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## Crossflow Surfactant-Based Ultrafiltration of Heavy Metals from Waste Streams

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### ABSTRACT

Five heavy metals (cadmium, lead, copper, nickel, and zinc) in a simulated wastewater, alone and together, were substantially removed by surfactant-based ultrafiltration using natural surfactants such as a derivative of cholesterol (deoxycholic acid) and lecithins. Selective and total removal of metal ions has been achieved by applying an appropriate level of surfactant-to-metal ratio (S/M). The underlying principle is to increase the size of the target metal ions by fixing them to larger surfactant macromolecules so they can be retained by a compatible membrane. Deoxycholic acid exhibited more efficiency in metal removal than did lecithin and sodium dodecyl sulfate. This research showed that transmembrane pressure had a minimal effect on metal removal whereas S/M had a substantial influence. The optimal S/M for considerable metal removal (99.9 + rejection ratio) is around 2.5 and 5 for deoxycholic acid and sodium dodecyl sulfate, respectively. The binding of metals to surfactant in the absence of membrane interferences was also determined by a centrifuge method.

### INTRODUCTION

Industrial wastewaters often contain a variety of toxic substances in dilute solutions. Removal of hazardous compounds from waste streams by conventional methods is usually not economical because of the large

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volumes of dilute wastewaters that need to be handled. Membrane separation technology, such as reverse osmosis (RO) and ultrafiltration (UF), can significantly reduce the waste volumes without a phase change, which results in low energy requirements. Surfactant-based UF, which combines the high flux of UF with the high selectivity of surfactants, has been applied to separate dissolved heavy metals and toxic organics from water using synthetic surfactants like sodium dodecyl sulfate (SDS) (1-3). However, synthetic surfactants have some disadvantages, such as the introduction of secondary pollutants into the treated effluent. Natural surfactants have some important potential advantages. They are not toxic, are biodegradable and abundant, and are expected to be much less expensive than synthetic ones. In this research, natural surfactants, such as the derivatives of cholesterol and lecithin, were used as a substitute for synthetic surfactants.

In general, UF is limited to handling pollutants with molecular weights from 300 to 300,000 because of the relatively large pore sizes of the membrane (4). However, smaller contaminants like heavy metals can be removed from solution by fixing them to larger surfactant macromolecules. At concentrations above the critical micellar concentration (cmc), 60-200 surfactant molecules will attach to each other, forming macromolecules or micelles. Therefore, metal cations associated with negatively charged micelles, which have a molecular weight in the range of 2,000 and 10,000, can be selectively removed by a compatible UF membrane with considerably higher permeate flow rates at lower pressure ranges than RO (5). The resulting permeate contains very low concentrations of metal ions and surfactant monomers and can be reused in manufacturing. The retentate, whose volume is now reduced from 1/10 to 1/100 of the original, can be reused and further treated by various chemical and physical methods. Successful separation is basically dependent on the type of surfactant and metal, surfactant-to-metal ratio (S/M), binding characteristics of surfactant to contaminants, and operating pressure. Selective removal of metal cations from wastewaters with surfactant-based UF can also be achieved by applying an appropriate level of S/M and a compatible type of membrane.

The goals of the present research were to determine the effects of surfactant types, metal types, and S/M on the system performance of crossflow surfactant-based UF. Three different operating procedures for varying metal and surfactant concentrations were conducted to determine the optimal S/M on selective and total removal of metal ions from solution with the best performing surfactant, deoxycholic acid (DCA). The cmc's of surfactants used in this study were also determined. Furthermore, the binding characteristics of two surfactants (DCA and SDS) to a mixture

of five heavy metals (Cd, Pb, Cu, Ni, and Zn) and solutions containing each metal were studied by a centrifuge method to determine the effects of membrane on metal separation.

Simulated wastewaters containing Cd, Pb, Cu, Ni, and Zn were prepared by placing a predetermined amount of their metal salts in solution. Their concentrations was set at typical effluent concentrations for metal finishing wastewaters from *EPA Treatability Manuals* (6). Experiments were performed with a solution of five metals, together and alone. Finally, a real industrial wastewater from a metal finishing facility containing Cu, Ni, Zn, and chromium (Cr) was utilized for this study.

## EXPERIMENTAL

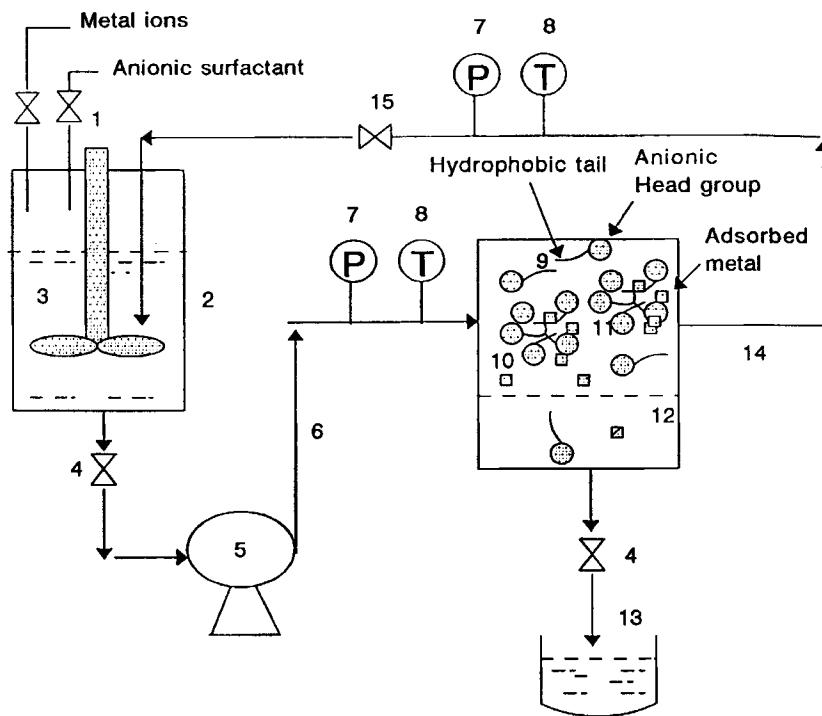
### Chemicals

A sodium salt of deoxycholic acid (DCA) and sodium dodecyl sulfate (SDS) were obtained from Sigma (St. Louis, Missouri) and used as received. Lecithins and soybean protein were obtained from Lucas Meyer (Decatur, Illinois) and Food Protein R&D Center (Texas A&M University, College Station, Texas), respectively. Cadmium chloride, zinc chloride, nickel sulfate, copper sulfate, and lead acetate, the sources of spike metal ions, were obtained from Sigma. Deionized water was used in preparing all solutions and reagents. Real wastewater was obtained from a metal finishing plant in Houston, Texas, which would like to remain anonymous.

