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UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

**USE OF LIGAND-MODIFIED MICELLAR-ENHANCED
ULTRAFILTRATION TO SELECTIVELY SEPARATE COPPER
IONS FROM WASTEWATER STREAMS**

A THESIS

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

MASTER OF SCIENCE

(Chemical Engineering)

BY

SUSAN BAKHTIARI SHADIZADEH

Norman, Oklahoma

1992

MASTER

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A THESIS

**APPROVED FOR THE SCHOOL OF CHEMICAL
ENGINEERING AND MATERIALS SCIENCE**

BY

John Scamehorn
Richard W. Tyle
Robert H. Shambaugh

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*To my parents,
Iran and Sohrab Bakhtiari,
and my family, Reza and Sohail Shadizadeh*

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ABSTRACT

The selective removal of target ions from an aqueous solution containing ions of like charge by ligand-modified micellar-enhanced ultrafiltration (LM-MEUF), is presented. In LM-MEUF, surfactant and specially tailored ligand are added to the contaminated stream. The surfactant forms aggregates called micelles, the hydrocarbon core of which the ligand complexed with the target species will solubilize. The surfactant is chosen to have the same charge type as the target ion; therefore, other ions (with similar charge) will not associate with the micelle, which makes the separation of the target ion selective. The solution is then processed by ultrafiltration, using a membrane with pore size small enough to block the passage of the micelles. In this study the divalent copper is the target ion in the solution containing divalent calcium. The surfactant is cetylpyridinium chloride (CPC) and the ligand is 4-hexadecyloxybenzyliminodiacetic acid (C_{16} BIDA). Experiments were conducted with batch stirred cells and the results have been compared to separation efficiency under equilibrium conditions. The experiments explored the separation that take place under a variety of conditions in the LM-MEUF process. Rejections of copper of up to 99.8 % are observed, with almost no rejection of calcium, showing that LM-MEUF has excellent selectivity and separation efficiency.

CHAPTER I

INTRODUCTION

Ground and surface water pollution is a vital problem on the earth. Large volumes of contaminated waste water are produced daily by industry. Concern is currently rising over ground and surface water contamination in the United States (1). Inexpensive and effective methods of water purification are needed and optimization of existing methods are necessary to fulfill the new requirements. The Environmental Protection Agency (EPA) of the United States has recently assessed the hazards caused by the elements Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Ag, Tl, and Zn as toxic pollutants, in addition to the radioactive species. When these ions are present at excessive levels in an aqueous discharge, the stream becomes unusable (2).

One effective method for separation of metal pollutants from aqueous streams is a new class of separation techniques developed at the University of Oklahoma called colloid enhanced ultrafiltration. The following Chapters represent results for the newest type of colloid-enhanced ultrafiltration technique, ligand-modified micellar-enhanced ultrafiltration (LM-MEUF). The use of LM-MEUF as a wastewater treatment technique is attractive for several reasons: it effectively removes cationic contaminants from polluted water streams, it removes a target ion only in the presence of other similar charged ions (e.g. calcium), the process is readily adaptable to treating large

quantities of contaminated waste water, and it allows for the direct recovery of the colloidal separation agent and the ligand for recycle to the original industrial process using changes in pH.

This study is focused on the selective removal of copper in the presence of calcium contaminants. Copper-laden wastewaters are produced in large quantities by industries such as metal plating plants. Another pollution problem is that abandoned metal mines can fill with acid mine water, polluting nearby drinking water aquifers with heavy metals. This study involves bench-scale experimental investigations and does not include an economic or scale-up design analysis for the LM-MEUF technique. However, the data reported in this thesis could be basis for rough estimates of economic and scale-up design parameters.

CHAPTER II

Background

Surfactants have properties that make them useful in separation processes. A unique property of surfactants is their ability to form micelles. At concentrations in excess of a certain concentration (the Critical Micelle Concentration or CMC), surfactants form aggregates called micelles, containing from 50 to 100 surfactant molecules. The surfactant which is not present as micelles exists primarily as unassociated molecules or ions in solution (monomer). At solution surfactant concentrations above the CMC, surfactant monomers are in dynamic equilibrium with the micelles (3). At concentrations above CMC, the concentration of monomer remains approximately constant. The micelles are roughly spherical in geometry and possess a hydrophobic core and a hydrophilic surface. The radius of the micelle is approximately equal to the length of fully extended hydrophobic group, surrounded by an outer region containing the hydrated hydrophilic groups (4). The micelle core is much like a hydrocarbon liquid and the solubility of many organic compounds in aqueous solutions is significantly higher in concentrated surfactant solutions due to dissolution of the organic solute into the micelle, a process known as solubilization. The extent of solubilization in the micelle varies depending on the nature of the solute and the surfactant. Generally, the more hydrophobic the solute, the more strongly it

will partition into the micelle (3). For ionic surfactants, the charged micellar surface has a high electrical potential due to the hydrophilic groups. As a result, oppositely charged ions (counterions) adsorb or bind on the micelle surface (20). This dual sequestering nature of the micelle (solubilization and counterion binding) makes them very useful in separation processes.

The family of colloid-enhanced ultrafiltration techniques encompasses four methods:

1. Micellar-enhanced ultrafiltration (MEUF)
2. Polyelectrolyte-enhanced ultrafiltration (PEUF)
3. Ion-expulsion ultrafiltration (IEUF)
4. Ligand-modified micellar-enhanced ultrafiltration (LM-MEUF).

