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Chelation and Foam Separation of Metal Ions from Solutions

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Abstract

An experimental study was conducted on the chelation and foam separation of trace amounts of cadmium, zinc, and lead from their water solutions. The chelation agents ethylenediaminetetraacetate (sodium salt), sodium diethyldithiocarbamate, and citric acid were used with sodium dodecylsulfate (SDS) as a foam-producing agent. The chelation agents did not produce metal complexes that were very surface active. The foam-producing agent produced metal ion complexes that were surface active and resulted in appreciable separation of the metal ions. The use of 100 ppm SDS resulted in separation of 90% of the zinc ions from solution containing 2 to 20 ppm zinc. At concentrations below and above this, the removal efficiency dropped significantly.

INTRODUCTION

The use of chelating agents to form complexes with metal ions in solution and the subsequent separation of the complexes from the bulk liquid by foaming have been recently studied as a method for removal of trace metals from water (*1*). The process involves the addition of an organic chelating agent to form a complex with a metal ion. The chelated metal ion complex is generally hydrophobic and migrates to a gas–liquid interface where it concentrates. In many cases the organic chelating agent is sufficiently surface active to result in the formation of a stable foam. In other cases a separate surfactant is added to produce a foam. The generated foam with the concentrated chelate metal–ion complex is subsequently collapsed.

Either metal cations or anions may be complexed. For metal cations, the complexing agent should have an anionic hydrophobic portion which can combine stoichiometrically with the metal cation. For instance, the surfactant sodium dodecylsulfate (SDS) has been used to complex lead ions (2+) in a study by Rubin and Lapp (*2*). The surfactant to metal ion concentration was 2 for removal of about 96% of the lead from a 0.1 m*M* solution at a pH of 9.0. Lower percentage removals were observed at lower pH values. This study also demonstrates the importance of regulating the pH in the solution; at low to intermediate pH values there are sufficient hydrogen ions to compete with the metal ions for the surfactant anions.

Other factors that affect the separation include: the concentration of metal ion and surfactant, the gas flow rate, the type of sparger used to generate bubbles, the column length, the bubble size, and the ionic strength. In the section that follows, a very simple mathematical model is developed to allow the prediction of these factors upon the separation efficiency. The model predictions will be qualitatively checked by comparison to results for the chelation and separation of metal ions of cadmium, lead, and zinc with the chelating agents citric acid, EDTA (ethylenediaminetetraacetic acid), and NDDTC (sodium diethyldithiocarbamic acid) with the surfactant SDS which can also act as a chelating agent.

Citric acid and EDTA are relatively common chelating agents used in a variety of industries including metal plating and finishing (*3*). Citric acid forms soluble, weakly bound complexes with metal ions, presumably by means of its hydroxyl groups. On the other hand, EDTA forms strongly bound complexes with metals by means of amine groups. The chelating agent NDDTC has been suggested as an agent for chelating and solvent extraction of heavy metals (*4*). This compound forms a neutral complex with the metal ion, almost quantitatively removed by solvent extraction. The surfactant SDS is an anionic surfactant which can also combine with the metal ions to produce a chelate (*5*).

BACKGROUND

In the bulk liquid phase in the foam generating section of the column, equilibrium between the associated chelating agent, in acid form, and its ionic form is assumed:

$$\mathrm{SnCh} \rightarrow n\mathrm{S}^+ + \mathrm{Ch}^{n-} \tag{1}$$

$$\mathrm{Ch}^{n-} + n\mathrm{H}^+ \rightleftharpoons \mathrm{HnCh} \tag{2}$$

In Reaction (2) the ionization constant, K_a, is defined as

$$K_a = \frac{[\mathrm{Ch}^{n-}][\mathrm{H}^+]^n}{[\mathrm{HnCh}]} \tag{3}$$

where $[\mathrm{H}^+]$, $[\mathrm{Ch}^{n-}]$, and $[\mathrm{HnCh}]$ correspond to the concentrations of hydrogen ion, chelate ion, and associated chelate in solution, respectively. SnCh is the chelating agent in salt form. If the concentration of the chelating agent is S, then we have

$$S = [\mathrm{HnCh}] + [\mathrm{Ch}^{n-}] \tag{4}$$

and Eq. (3) can be rearranged to

$$K_a = \frac{[\mathrm{Ch}^{n-}][\mathrm{H}^+]^n}{S - [\mathrm{Ch}^{n-}]} \tag{5}$$

Further rearrangements give

$$[\mathrm{Ch}^{n-}] = \frac{SK_a}{K_a + [\mathrm{H}^+]^n} \tag{6}$$

If $K_a \gg [\mathrm{H}^+]^n$,

$$\log\,[\mathrm{Ch}^{n-}] = \log S \tag{7}$$

If $K_a \ll [\mathrm{H}^+]^n$,

$$\log\,[\mathrm{Ch}^{n-}] = \log SK_a + n\mathrm{pH} \tag{8}$$

When chelate-producing metal ions are present, the following reactions take place:

$$m\mathrm{Ch}^{n-} + n\mathrm{M}^{m+} \rightleftharpoons \mathrm{M}_n\mathrm{Ch}_m \tag{9}$$

The stability constant, K_s, for this reaction is

$$K_s = [\mathrm{Ch}^{n-}]^m[\mathrm{M}^{m+}]^n \tag{10}$$

If the metal chelate is quite stable, i.e., K_s is too small, then almost all of the metal will turn to chelate.