### Methods

Conductivity experiments were performed to determine the cmc's of ionic surfactants at various concentrations ranging from 0.2 to 40 g/L. The conductivity measurements were done using a Hanna HI 8333 conductivity bridge (Hanna Instruments, Limena, Italy).

Crossflow UF runs were made by using a bench-top crossflow system with an effective membrane area of 138.7 cm<sup>2</sup>. A schematic flow diagram of this system is shown in Fig. 1. Membranes of the RGO3 type (Osmonics Inc., Minnesota) are made from anisotropic acrylanitryl which have a molecular-weight-cut-off (MWCO) around 2000 daltons. Membranes were soaked in deionized water to clean the protective glycerol layer which was applied before shipment. A new membrane was used in each experiment. The feed solution flowed tangentially across the membrane surface to reduce the effects of concentration polarization and membrane fouling. The pressure drop across the membrane was maintained at 276 kPa (40 psi) unless mentioned otherwise, and the temperature was set at 30°C. Plain water runs were done before and after separation trials to correlate



1) Air mixer	9) Surfactant monomer
2) Feed Tank	10) Unadsorbed metal
3) Feed solution	11) Micelle
4) Control valve	12) UF membrane
5) Feed pump	13) Permeate
6) Feed	14) Retentate
7) Pressure gauge	15) Pressure regulator
8) Thermometer	

FIG. 1 Schematic flow diagram for crossflow surfactant-based ultrafiltration.

the behavior of the different pieces of membranes and to observe the degree of membrane fouling, respectively. Three different operating conditions were used; (1) fixed S/M (a batch system), (2) increasing S/M; (3) decreasing S/M. Case 1 is conducted to screen and quantify the effects of different surfactants on system performance. Case 2 is performed to evaluate the feasibility of selective and total removal of metal ions. Case 3 is carried out to study the holding capacity of surfactants with respect to heavy metals and establish a breakthrough curve for each surfactant.

For the case of fixed S/M, the feed tank initially contained a 4-L solution of metals and surfactant. This volume was concentrated to around 3 L. No surfactants or metal ions were added into the feed solution during the experiment.

For the case of increasing S/M, the feed tank initially contained a 4-L solution of metals and surfactant. After the collection of 250 mL permeate, 2 g surfactant was added into the feed tank. The collected permeate at each interval was put back into the feed solution to keep the concentration of each metal as constant as possible.

For the case of decreasing S/M, the feed tank initially contained a 3-L solution of metals and surfactant. After the collection of 500 mL permeate, a 500-mL solution containing the same metal concentrations as the initial feed solution was added into the feed tank.

Metal concentrations in the feed and permeate samples were determined by using a Varian 975 Atomic Adsorption Spectrophotometer. Due to the low solubilities of lead sulfate and cadmium hydroxide, the feed solution was filtered when apparent suspended solids or precipitates existed. A new calibration curve was prepared for each analysis to ensure the accuracy of readings.

Centrifuge experiments were conducted to determine the membrane interferences with the binding of surfactants and metal ions. Various amounts of surfactant were added into several solutions with fixed metal concentrations. After a 30-minute reaction time, the samples were centrifuged for 10 minutes at 10,000 rpm (Sorvall, Du Pont Instruments) and then filtered through a 0.45-micrometer filter (Whatman Filter Company). The micelles containing absorbed metals and metal precipitates were separated from the liquid phase containing free metal ions and surfactant monomers. The liquid-phase samples were analyzed for their metal contents by using the atomic adsorption spectrophotometer, and the amounts of precipitated metals were determined by mass balance.

## DEFINITION AND THEORY

### Determination of Surfactant cmc

The cmc of an ionic surfactant was determined from a plot of equivalent conductivity versus square root of concentration. Equivalent conductivity,  $\Lambda_0$  ( $\text{m}^2/\text{mol}\cdot\text{ohm}$ ), is the ratio of conductivity to corresponding surfactant concentration in solution and defined as

$$\Lambda_0 = K_0/C_s \quad (1)$$

where  $K_0$  and  $C_s$  are conductivity ( $\text{ohm}^{-1}\cdot\text{m}^{-1}$ ) and concentration ( $\text{mol}/\text{L}$ ) of surfactant in solution, respectively.

The behavior of ionic surfactants below the cmc is similar to that of conventional electrolytes. The equivalent conductivity decreases slightly but linearly against the square root of concentration in accordance with Onsager's equation (7). Beyond the cmc, there is a large decrease in equivalent conductivity that is due to incomplete dissociation of surfactant in micellar form. As a result, the micelles are less-efficient carriers of charge than the equivalent number of fully dissociated monomers. Therefore, the intersection of two lines in this plot gives the cmc of an ionic surfactant (Fig. 2).

### Metal Removal by Surfactant-Based UF

The efficiency of a UF process to retain a specific component is mainly characterized by the rejection ratio (rate),  $R$ , defined as

$$R = 1 - C_p/C_r \quad (2)$$

where  $C_p$  is the concentration of the components in the permeate and  $C_r$  is the concentration of the components in the retentate.