Micellar-enhanced ultrafiltration (MEUF) involves the addition of surfactants to polluted water. The surfactants form micelles, which interact with pollutant in the aqueous stream. Dissolved organics in solution will tend to solubilize or dissolve in the micelle. If the surfactant has an opposite charge to a multivalent ion in solution, these counterions will bind to the micelles. The solution is then treated in an ultrafiltration unit with membrane pore sizes small enough to reject the micelles. The result is that the micelles with their solubilized organics and bound ions become concentrated in the retentate (the solution not passing through membrane). The permeate (the solution passing through membrane) contains very low concentrations of organic solute and surfactant, and it can be discharged or recycled. The retentate contains very high concentrations of both solute and surfactant and has a much lower volume than the original process stream. Therefore, subsequent further purification or

disposal of this retentate is less expensive and requires less energy than treating the original stream. The MEUF process has been employed to remove dissolved nonionic organics (5-12), multivalent cations or anions (12-15), and mixtures of nonionic organic and divalent actions (16).

Polyelectrolyte-enhanced ultrafiltration is identical with MEUF except that a Polyelectrolyte is utilized as the colloid instead of surfactant. Since polyelectrolytes can not solubilize organics to significant extent, in PEUF a soluble polyelectrolyte is added to a solution containing oppositely charged ionic contaminants. The target solute binds to the polyelectrolyte due to electrostatic attraction and the solution is treated by ultrafiltration with a membrane possessing a pore size small enough to reject the polyelectrolyte from the solution. This method can be used to effectively remove multivalent ionic elements (17).

Ion-expulsion ultrafiltration is one of the newest methods of colloid-enhanced ultrafiltration techniques (18). It is well known that ionic micelles and polyelectrolytes in aqueous solutions bind a certain fraction of dissolved counterions (19-24). Ion-expulsion ultrafiltration is explained by the fact that the concentration of free counterions (e.g., Cl^- in CPC solutions) is a constant fraction of total colloid concentration. For example, colloids of cetylpyridinium chloride (CPC) and sodium dodecyl sulfate have 60 to 80 percent fractional counterion binding (19-21) at surfactant concentrations ranging from just above the CMC to several tenths molar. Similarly, polysulfonate has fractional counterion bindings of 65-80 % (24). Therefore, the concentration of co-ions (ions of like charge as the CPC) is less than concentration of unbound counterions in solution.

Ion-expulsion ultrafiltration uses the charge characteristics of a colloid to expel a like charged target species across a membrane in an ultrafiltration process. The membrane has pores which are small enough to inhibit the movement of the colloid while allowing passage of the target species.

If the unassociated co-ion and counterion are in equilibrium across the membrane between retentate and permeate, the ion activity product activity of each neutral electrolyte pair will be the same across the membrane. The resulting equilibrium concentration of each ion in solution in the permeate can be deduced from a Donnan equilibrium calculation (25-26). Figure II-1 illustrates a numerical calculation using the Donnan assumption to show the equilibrium separation which could occur using the ion-expulsion technique to expel copper using cetylpyridinium chloride (CPC). Two assumptions are made in Donnan calculation; the species activities can be approximated by their concentrations and the CPC has 80 percent counterion binding. The calculations show that if Donnan equilibrium is satisfied, the permeate copper concentration is 21.5 times greater than in the retentate (18). Qualitatively, the like-charged colloid can be viewed as repelling the target co-ions or pushing them from the vicinity of the colloid through the membrane. The effect is due to electrostatic repulsion.

	retentate solution
concentration of CPC	$[CPC] = 0.100 \text{ M}$
initial copper concentration	$[Cu^{+2}] = 1.00 \times 10^{-4} \text{ M}$
initial chloride concentration	$[Cl^-] = 0.2 \times 0.10 = 0.02 \text{ M}$
ion product constant	$[Cu^{+2}] [Cl^-]^2 = 1.0 \times 10^{-4} (0.02)^2$ $4.0 \times 10^{-8} \text{ M}^3$
ultrafiltration membrane	-----
by electrical neutrality	$2[Cu^{2+}] = [Cl^-]$
ion product constant	$[Cu^{+2}] [Cl^-]^2 = 4 [Cu^{2+}]^3 =$ $4.0 \times 10^{-8} \text{ M}^3$
permeate copper concentration	$[Cu^{2+}] = 2.15 \times 10^{-3} \text{ M}$
	permeate solution

Figure II-1: Example of Donnan Equilibrium Calculation in IEUF (18).

The use of ion-expulsion to expel target species has been extremely limited due to membrane polarization (17,39).

Ligand modified-micellar enhanced ultrafiltration (LM-MEUF) is a new separation technique based on MEUF that is designed to selectively remove metal ions from aqueous streams (27). In this process a ligand is added to the polluted solution in addition to the surfactant prior to ultrafiltration. The ligand will solubilize in the hydrophobic core of the micelle and the chelating head group will reside in the polar, hydrophilic region (28). The ligand is designed to selectively form a complex with the target ion. The aqueous stream is then passed through an ultrafiltration membrane with pore size just small enough to reject the micelles. The metal ion bound to the micelles via the ligand remains in the retentate solution, while the unbound ions are free to pass through the membrane. One important feature of the LM-MEUF is that the ligands can exhibit pH dependent metal binding behavior. This can be advantageous in the LM-MEUF process, enabling the recovery of used ligand or micelle-solubilized ligand by lowering the pH. However, for optimum metal-complexion it is often desirable to work at pH of 5 to 7 (32), a pH which is commonly encountered in natural waste water streams. The schematic of the LM-MEUF system is represented in figure II.2.

Figure II-2: Diagram of a LM-MEUF unit for the removal of cationic metal species from an aqueous stream (27).

LM-MEUF has shown to be extremely successful for the separation of copper ions from aqueous solutions that also contain calcium ions with rejection values up to 99.2% for copper using dodecyliminodiacetic acid (NIDA) as the ligand in cetyl pyridinium chloride (CPC) solutions (27).

