therefore, the proportion of copper bound with the ligand decreases as the copper concentration in retentate solution increases. In the experiments described in Fig. 3, the copper concentration in the retentate never exceeds the stoichiometric amount which could be bound by the ligand. The calcium concentration in the permeate is unaffected by the retentate copper concentration. This confirms that the tendency of the ligand to complex the calcium is small.

Figure 4 shows that the permeate copper concentration decreases as the retentate surfactant concentration increases. Increasing the concentration of the surfactant in the retentate should decrease the ability of Ca^{2+} to compete with Cu^{2+} for ligand binding by increasing the ion-expulsion effect. Any tendency of Ca^{2+} to bind to the ligand in the micelle would therefore

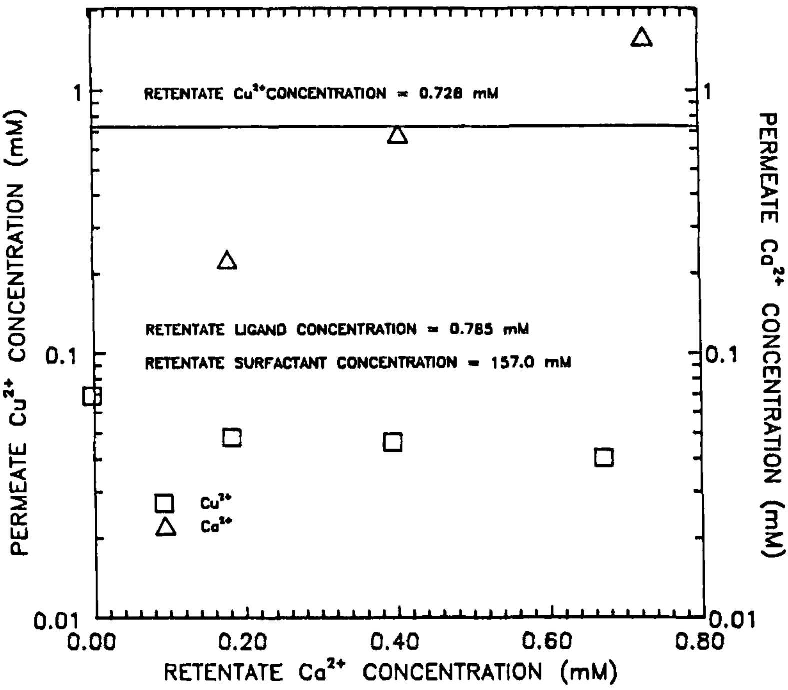

FIG. 5. Effect of retentate calcium concentration on separation.

be reduced by the presence of additional surfactant and of the Cu^{2+} to bind to the ligand in the micelle would increase as surfactant concentration increases.

Figure 5 demonstrates that as the retentate calcium concentration increases, the permeate calcium concentration increases, but the permeate copper concentration decreases. This latter effect is probably due to a reduction in the ion-expulsion effect as the electrolyte concentration in solution increases. Since the ion-expulsion effect would tend to result in a higher copper concentration in the premeate, an increase in retentate calcium concentration reduces the permeate copper concentration.

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