In order to observe the effects of concentration polarization, gel layer formation, and membrane fouling on removal of metal ions, a long-duration run is preferred. An index called volumetric concentration factor (VCF) is used to determine how many times the feed concentration has

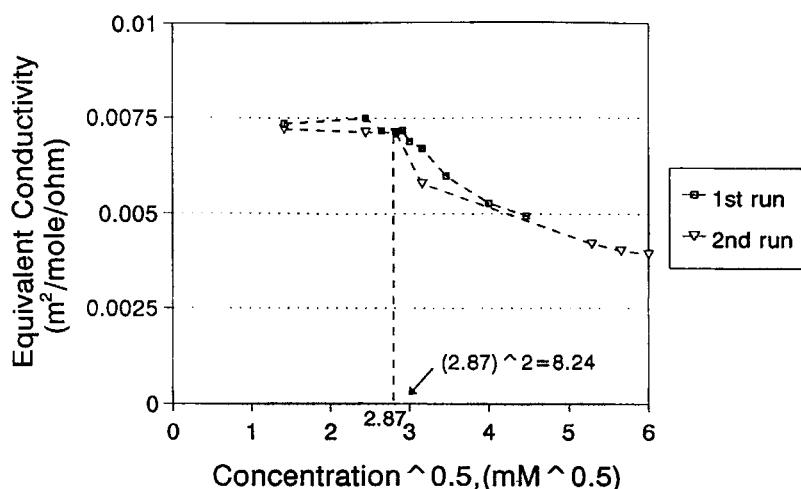


FIG. 2 Critical micellar concentration (8.27 mM) of SDS.

been concentrated. The VCF is defined as

$$VCF = V_f/V_r \quad (3)$$

where  $V_f$  and  $V_r$  are the volume of feed and retentate, respectively.

### Metal Removal by Centrifugation

The removal efficiency,  $K$ , of the metal is defined as

$$K = 1 - M_a/M_t \quad (4)$$

where  $M_a$  is the amount of metal present in the aqueous phase and  $M_t$  is the total amount of metal in the mixture.

## RESULTS AND DISCUSSION

The results and discussion are divided into three major sections. They are: 1) determination of cmc by conductivity experiments, 2) crossflow UF process, and 3) centrifuge experiments.

### Conductivity Experiments

Table 1 gives the cmc's of surfactants used in the present study. The good agreement between the measured cmc's and the literature values indicates the reliability of the conductivity method. The breakpoint in Fig. 2 shows the cmc of SDS. There is no cmc information available in the literature for lecithin. Lecithins and DCA are good surfactants because they have high molecular weight, form large-size micelles in the retentate, and have small cmc's that minimize surfactant monomers in the permeate.

TABLE 1  
Critical Micellar Concentration of Various Surfactants Determined by the Conductivity Method

Surfactant	Measured value (mM)	Reported value <sup>a</sup> (mM)	Molecular weight
Centrolex F	2.7–4.0	—	750
M-C-Thin	1.3–2.7	—	750
SDS	8.0–8.5	8.27	283
DCA	4.8–6.0	5.0	414.6

<sup>a</sup> The reported values of cmc were obtained from the 1992 Catalog of Sigma Chemical Company.

### Crossflow UF Experiments

The effect of transmembrane pressure on the flux of distilled water using the same piece of membrane (RGO3, 2000 MWCO) was studied to observe membrane compaction. The increases in pressure from 138 kPa (20 psi) to 690 kPa (100 psi) increased the flux from 25 to 172 L/h/m<sup>2</sup>, respectively (Fig. 3). There was no membrane compaction at this pressure range (138–690 kPa). 276 kPa was selected as the operating pressure.

The fluxes with plain water were measured before the experiment and after the cleaning to determine the permanent fouling of membrane. The results and cleaning procedures are summarized in Table 2. The cleaning procedures were very promising and resulted in higher flux. The deposits on the membrane surface can be removed by this cleaning procedures except at the high concentration of DCA.

### Factors Affecting the Permeate Flux (fixed S/M ratio)

An index called "normalized flux" is designed to minimize the deviations coming from the nonuniform pore size distribution of membranes. It is defined as the ratio of the flux of separation trial to that of a plain water run using the same piece of membrane.

**Metal Concentrations.** The effect of metal concentrations on the permeate flux using lecithin (Centrolex F) is shown in Fig. 4. The concentration of lecithin was maintained at 8.9 mM. The normalized flux decreases

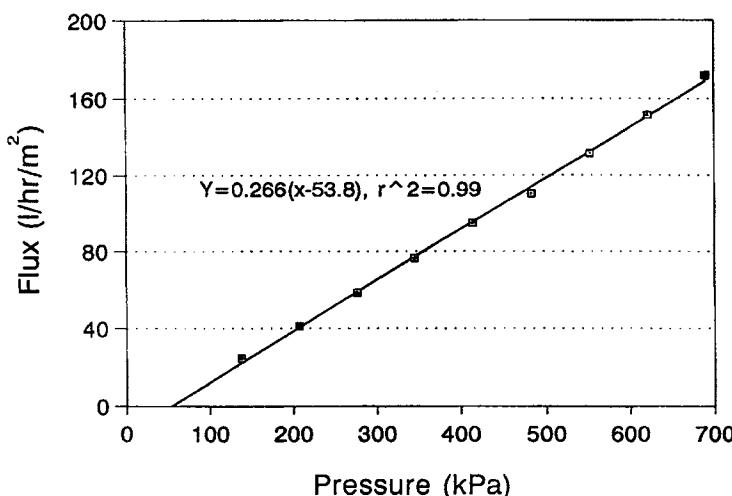


FIG. 3 Pure water flux at different pressures.

TABLE 2  
Results of Fouling Experiments and Cleaning Procedures<sup>a</sup>

Surfactant and concentration	Plain water flux before experiment (L/h/m <sup>2</sup> )	Plain water flux after cleaning (L/h/m <sup>2</sup> )
8 mM DCA	79.5	85.9
16 mM DCA	63.0	68.0
24 mM DCA	75.8	80.5
64 mM DCA	62.8	51.4
28 mM SDS	73.4	76.5

<sup>a</sup> Cleaning procedures:

1. Pump retentate out
2. Flush the system with 1 gallon of tap water
3. Recirculate 60 g/2 gal Terg-A-Zyme for 5 minutes and then flush
4. Flush with 1 gal tap water
5. Recirculate 6 g/2 gal D-Acid-HD for 5 minutes and then flush
6. Flush the system with 5 gal distilled water
7. Analyze the collected permeate sample for residual metal ions.

with increased metal concentration, except for lead. This irregularity is caused by the precipitates of lead-lecithin complexes, which deposit and form a gel layer on the surface of membrane. The permeate fluxes of metal mixture and plain water are listed in Table 3.