The primary focus of this thesis is to study the selective separation of copper by the ligand C_{16} BIDA in CPC solution in the presence of calcium, from aqueous streams. Figure II.3 shows the structure of the CPC and C_{16} BIDA. The effect of changes in concentration of CPC, Cu, Ca, ligand and added electrolyte in the feed on the separation efficiency has been studied here. The flux of the permeate and the Krafft point of retentate (two important operating variables) have been studied. The results of the separation experiments by ultrafiltration (stirred cell) have been compared to the results for separations at near equilibrium conditions.

Semi-equilibrium dialysis (SED) is an experimental technique used to measure (equilibrium) separations in colloid-enhanced ultrafiltration operations (18,19). It has been found that when the target species is rejected, these separations are often near equilibrium under practical operating conditions. Figure II.4 is an illustration of an SED experiment for the selective removal of a metal contaminant.

The effectiveness of the separation process in retaining the target species in the retentate can be shown in terms of rejection values. The % rejection is defined by equation 1,

$$\% \text{ Rejection} = [1 - (\text{permeate})/(\text{retentate})] \times 100 \quad (1)$$

CPC

C₁₆BIDA

Figure II-3: Structures of the surfactant (CPC) and the ligand (C₁₆BIDA) used in the LM-MEUF study.

Figure II-4: Representation of a LM-MEUF experiment using the SED technique. (A) is at time = 0 and (B) is at time = 20-24 hours (system is reached the semi-equilibrium) (31).

CHAPTER III

EXPERIMENTAL

3.1 Materials

Copper chloride dihydrate, calcium chloride dihydrate and sodium chloride were purchased from Fisher Certified ACS grade and were dried in an oven at 240 °C for 24 hours in order to dehydrate them. These material are very hydroscopic therefore they were stored in a desiccator and have been used as needed. N-hexadecylpyridinium chloride monohydrate (Cetylpyridinium Chloride or CPC) was obtained from Hexcel Chemical Co. The CPC purchased was pharmaceutical grade, had a molecular formula of $C_{21}H_{37}NCl$ and formula weight of 358. The purity of CPC was confirmed by surface tension and HPLC analysis. Deionized (DI) water used in all of the experiments was house DI water which had been passed through two cartridges (organic removal and ion exchange) in a Barnstead water system. The ligand, 4-hexadecyloxybenzylinodiacetic acid ($C_{16}BIDA$), was synthesized in the Chemistry Department of University of Oklahoma (31).

Five types of gases were used in the analysis. Nitrogen was supplied by Big Three Industrial Gas Inc. Prepurified grade argon and atomic absorption grade

acetylene and nitrous oxide were obtained from Linde Specialty Gases. Finally, the house air used as an air source was simply ambient air which has been passed through several filters and water removal traps.

For the stirred cell experiments, Spectrum cellulose acetate membranes with a molecular weight cut-off of 10,000 (10 K) and a diameter of 76 mm, was used.

Other materials used in this study were: HPLC grade methanol (J. T. Baker), certified buffer solutions with pH 4 and pH 7 (Fisher Scientific), copper and calcium reference solution for atomic absorption spectrometer analysis (Fisher Scientific).

3.2 Experimental Equipment

Figure III.1 is a schematic of the stirred cell. The ultrafiltration stirred cell used in the experiments was purchased from Spectrum and had the following specifications (33):

Model Number	S76-400
Height	9.0 inches
Diameter	4.75 inches
Capacity	400 mL
Membrane Diameter	76.0 mm
Filtration Area	38.5 cm ²

Maximum Operation Temperature	60.0 °C
Maximum Operation Pressure	70 psi (483 KPa)

The cell was wrapped with 1/4 inch OD Tygon tubing for temperature control. Water from a temperature bath was circulated through the tubing. A Haake D1 heated circulating pump was used to heat and circulate the water. The stir bar was operated by using a Fisher Thermix model 220T magnetic stirrer. A Teflon coated, pyramidal shaped stir bar was used to ensure adequate mixing within the cell.

Typical stirred cell experiments began with preparation of the feed solution. The ultrafiltration membrane was soaked in the feed solution before the actual ultrafiltration experiment was conducted. Before assembling the apparatus, the stirred cell was carefully rinsed by DI water and dried with laboratory air. The presoaked membrane was then placed on the cell base and carefully sealed.

Figure III-1: Diagram of stirred cell used for ultrafiltration experiments.

Great care was taken to ensure that the membrane did not have any defects or ripples in its surface which can lead to tearing of the membrane by the stirrer during the ultrafiltration experiment. After placement of the membrane, the stirred cell apparatus was assembled. The assembled cell was wrapped with flexible Tygon tubing which was attached to a water bath for temperature control. Three hundred milliliters of feed solution was pipetted into the cell via the removable pressure relief valve. The rate of spin of the magnetic stir bar was set at 860 RPM using a calibrated stroboscope supplied by the Sargent Welch Scientific Company. The cell was allowed to come to thermal equilibrium before being pressurized with nitrogen. Samples were removed through the sampling port located in the base of the stirred cell. The samples were weighed and the sample collection time was determined using a conventional stopwatch.

Measurement of pH

All pH measurements were made on a Markson pH meter model 6102 using a Markson Epoxy bodied combination electrode (Q-830). The pH meter was standardized using standard buffer solutions (pH 4.00 and 7.00) obtained from Fisher Chemical Co. All solutions were adjusted to pH 5.5 ± 0.5 using HCl and NaOH obtained from Fisher Chemical Co. The pH meter electrode had the following manufacture specifications (33):

Model Number Q-830

Length 3.5 inch and Diameter 0.5 inch

Epoxy bodied combination electrodes

porous, inert, Teflon junction (resists clogging in even the most troublesome solutions)