**Surfactant Types.** The effect of surfactant types on the permeate flux is shown in Fig. 5. Each surfactant due to its different structure resulted

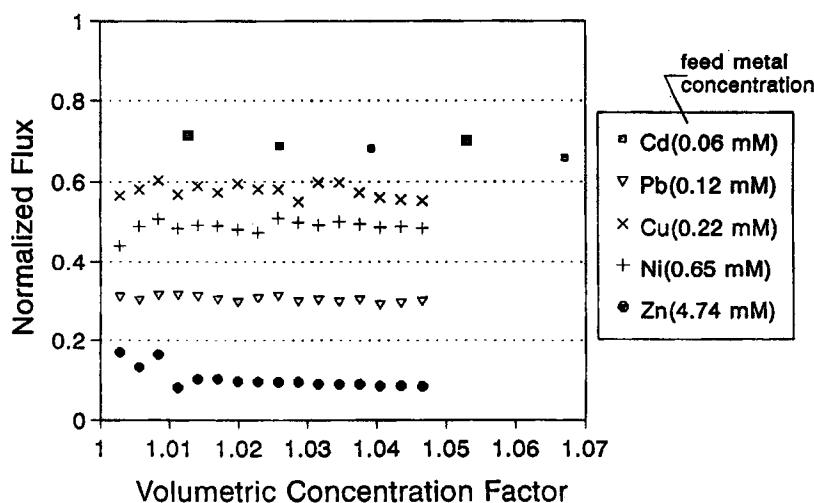


FIG. 4 Normalized flux at various metal concentrations.

TABLE 3  
Comparison of Removal of Various Divalent Ions Using Different Lecithins<sup>a</sup>

Metal (mM)	Lecithin (mM)	Average flux (L/h/m <sup>2</sup> )		Lecithin/ metal ratio	Final rejection (%)
		Permeate	Plain water		
Cd (0.06)	Centrolex F (8.9)	42.7	59.7	142.86	99.9+
Pb (0.12)	Centrolex F (8.9)	15.9	52.0	71.43	98.7
Cu (0.22)	Centrolex F (8.9)	30.5	52.4	40.00	95.1
Ni (0.65)	Centrolex F (8.9)	25.7	54.2	1.37	69.9
Zn (4.74)	Centrolex F (8.9)	6.7	69.7	1.88	47.4
Zn (4.74)	M-C-T (17.8)	14.0	52.4	3.76	68.4

<sup>a</sup> Temperature = 30°C; pressure drop = 276 kPa (40 psi); molecular weight of Centrolex F and M-C-Thin HL66 lecithin = 750; MWCO of RGO3-type membrane = 2000; initial volume = 4 L; volumetric concentration factor: copper = lead = nickel = zinc (Centrolex F) = 1.05; zinc (M-C-Thin) = 3.36; cadmium = 4.15.

in different permeability. The permeate fluxes remained nearly constant after the concentration of metal mixture and surfactant were concentrated two and a half times except in the case of protein. Some deposits of protein were observed on the surface of the membrane after the cell was opened. This indicated extensive membrane fouling at a high volumetric concentration factor. The effects of gel layer formation and membrane fouling were

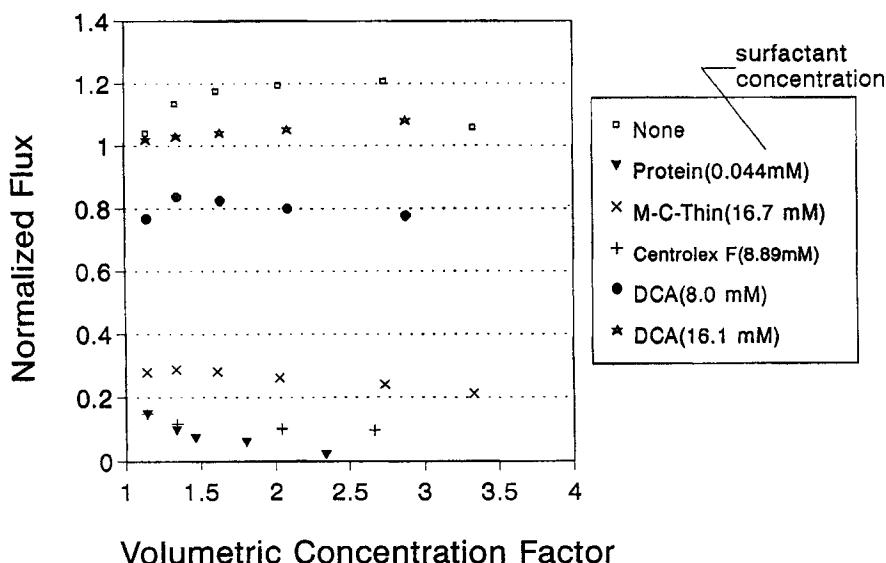


FIG. 5 Normalized flux at various surfactant concentrations.

not significant with surfactants DCA, M-C-Thin lecithin, and Centrolex F lecithin. DCA had the best performance and therefore was chosen for further study (Table 4 and Fig. 5).

**Surfactant Concentrations.** The effect of DCA concentration on permeate flux is given in Figure 5. The permeate flux at 16 mM is lower than at 8 mM. This is due to the high viscosity of the feed solution at a high surfactant concentration.

### **Factors Affecting the Rejection Ratio (fixed S/M)**

A mixture of five heavy metals (Cd, Pb, Cu, Ni, and Zn) was prepared to simulate real industrial wastewaters. The composition of the mixture is obtained from *EPA Treatability Manuals* (Tables 3 and 4) (6). The rejection ratio was calculated using the *measured* feed and permeate metal concentrations to eliminate the effect of metal precipitation.

**Membrane.** Table 4 illustrates the metal ion rejection ratio of the membrane RGO3 (2000 MWCO). In the absence of surfactant, Pb was rejected the most (50.5%) and Ni the least (17.7%) when the volumetric concentration factor reached the level of 3.4. It is interesting to observe that the permeate flux of the mixture was higher than that of plain water using the same piece of membrane (69.3 versus 59.5 L/hr/m<sup>2</sup>). One way to explain this phenomenon is that the membrane was conditioned by the feed solution during the separation. Metal ions in a mixture will pass through a membrane much easier when it is soaked in the same mixture first (2).

**Metal Types and Concentrations.** The effect of metal types and concentrations on the rejection coefficient at a constant soybean lecithin (Centrolex F) concentration (8.9 mM) is shown in Table 3. The final rejection ratio reaches the highest value for Cd (99.9 + %) and the lowest for Zn (47.4%). A higher initial feed metal concentration caused a lower rejection ratio and a lower permeate flux with Centrolex F lecithin (Table 3). This is mainly due to an increase in metal concentration that reduces the electrical surface potential of the negatively charged micelles. This decreases the driving force for separation.

**Surfactant Types.** The effect of surfactant type on the removal of a metal mixture is listed in Table 4. The performances of lecithin and protein were poor compared to that of DCA. The amphoteric characteristics of lecithin and protein result in weaker binding forces to metal cations than anionic surfactants such as DCA. In addition, the structures of surfactant aggregates in aqueous phase are spherical micelles for DCA and a flexible bilayer or vesicles for lecithin. Although protein has a lower S/M than lecithin and DCA, its flux decreased rapidly during the run. Some deposit

TABLE 4  
Removal of Metal Ions in Mixture Using Different Surfactants<sup>a</sup>

Retentate concentration		Average flux (L/h/m <sup>2</sup> )		Final rejection (%)	
Metal (mM)	Surfactant (mM)	Permeate	Plain water	S/M	
Cd (0.06)	None	69.3	59.5	—	20.9
Pb (0.12)					50.5
Cu (0.22)					44.0
Ni (0.65)					17.7
Zn (4.74)					26.2
Cd (0.06)	Centrolex F (8.89)	5.0	66.5	1.54	40.3
Pb (0.12)					90.4
Cu (0.22)					35.5
Ni (0.65)					21.0
Zn (4.74)					44.4
Cd (0.06)	M-C-Thin HL66 (16.7)	15.5	56.2	3.07	77.6
Pb (0.12)					94.2
Cu (0.22)					52.2
Ni (0.65)					55.6
Zn (4.74)					72.8
Cd (0.06)	Protein (0.044)	6.4	58.8	0.008	68.0
Pb (0.12)					99.9 +
Cu (0.22)					98.0
Ni (0.65)					24.1
Zn (4.74)					65.5
Cd (0.06)	DCA (8.0)	80.0	79.5	1.38	90.9
Pb (0.12)					97.7
Cu (0.22)					98.7
Ni (0.65)					24.2
Zn (4.74)					89.8
Cd (0.06)	DCA (16.1)	52.3	63.0	2.78	99.9 +
Pb (0.12)					99.9 +
Cu (0.22)					99.9 +
Ni (0.65)					99.9 +
Zn (4.74)					99.9 +

<sup>a</sup> Temperature = 30°C; pressure drop = 276 kPa (40 psi); initial volume = 4 L; volumetric concentration factor: W/O surfactant = 3.36; Centrolex F = 2.34; M-C-Thin = 3.36; protein = 2.55; DCA (8 mM) = 2.86; DCA (16.1 mM) = 2.86.

of proteins on the surface of the membrane after the membrane cell was opened indicated extensive membrane fouling at a high volumetric concentration factor. DCA, a biological detergent, has an inherent advantage over other surfactants due to its capability of cleaning the membrane during separation. It reduces the effects of gel layer formation and membrane fouling. DCA has a higher flux and rejection ratio than other surfactants (Table 4). Therefore, DCA was selected for further experiments.

**Surfactant Concentration.** As the retentate surfactant concentration increases relative to the retentate metal concentrations in a mixture (Table 4), the permeate metal concentration decreases. This is due to increasing the fraction of surfactant in micellar form by increasing the relative concentration of the surfactant. A larger fraction of total surfactant present in micellar form will tend to increase the separation efficiency.

#### **Selective Removal of Metal Ions (Increasing S/M)**

The effect of varying the surfactant concentration while holding the retentate metal concentration constant is shown in Fig. 6 (DCA with each metal at 40 psi), Figs. 7 and 8 (DCA with metal mixture at 40 and 80 psi, respectively), and Fig. 9 (SDS with metal mixture at 40 psi). Metal ions at a concentration of 5 mM can be considerably removed by DCA at a

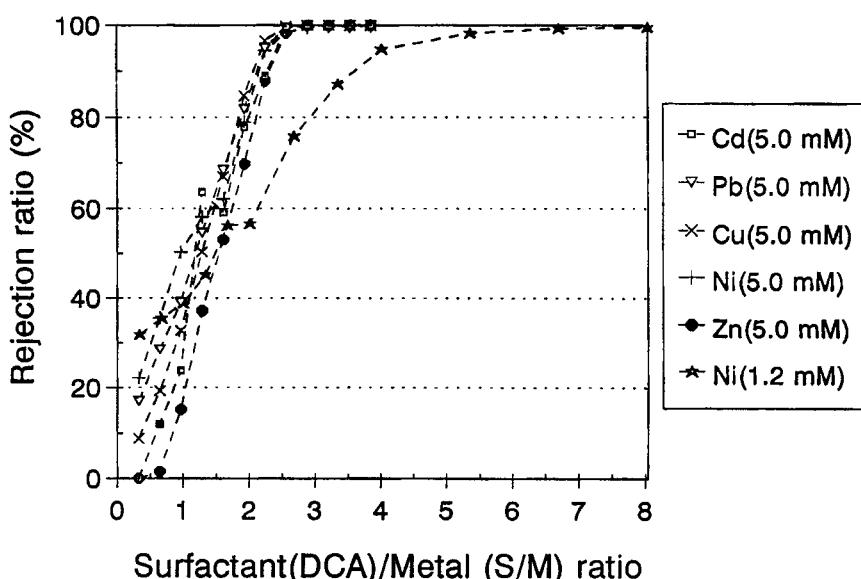


FIG. 6 Effect of S/M of DCA on the removal of each metal at 40 psi.