Sealed-body design filled with KCl/Ag/AgCl

Full 0-14 pH range

Operable from 0-70 ° C and up to 100 psi

3.3 Experimental Procedures

Ultrafiltration

Ultrafiltration experiments were performed using a Nuclepore 400 mL batch-stirred cells, wrapped with Tygon tubing containing circulating water for temperature control. The pressure on the retentate side was induced by nitrogen gas. Pressure in all the experiments were 60 psig except two runs that were at lower pressures of 40 and 20 psig. The temperature for all the runs was 25 ° C. Nuclepore anisotropic cellulose acetate membranes of 76 mm diameter were used. These were soaked in the feed solution to saturate the membrane for 24 hours before the run was started. The permeate solution initially removed from the stirred cell during the experiment was highly concentrated in the target species. By soaking the membrane in the feed solution, the experimental condition were achieved more rapidly. Hence, the first permeate sample was assumed to be representative of the expulsion of the target

species due to the presoaking. After the cell was assembled and the feed solution loaded into the cell chamber, the temperature of the cell was allowed to equilibrate at 25 ° C for 30 minutes. The stir bar speed was set at 840 rpm. The effect of stir bar speed on flux and separation characteristics has been studied previously by Dunn et.al. (34). The stir bar rate of 840 rpm was found to be a good speed to minimize concentration polarization while not allowing the vortex to reach the membrane surface when the desired amount of permeate had been withdrawn. Membranes having 1,000 Dalton molecular weight cut-off were used. The cell was initially filled with 300 mL of surfactant solution and permeate collected at approximately 5 minute intervals. No more than 200 mL of permeate was collected during any given run. From each run, ten samples were collected which included, feed, 8 permeate samples (25 mL each), and one retentate sample. Feed, permeate, and retentate concentrations were determined using HPLC for CPC and SpectrAA-20 for copper and calcium.

Stirred cell membranes were used for several experiments before being discarded. After each stirred cell run, the membrane was carefully removed from the apparatus, rinsed with DI water and soaked in DI water for 24 hours, during which the water has been changed periodically. The membrane was then placed in a new feed solution before being used in the next run as explained above. Membranes were carefully inspected before each run to ensure that no noticeable blemishes or abnormalities existed on the membrane surface. Stirred cell membranes were used until noticeable imperfections were found in the membrane during routine inspection.

3.4 Sample Analysis

3.4-1 Atomic Absorption Spectrometer Analysis

Atomic absorption spectrometry was used to determine the calcium and copper content in the experiments. The following atomic absorption (AA) spectrometry equipment was used:

SpectrAA 20 Atomic Absorption Spectrometer

GTA-96 Graphite Tube Atomizer

PSD 96 Programmable Sampling Device

Ex-800 Dot matrix Printer

All of the AA equipment was manufactured by Varian, except for the dot matrix printer which was manufactured by Epson.

There are two methods of analysis that can be conducted with the Varian SpectrAA-20; one is the flame method and the other one is the furnace method. The flame method was utilized for high concentration solutions (2-4 ppm concentrations) while the furnace was more sensitive and was utilized to analyze samples with lower concentrations.

The analysis of samples containing colloid by AA Spectrometry is greatly complicated by the change in viscosity of the samples owing to the differing concentrations of colloid. This problem was overcome by adding a measured average colloid concentration in the retentate to the standards.

The graphite tube atomizer was utilized when the concentrations were below the flame detection limit, which is 2-8 ppm for copper and 1-4 ppm for calcium. In a graphite tube furnace, the sample is injected into a small graphite tube by an automatic sampling device. Hence, the viscosity of the sample is of no consequence to the analytical procedure. However, there might be some interference that should be considered. After injection of the sample into the graphite tube, the sample is slowly dried by gradually heating the graphite tube by an electric current, while blowing prepurified Argon gas over the sample. After the sample has been dried, the gas blow is stopped, and the temperature is violently rammed up to 2,300 ° C in less than a second. The rapid temperature change dislodges the dried sample from the wall of the furnace and the emission characteristics of the sample can be observed by AA (42). Figure III.3 is a reproduction of the actual absorption of a sample superimposed on the temperature profile of the analysis. Figure III.2 is a sample analysis program.

Atomic absorption standards were prepared from the certified reference solution (Fisher Scientific). For flame analysis, the doped concentration of surfactant (CPC) in the standards were matched to that in the midpoint permeate sample. Each copper and calcium sample was analyzed three times and the signal averaged to ensure that reproducible results were obtained. Linear least squares analysis of the standards has been used for the calibration curve. Typical atomic absorption calibration graphs for

copper and calcium in 0.5 mM CPC solution using graphite furnace (for copper only) and flame (copper and calcium) atomic absorption analysis are shown in Figures III 4., 5, and 6 respectively. The concentration of samples analyzed by the graphite furnace AA were in the range of 0.1-0.5 micromolar, which is within the linear range of the calibration curve. The feed and retentate solutions were diluted to the concentration range of the calibration curve with doubly distilled water. A surfactant concentration of 0.5 mM was used as the blank for each analysis.

0.663		PROGRAM 16	Cu		
		STANDARD 3	REPLICATE 1		
		ABSORBANCE	CONCENTRATION	SAMPLER AUTOMIX	
		PEAK HEIGHT	3.0 (sec)	BC OFF	
AUTOMATIC RUN PAUSED PRINTING					
		FURNACE PARAMETERS			
STEP NO.	TEMPERATURE (°C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	85	5.0	3.0	NORMAL	NO
2	95	40.0	3.0	NORMAL	NO
3	120	10.0	3.0	NORMAL	NO
4	800	5.0	3.0	NORMAL	NO
5	800	5.0	3.0	NORMAL	NO
6	800	2.0	0.0	NORMAL	NO
7	2300	1.1	0.0	NORMAL	YES
8	2300	2.0	0.0	NORMAL	YES
9	2300	2.0	3.0	NORMAL	NO
10					
STEP INSERT		STEP DELETE	OTHER STEPS	SIGNAL GRAPHICS	

Figure III-2: Example of graphite furnace microprocessor program.