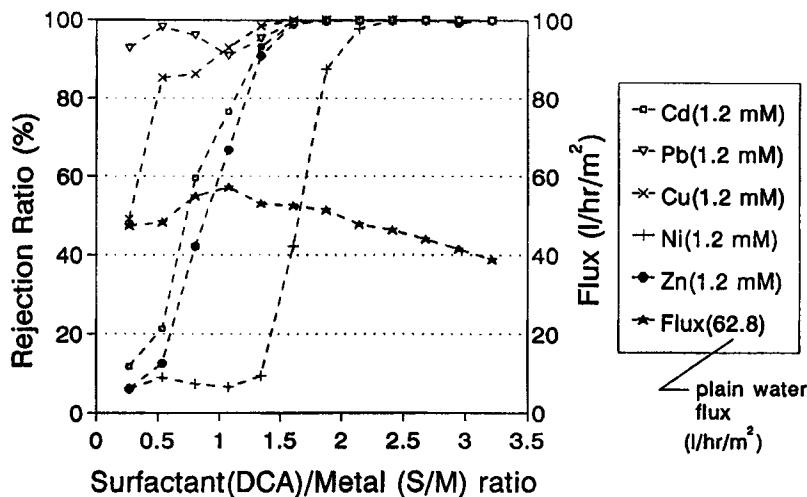


FIG. 7 Effect of S/M of DCA on the removal of metals in mixture at 40 psi.

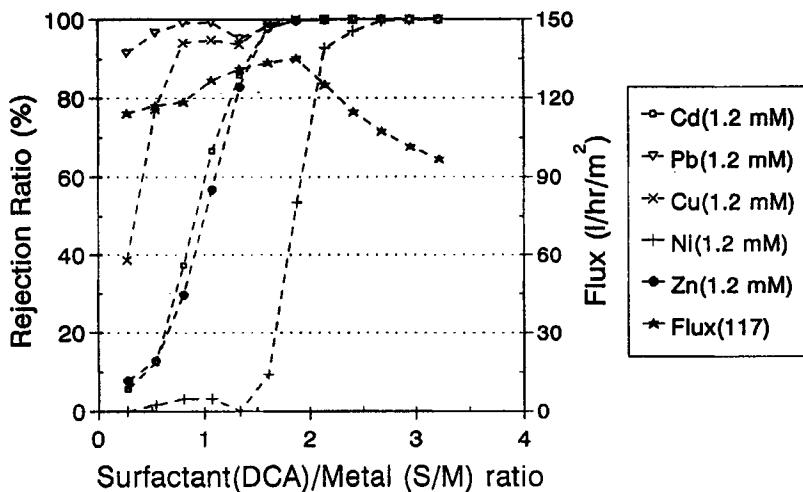


FIG. 8 Effect of S/M of DCA on the removal of metals in mixture at 80 psi.

S/M above 2.5 (Fig. 6). For the case of a lower nickel concentration (1.2 mM), nickel is not totally removed at a S/M of 2.5 because the concentration of DCA (only 3 mM at this level of S/M) does not reach its cmc (5 mM). So a higher S/M ( $S/M > 8$ ) is needed to remove all the nickel ions at a lower concentration. The performance of DCA is better than that of

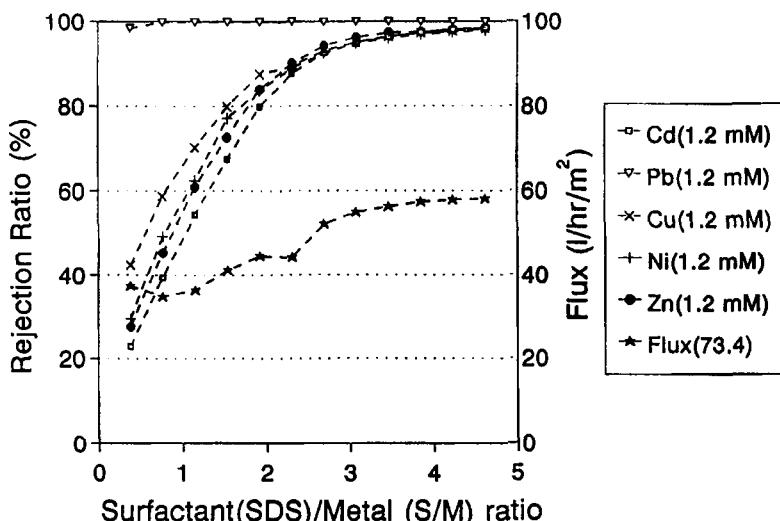


FIG. 9 Effect of S/M of SDS on the removal of metals in mixture at 40 psi.

SDS for the removal of the same metal concentrations in a mixture (Figs. 7 and 9). DCA requires a critical S/M of 2.5 compared to 5 for SDS to substantially remove all the metal ions in a mixture. A lower critical S/M indicates better performance of the surfactant. The flux increased with S/M using SDS as the surfactant while the flux decreased with S/M using DCA. This may be caused by a different interaction between the micelles and the membrane surface. The performance of DCA (S/M) is the same whether metal ions are in a mixture or in an individual metal solution. The trend of DCA for the removal of individual metal is similar for each metal (Fig. 6). But for DCA the removal of the five heavy metals together, competitive binding occurred (Figs. 7 and 8). Therefore, selective removal of metal ions in a mixture can be achieved by applying an appropriate amount of surfactant. In a solution containing five heavy metals, selective removal of copper from nickel can be accomplished by using a S/M of around 1.4. The affinity of metal ions for the surfactant is Pb > Cu > Cd > Zn > Ni for DCA and Pb > Cu > Ni > Zn > Cd for SDS (Figs. 7 and 9, respectively). A high operating pressure (80 psi) did not increase the metal rejection significantly, but it did increase the permeate flux almost two times compared to that of 40 psi (Fig. 8). The metal ions can be removed with a surfactant concentration below its cmc (Figs. 6–9). This means that metal is removed by forming metal complexes at a surfactant concentration below the cmc and by forming both metal complexes and metal micelles at a surfactant concentration above the cmc.

### **Total Removal of Metal Ions (fixed S/M)**

The optimal S/M for DCA on total removal of metal ions present in a mixture is around 2.5 (Fig. 7). An experiment was performed to confirm the rejection capacity of DCA using a concentration of 16.1 mM to treat a simulated industrial wastewater which contained 5.79 mM of total metal ions. The results from this experiment are given in the bottom section of Table 4. All metal ions present in a mixture can be substantially removed by DCA at a S/M of 3. This means that roughly three surfactant molecules are needed to bind a metal ion at a surfactant concentration above its cmc. DCA has an outstanding capability for total and selective removal of metal ions present in a simulated wastewater with relatively high permeate flux.

### **The Holding Capacity of Surfactant to Metals (decreasing S/M)**

The breakthrough curve of DCA (24 mM) for holding the metal ions (5.79 mM) in a mixture of 3 L is shown in Fig. 10. The order of metal ions detected in the permeate was Ni > Zn > Cd > Cu > Pb. This order matches the affinity determined previously and shown in Fig. 7.

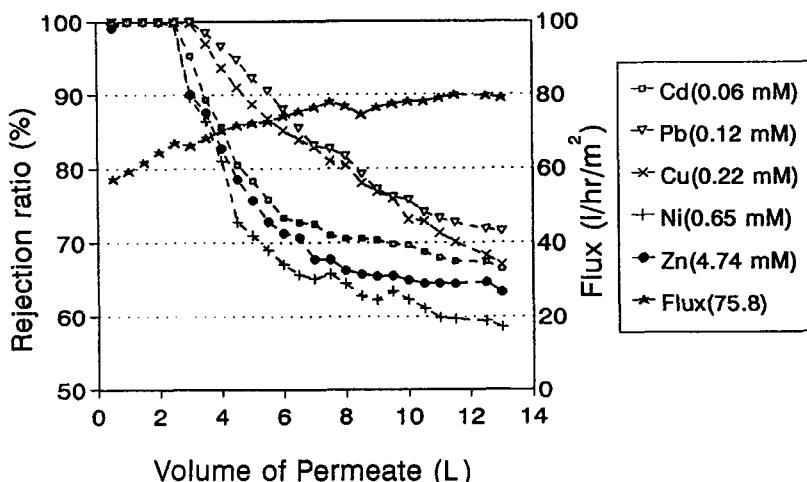


FIG. 10 Breakthrough curve of DCA in metal mixture.

### ***Application to Real Industrial Wastewater (fixed S/M)***

M-C-Thin lecithin was applied to treat a real wastewater which was collected from a commercial electroplating facility in Houston, Texas. Initially the raw wastewater was pretreated by a microfilter to remove the particles and colloids. This wastewater contained copper (0.08 mM), nickel (0.65 mM), chromium (0.32 mM), and a trace amount of zinc. The flux decreases slightly from 20 to 11 L/h/m<sup>2</sup> with an increase in the volumetric concentration factor (Fig. 11). The final rejection ratio for metals increases slightly with the volumetric concentration factor except for Cr which increases significantly. This may be due to the low reaction ratio of the binding between Cr and M-C-Thin lecithin.

### **Centrifuge Experiments**

The absorption capacities of the two best performing surfactants (DCA and SDS) to metal ions were examined in the absence of a membrane. A mixture of five metals and a solution containing each metal were used in this study. Two assumptions were made. One was that the filter paper did not absorb or reject any free metal ions. The other was that the micelles were removed completely by the centrifuge and filtration process. The ability of DCA to remove each metal ion is much better than that of SDS (Figs. 12 and 13). At a S/M of DCA that is slightly above its critical level

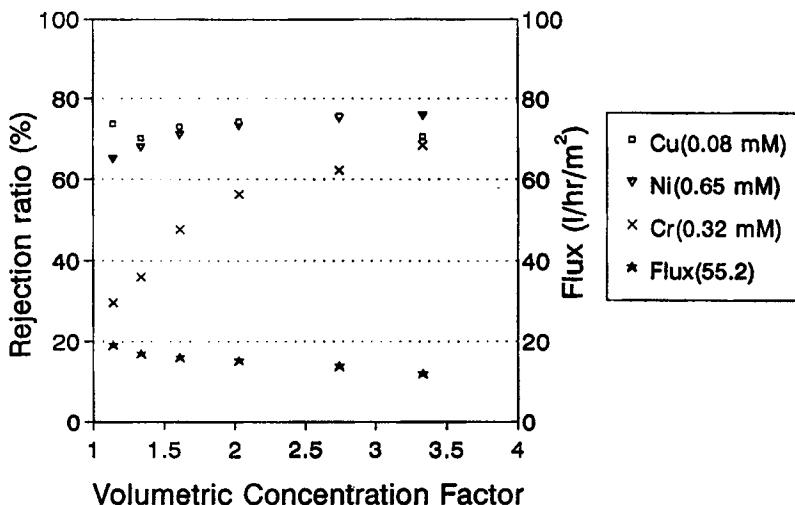


FIG. 11 Removal of metal ions from industrial wastewater using M-C-Thin lecithin.