Figure III-3: Example of absorbance signal from graphite furnace.

Figure III-4: Calibration graph for the analysis of calcium in 0.5 mM CPC using flame AA.

Figure III-5: Calibration graph for the analysis of copper using flame AA.

Figure III-6: Calibration graph for the analysis of copper using graphite furnace AA.

3.4-2 Uv-vis Spectrophotometric Analysis

Spectrophotometric analyses were performed with an HP8452A diode-array spectrophotometer, using a 1 cm cell with 10 second signal-averaging and using 3 confirmation wavelengths. CPC absorbs light at ~ 260 nanometers and interferes with the spectrum of C₁₆BIDA; therefore the HPLC method was used to determine the concentration of the CPC .

3.4-3 HPLC Analysis

High performance liquid chromatography (HPLC) was used to determine the CPC concentrations in the feed, permeate and retentate. The HPLC unit consisted of reservoirs for either one or two solvents, a valve to change between the two solvents, a constant flow rate pump, an injector valve for introducing the sample to be measured, a packed column to separate the components of the injected sample solution, a conductivity or ultraviolet detector to measure a specific property of the surfactant in the injected sample solution, and an integrator to integrate the property measured by the detector and to control the solvent change valve. The HPLC equipment used in this study was a Tracor Model 951A Pump or a Beckman Model 110B Pump, a Rheodyne injector Valve, and Anger Scientific Model 368140Q Solenoid/Valve

Assembly, Rheodyne (20, 100, 500, and 1000 microliter) Sample Loops, a Tuberculin 1 mL Syringe, a Varian 4270 Integrator/Plotter, and a Tracor Model 970A Ultraviolet Detector.

The HPLC packed column used in this study was prepared from materials ordered from Alltech Assoc., Inc. The column tubing had an outer diameter of 0.25 inch, an inner diameter of 4.6 mm, and was cut into lengths of 4.5 inches. Two micron (1/4 inch OD, 1/32 inch thick) stainless steel porous frits were placed at the inlet and outlet of each column in order to retain the packing material in the column and to protect the packing material and the detection meter measuring cells from injected impurities. Optiflow 0.25 inch column end fittings were then tightened onto each end of the column in order to seal the end fitting ferrules onto the column. Before the end fittings were used, the inlet holes of both end fittings were drilled out to a diameter of 0.058 inches and the insides of the end fittings (facing the packing material) were flared out to a diameter just smaller than the frits. The end fittings were altered in order to allow the solutions flowing through the end fittings to contact a larger frit surface area, and to thereby, reduce the excessive pump pressures resulting from a build up of injected impurities and pieces of the pump seals on the frits.

The HPLC columns were then packed with Whatman Partisil ODS II, using a Micromeritics Model 705 Stirred-Slurry Column Packer. The ODS II packing materials contained octadecyl groups chemically bonded onto reverse phase silica. Both of these packing materials were ten microns in particle size. The ODS II was packed using HPLC grade methanol (MeOH).

Preparing the solvent mixtures and the column prior to the HPLC analysis of the surfactant solutions was extremely important in order to obtain accurate results. The necessary preparations included premixing and then degassing the solvent mixtures, and checking the column before use. These preparations were necessary to prevent the most prevalent HPLC problems that might otherwise arise.

Solvent mixtures were prepared the night before use, in order to insure that the solvents were well mixed, the solvents were at room temperature, and that most of the air dissolved in the solvents was removed. Two liters of the solvent mixture was prepared at a time, using a one liter graduated cylinder. The solvent mixture was then well shaken and placed on a stir plate with a stir bar in the solution and degassed for 30 minutes under a vacuum.

In case of residue accumulation on the frits, the frits were cleaned with compressed air or replaced, if necessary. While the end fittings and frits were removed, the column inlet packing material was carefully checked. If there was any void volume at the column inlet, it was filled in with a thick slurry of 100% MeOH and packing material, using a spatula and a small beaker. If the inlet packing material was discolored (yellow), the packing material at the column inlet was replaced. Color changes in the packing material indicate that the packing material is contaminated and must be replaced.

After the column was ready, the pump flow rate was reduced to 0.01 mL/minute while the column inlet was connected to the outlet of the injector valve and the column outlet was connected to the detection meter. The detection meter was then turned on,

the detection meter attenuation was set, and the pump flow rate was increased again to 3 mL/minute. The integrator program was run several more times while checking for air and leaks in the HPLC system. The system was on for 30 minutes in order to reach an steady pump pressure of 1,800-2,200 psig. MeOH was continuously pumped through the column and the attenuation of the integrator was set. Once the solvent baseline leveled out, the detection meter and the integrator/plotter were zeroed out, and then the integrator peak threshold was evaluated and set. Determining the integrator peak threshold at a constant solvent baseline allowed the integrator/plotter to distinguish between the baseline noise and the surfactant peaks. At this point, a constant solvent baseline insured that the HPLC system was ready for the CPC analysis. A typical HPLC calibration graph for CPC using uv.spectrum is shown in Figure III.7. A linear least squares fit with an $r^2 = 0.9986$ has been used to correlate the data. The CPC concentration determined by HPLC was below the CMC value of 0.88 mM, as was expected (9).

After the HPLC analysis, the column was prepared for storage by flushing with 100 % MeOH for fifteen minutes, in order to clean the packing material. Calibration curves were determined using the HPLC analysis of the CPC standard solutions, by performing a linear least squares fit of the CPC peak heights versus the average CPC concentrations. The CPC concentration in the feed, permeate and retentate solutions was then calculated using the average of the CPC peak heights.

Figure III-7: Calibration graph for the analysis of surfactant (CPC) using HPLC.