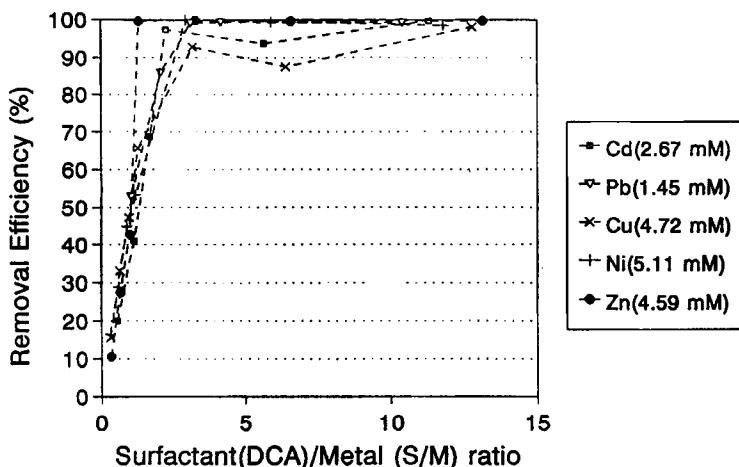


FIG. 12 Removal efficiency of DCA for each metal.

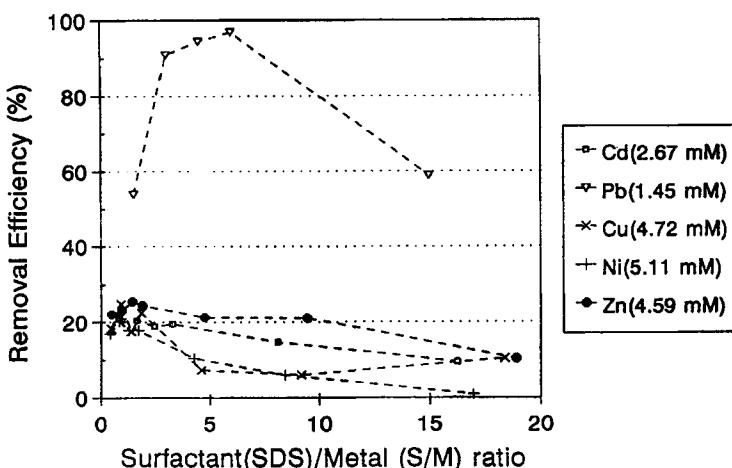


FIG. 13 Removal efficiency of SDS for each metal.

(S/M = 2.5), all five metals except Cd and Cu were entirely removed in solutions containing each heavy metal. For the case of a mixture containing the same concentration of each of the five metals, DCA still exhibited a better performance than did SDS (Figs. 14 and 15). The optimal S/M of DCA is 2.5 in the presence of a membrane and 4 in the absence of a membrane (Figs. 7 and 14). This is a clear indication of membrane rejec-

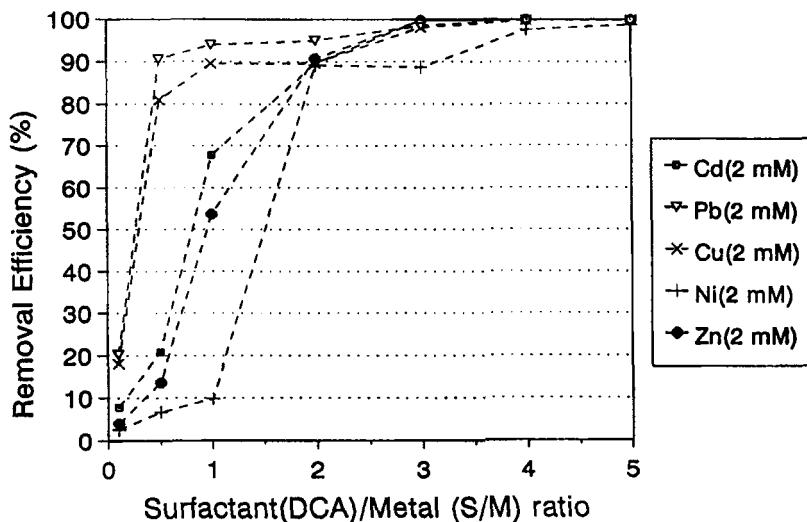


FIG. 14 Removal efficiency of DCA for metal ions in mixture.

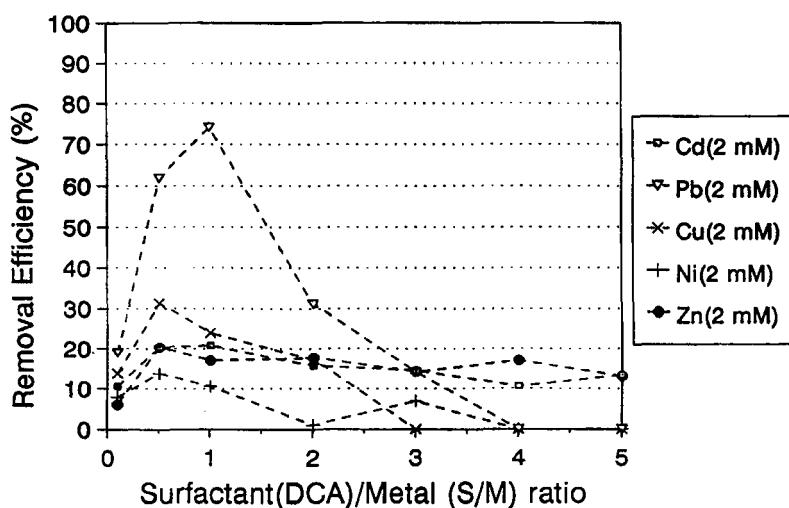


FIG. 15 Removal efficiency of SDS for metal ions in mixture.

tion and/or absorption of some metals. The affinity of metal to DCA is  $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$  (Fig. 14). This order is the same as that in crossflow UF runs.

## CONCLUSIONS

Identification of cmc's of ionic surfactants using conductivity methods is shown to be reliable. Selective and total removal of metal ions present in a simulated industrial wastewaters is achieved by applying an appropriate level of S/M. The performance of DCA on metal separation is better than that of the other surfactants, including SDS. Membrane did reject/adsorb some metals. The binding of metals to surfactant can be determined in the absence of membrane interferences by a centrifuge method.

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