Chapter IV

Use of LM-MEUF for Selective Separation of Copper with C₁₆BIDA and CPC

4.1 Introduction

As described in chapter II, LM-MEUF is a process which offers a selective method for removing the divalent cationic copper from wastewater streams. Often in wastewater streams, along with the target toxic metals, there are relatively innocuous ions of the same charge as the target ion. For example, in a wastewater containing copper and calcium, calcium isn't in the hazardous list of the EPA, hence, it is desirable to separate and remove only copper and leave the calcium. Furthermore, if this technique is used to recover an precious element it is desirable to recover the target specie alone in order to lower the cost. Therefore, the ability to selectively separate a target metal ion is not only environmentally beneficial but also economically desirable.

This chapter discusses the results of LM-MEUF experiments which utilized C₁₆BIDA and CPC to remove copper from water. Experiments were conducted in stirred cell and the results compared to those from semi-equilibrium dialysis experiments. From the SED results, it has been determined that the ligand binds to

copper with a mixed stiochiometry of one to one and/or two to one then solubilizes into the micelle of CPC (31).

4.2 LM-MEUF of Copper in a Ultrafiltration Unit

Ultrafiltration experiments have been performed in batch stirred cells. Both flux and rejection have been studied.

Figure IV.1 is a typical plot of the copper retained in the retentate as a function of feed removed as permeate for pressure of 60 psig (414 KPa) in the stirred cell unit. The rejection has been calculated for the midpoint of each run (after 100 mL of a total of 200 mL has been collected) by utilizing equation 1 on page 11.

For each run, feed, permeate and retentate concentrations of Ca, Cu, and CPC have been determined and the results at midpoint has been presented. Feed and retentate has been analyzed to compare the mass balance prediction to the actual concentrations to assure the accuracy of the analysis.

The experimental results for all runs made are given in Tables 1,2,3,4,5, and 6. As shown in Table 5, surfactant rejection of more than 99% has been observed. The separation experiments determine the % rejection of copper by C₁₆BIDA and CPC with copper alone or in the presence of calcium, while varying copper, calcium, ligand, surfactant, and sodium chloride concentrations at feed pH = 5.5. Plots of the concentrations of copper and calcium in permeate versus [variable element]_{Ret.} are

shown for each set of experiments. A low concentration of copper in the permeate translates to a high copper rejection value. For each Figure, 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 Figures IV. 2, 3, 4, 5. For example, in Figure IV.2 , the retentate calcium concentration varies from 0.540 to 0.603 mM for the data shown. Therefore, an average value of 0.575 mM is shown in the plot. The reason that it is 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 tables at the midpoint.

Figure IV-1: Typical graph of retentate copper concentration versus retentate volume.

As shown in table 4 , when no ligand is added to the solution, the % Rejection of both copper and calcium is almost the same and very poor (Cu Rejection % = 42.39 and Ca Rejection % = 41.15). This run has been repeated three times and the results were consistent (rejection = + 4%). Since we did not observe a very strong ion expulsion effect in this particular experiment, an additional run with only copper and CPC have been made. For this run, where an initial concentration of copper was 0.5 mM, the permeate copper concentration of 0.545 mM at midpoint has been seen which results in a rejection of 4.9 %. If the concentration of CPC is increased, then the concentration of the copper and calcium can increase in the permeate (as was observed here) to a level that is higher than their concentration in the retentate. This is due to the ion-expulsion effect and is the basis for a separation technique called ion-expulsion ultrafiltration (17,39). The positively charged micelle rejects the positively charged copper and calcium. As seen in Fig. IV.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. Fig. IV.4 shows that the calcium concentration in the permeate increases as the surfactant (CPC) concentration in the retentate increases, reflecting an increased ion-expulsion effect.

Figure IV.5 shows that an increase in $C_{16}BIDA$ concentration in the retentate causes a decrease in the permeate copper concentration and an increase in the calcium concentration in permeate. A rejection as high as 99.8 % at an added concentration of 2.00 mM ligand for copper and almost no rejection of calcium indicates the extremely high removal efficiency and selectivity.

Figure IV.2 shows that the permeate copper concentration increases as the retentate copper concentration increases. This is expected at high concentrations of Ca^{2+} and Cu^{2+} with a cationic surfactant. As seen in Table 1, the rejection of copper decreases as the retentate copper concentration increases. The permeate calcium concentration increases as the retentate copper concentration increases due to a lower concentration of uncomplexed ligand.

Figure IV.4 shows that the permeate copper concentration decreases as the retentate CPC concentration increases. Increasing the concentration of the surfactant in the retentate should increase ligand solubilization and, hence, copper rejection.

Table 1 : Results of ultrafiltration experiments of C₁₆BIDA in CPC solutions with [C₁₆BIDA]₀ = 1.00 mM, [CPC]₀ = 100 mM, [Ca²⁺]₀ = 0.50 mM .

All concentrations in mM.

Feed pH = 5.50

Temp = 25 °C

P = 60 psig (414 KPa)

[Cu] ₀	[Cu] _{per}	[Cu] _{ret}	Cu Rej.% ^a	[Ca] _{per}	[Ca] _{ret}
0.10	0.000165	0.1500	99.89	0.3815	0.5402
0.20	0.000200	0.2908	99.93	0.4169	0.5641
0.325	0.000322	0.5023	99.93	0.3274	0.5884
0.50	0.0020	0.7631	99.74	0.5846	0.6037
0.75	0.0494	1.5080	96.79	0.6139	0.5791

Above runs show an average of 99.63% CPC rejection.

^a Rejection (%) = 100 x (1 - [permeate]/[retentate]).

₀ Indicates initial concentrations.

_{per} Indicates midpoint permeate concentrations.

_{ret} Indicates midpoint retentate concentrations.

Table 2: Results of ultrafiltration experiments of C₁₆BIDA in CPC solutions with [C₁₆BIDA]_o = 1.00 mM, [CPC]_o = 100 mM, [Cu²⁺]_o = 0.50 mM.

All concentrations in mM.

Feed pH = 5.50

Temp = 25 °C

P = 60 psig (414 KPa)

[Ca] _o	[Cu] _{per}	[Cu] _{ret}	Cu Rej. % ^a	[Ca] _{per}	[Ca] _{ret}
0.0 ^b	0.000178	0.7399	99.97	0.000	0.000
0.5	0.0020	0.7631	99.74	0.5846	0.6037
1.0	0.00100	0.7684	99.87	1.0860	1.0015
2.0	0.0001030	0.679	99.98	1.8840	1.9283
5.0	0.000391	0.768	99.95	5.7477	4.4950

Above runs show an average of 99.63% CPC rejection.

^a Rejection (%) = 100 x (1 - [permeate]/[retentate]).

^b All permeate and retentate results reflect an average of two ultrafiltration runs.

_o Indicates initial concentrations.

_{per} Indicates midpoint permeate concentrations.

_{ret} Indicates midpoint retentate concentrations.

Table 3: Results of ultrafiltration experiments of C₁₆BIDA in CPC solutions with
[C₁₆BIDA]_o = 1.00 mM, [Cu²⁺]_o = 0.50 mM, [Cu²⁺]_o = 0.50 mM.

All concentrations in mM.

Feed pH = 5.50

Temp = 25 °C

P = 60 psig (414 KPa)

[CPC] _o	[Cu] _{per}	[Cu] _{ret}	Cu Rej. % ^a	[Ca] _{per}	[Ca] _{ret}
100	0.0020	0.7631	99.74	0.5846	0.6037
150	0.000195	0.7207	99.97	0.4697	0.5143
200	0.0000707	0.7910	99.99	0.5244	0.4339

^a Rejection (%) = 100 x (1 - [permeate]/[retentate]).

_o Indicates initial concentrations.

_{per} Indicates midpoint permeate concentrations.

_{ret} Indicates midpoint retentate concentrations.

Table 4: Results of ultrafiltration experiments of C₁₆BIDA in CPC solutions with
[CPC]₀ = 100 mM, [Cu²⁺]₀ = 0.50 mM, [Ca²⁺]₀ = 0.50 mM .

All concentrations in mM.

Feed pH = 5.50

Temp = 25 ° C

P = 60 psig (414 KPa)

[C ₁₆ BIDA] ₀	[Cu] _{per}	[Cu] _{ret}	%Cu Rej. ^a	[Ca] _{per}	[Ca] _{ret}
0.0 ^b	0.3312	0.5749	42.39	0.3312	0.5628
0.5	0.0154	0.7422	97.92	0.4030	0.5822
1.0	0.0020	0.7631	99.74	0.5846	0.6037
2.0	0.0000769	0.7513	99.98	0.4866	0.5240
0.0 ^c	0.5453	0.5736	4.90	0.000	0.000

^a Rejection (%) = 100 x (1 - [permeate]/ [retentate]).

^b All permeate and the results reflect an average of two ultrafiltration runs.

^c Feed solution for this run contained only copper and CPC.

₀ Indicates initial concentrations.

_{per} Indicates midpoint permeate concentrations.

_{ret} Indicates midpoint retentate concentrations.

Figure IV-2: Effect of retentate copper concentration on separation.

Figure IV-3: Effect of retentate calcium concentration on separation.

Figure IV-4: Effect of retentate surfactant concentration on separation.

Figure IV-5: Effect of retentate ligand concentration on separation.

Figure IV.3 is a plot of permeate Cu^{2+} and Ca^{2+} concentration vs. retentate Ca^{2+} concentration. As the retentate Ca^{2+} concentration increases, the permeate copper concentration decreases due to a reduced ion-expulsion effect, then increases, due to competition of the calcium with the copper for complexation sites on the ligand at high Ca^{2+} retentate concentrations.

4.2-1 Effect of Electrolyte on the Separation Process

Separation experiments were performed in the presence of added electrolyte in order to study the effects of increased ionic strength on the separation process.

Figure IV.6 and Table 5 show that permeate copper and calcium concentrations as function of the initial electrolyte concentration (NaCl). It shows as we increase the concentration of electrolyte, the copper rejection increases, but selectivity decreases because the calcium concentration in the permeate decreases as well. The decrease in both copper and calcium concentration in the permeate can be explained by the ion expulsion effect. As the total ionic strength increases in solution, the ion expulsion effect decreases because of the reduction in the absolute value of the electrical potential on the colloid surface (35).

Table 5: Results of ultrafiltration experiments of C₁₆BIDA in CPC solutions with
[C₁₆BIDA]₀ = 1.00 mM, [CPC]₀ = 100 mM, [Cu²⁺]₀ = 0.50 mM, [Ca²⁺]₀
= 0.50 mM .

[NaCl] ₀	[Cu] _{per}	[Cu] _{ret}	Cu Rej. %	[Ca] _{per}	[Ca] _{ret}
0	0.00200	0.7631	99.74	0.5846	0.6037
100	0.000963	0.7443	99.87	0.3080	0.5517
200	0.000602	0.7826	99.92	0.2371	0.6159

All concentrations in mM.

Feed pH = 5.50

Temp = 25 ° C

P = 60 psig (414 KPa)

Figure IV-6: Effect of retentate electrolyte concentration on separation.

4.2-2 Krafft Point of Retentate

Krafft point is defined as the melting point of the hydrated solid agent (36). Studies have shown that cationic surfactants have much lower Krafft temperatures than anionic surfactants of the same alkyl chain length. Therefore, high molecular weight cationic surfactants, such as CPC, can be used at room temperature. Practical separations based on the water soluble colloids must operate at temperatures above the Krafft point. This section discusses measurements of the Krafft points of retentate solutions.

It is well known that the Krafft point as well as solubilities of ionic surfactants are affected by the addition of salts (37). In order to determine semiqualitatively the effect of added salts on Krafft points of CPC for each experiment the Krafft temperature of the retentate has been measured.

The Krafft points have been measured for retentate by a relatively simple method. The solutions (retentates) have been freeze-dried and then their temperature slowly increased in a water bath, while monitoring the temperature. The Krafft point is the temperature at which the surfactant crystals dissolve.

The retentates used for the ultrafiltration runs all had Krafft temperatures lower than 23 °C . Therefore, surfactant precipitation did not occur in these systems.

4.2-3 Effect of Pressure on the Separation

Ultrafiltration is a pressure driven process. Pressure is induced on the solution by nitrogen gas. As pressure is elevated, the flow rate will increase. However, there is a maximum pressure that an stirred cell is designed to withstand (70 psig or 483 kPa). Problems with membrane compression occurs at higher pressures. Thus, all of the experiments have been performed under induced pressure of 60 psig (414 kPa).

Since separation efficiency, as well as flow rate, is a function of pressure. Ultrafiltration experiments were performed under three different pressures. For these three experiments, the initial concentrations of calcium, copper and CPC were the same, with only pressure being varied. The results are shown in Table 6 and Figure IV.7. The ion-expulsion effect can be substantially affected by dynamic effects at high pressures leading to higher ion concentrations in the permeate at high pressures (39). At a low enough pressure, the stirred cell ultrafiltration is at equilibrium. At low pressure of 20 psig, the results are comparable to results obtained from SED experiments. As discussed in chapter III, the SED experiments indicate the separation efficiency at equilibrium. Therefore, at a low pressure of 20 psig, the separation is nearly at equilibrium.

Table 6: Results of Ultrafiltration Experiments of CPC Solutions with $[CPC]_0 = 100$ mM, $[Cu^{2+}]_0 = 0.50$ mM, $[Ca^{2+}]_0 = 0.50$ mM Under different applied pressures.

P (psig)	$[Cu]_{per}$	$[Cu]_{ret}$	Cu Rej.%	$[Ca]_{per}$	$[Ca]_{ret}$
20	0.5602	0.5883	4.77	0.5848	0.4811
40	0.3342	0.5948	43.81	0.3626	0.5819
60	0.2720	0.5237	48.06	0.272	0.5849

All concentrations in mM.

Feed pH = 5.50

Temp = 25 °C

Figure IV-7: Permeate copper concentration as a function of pressure.

4.2-3 Flux

In order to develop a design for a commercial system and evaluate the economic feasibility of the process, flux data is needed as well as rejections. Since, membranes are expensive, it is desirable to minimize the membrane area required to treat a stream at a specific flow rate, in an ultrafiltration process. The higher the flux per unit area of membrane, the lower the required membrane area and lower the capital cost.

All flux data are reported as absolute flux and relative flux (flux/ flux of pure water under the same conditions). Flux differences have been seen in membranes from the same lot. Therefore, for each new membrane a pure water run has been done to be used for calculating the relative flux for the given membrane. In membrane processes, species that are rejected by the membrane accumulate on the membrane surface. The concentration of rejected colloid on the membrane surface is always higher than in the bulk solution; this causes concentration polarization or flux reduction (10). According to the gel polarization model, colloids accumulate on the membrane surface and form a gel layer there. Permeate flux is reduced by the hydraulic resistance of the gel layer (34).

Figure IV.8 represents an absolute flux ($L/m^2.hr$) versus retentate CPC concentration. Figure IV.9 represents relative flux as a function of retentate CPC concentration. When the solution concentration is equal to the gel concentration, the

flux is zero (10). Therefore, in order to avoid low flux rates, the highly viscous solutions obtained at high CPC concentrations should be avoided. The surfactant is so much more concentrated than the ligand or target ions that the CPC concentration controls the concentration polarization behavior (10).

The general conclusion from the flux data is that substantial flux reduction in LM-MEUF does not occur until a fairly high concentration of CPC is present in the retentate.

Figure IV-8: Absolute flux for LM-MEUF.

Figure IV-9: Relative flux for LM-MEUF.

4.3 Separation Efficiency at Equilibrium

The efficiency of the separation process has been studied at equilibrium utilizing C₁₆BIDA and CPC with copper alone or in the presence of calcium, while altering other parameters. The conditions of the studies were comparable to those used in ultrafiltration, feed pH was 5.5 and all the experiments were performed at 25 °C. The parameters that were varied include the copper, calcium, ligand, and CPC concentration.

For example, at an initial concentration of 0.75 mM of copper the permeate concentration of copper from SED experiments was found to be ~ 0.05 mM while that from stirred cell ultrafiltration is 0.0494 mM (Table 1).

CHAPTER V

CONCLUSIONS

1. **Excellent rejection of copper and expulsion of calcium are simultaneously achieved. Using LM-MEUF yielding both high separation factors and selectivity for the target ion copper.**
2. **Added sodium chloride increases the rejection of copper ions and reduces the calcium expulsion .**
3. **The rejections of copper from LM-MEUF obtained from ultrafiltration agree closely with equilibrium results.**
4. **The flux data does not demonstrate severe concentration polarization effects until a fairly high concentration of CPC is reached in the retentate.**

CHAPTER VI

FUTURE WORK

1. Experiments should be conducted to determine how effective this technique is using the spiral wound ultrafiltration unit and under what conditions the maximum separation can be achieved.
2. A detailed study of methods to recover and reuse the ligand and surfactant should be conducted.
3. The results of this study should be compared to the model developed by our group (34).
4. A different ligand with shorter hydrocarbon chain should be used in order to be able to analyze the ligand concentration in the permeate.
5. A detailed design study should be made to calculate the approximate costs of removing target species from an industrial waste stream using LM-MEUF.

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