At low pH ($< 1/n\ \mathrm{p}K_a$) there will be less chelating agent available to chelate a certain amount of metal. In other words, at constant chelate concentration a lower percentage of metal will be removed at low pH.

The curve of log $[\mathrm{Ch}^{n-}]$ vs pH in Fig. 1 reveals that there is a minimum pH below which the concentration of free chelate decreases with decreasing pH. Above this pH value the concentration of free chelate and consequently metal chelate will be independent of pH.

If the metal chelate is appreciably hydrophobic, it will transfer to the gas–liquid interface. The mass transfer process can be approximated as diffusion from a bulk liquid to a bubble surface, i.e.,

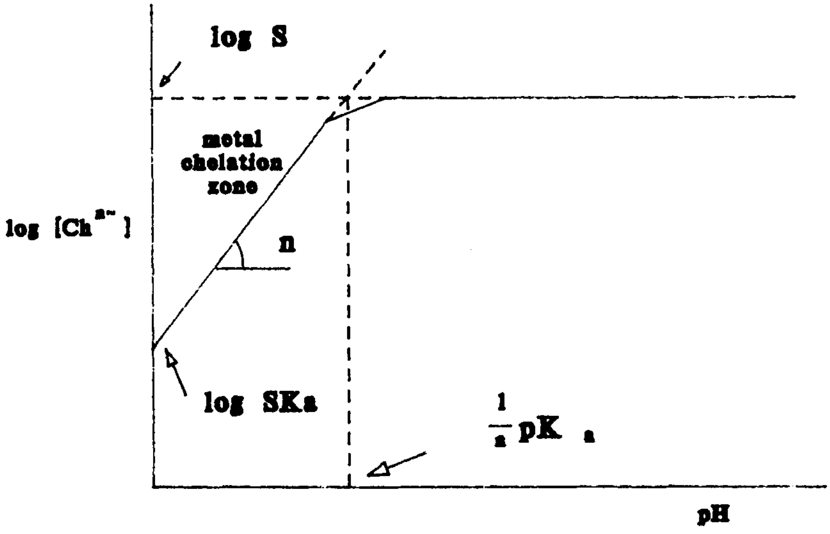

FIG. 1.

$$dC_b/dt = K(A/V)(C_s - C_b) \tag{11}$$

where C_b and C_s are the bulk and surface phase concentrations, respectively, A/V is the total bubble surface area to liquid volume ratio, K is a mass transfer coefficient, and t is the liquid residence time. This expression assumes that the liquid phase is well mixed. Liquid pool HTU (heigh equivalent of a theoretical plate) values are reported between 10 and 30 cm (*1*) which implies equilibrium between the exiting streams in the liquid leaving with the foam and that exiting the liquid pool.

At low concentrations of surfactant, equilibrium between the bulk phase and the surface follows a linear adsorption relationship, i.e.,

$$\Gamma = K_e C_b = C_s \delta \tag{12}$$

where Γ is the surface concentration (moles/unit surface area), K_e is a surface equilibrium coefficient, and δ is the "thickness" of the surface layer. At high bulk concentrations, the interface is saturated and Γ equals its value for saturation, Γ_s.

For the latter case the concentration, C_f, for collapsed foam at any position in the foaming section of the column can be related to Γ_s and C_b in the foaming section of the column:

$$C_f Q_f = \Gamma_s (A/V_g) Q_g + C_b Q_f \tag{13}$$

where Q_f is the flow rate of collapsed foam, A/V_g is the surface area of the bubbles/volume of gas, and Q_g is the gas flow rate. If the entrained bulk liquid leaving the liquid pool is in equilibrium with the bubble surface, no additional mass transfer will occur during the rising of the foam. Therefore, C_b will equal C_p, the pool concentration. An overall material balance can also be made to relate these concentrations to the inlet or initial concentration of chelated metal ion, C_i, in the foam column, i.e.,

$$C_i V_i = C_p V_p + C_f V_f \tag{14}$$

where V_i is the initial volume of liquid in the foam column or the inlet flow rate for a continuous system, V_p is the pool volume or flow rate of liquid leaving the bottom of the column, and C_f and V_f are the average concentration in the collapsed foam and total volume of collapsed foam for a batch run or are the exiting concentration in the collapsed foam and the collapsed foam flow rate for a continuous run.

The operation of the column can be expressed in terms of C_f, the concentration in the collapsed foam, and C_f/C_p, the ratio of the foam concentration to the pool concentration (an enrichment ratio). The above expressions can be solved for these, i.e.,

$$C_f = \frac{C_i(V_i/V_p) + \Gamma_s(A/V_g)(Q_g/Q_f)}{1 + (Q_f/V_p)} \tag{15}$$

$$\begin{aligned} C_f/C_p &= 1 + \Gamma_s(A/V_g)(Q_g/Q_f)/C_p \\ &= \frac{C_i(V_i/V_p) + \Gamma_s(A/V_g)(Q_g/Q_f)}{C_i(V_i/V_p) - \Gamma_s(A/V_g)(Q_g/V_p)} \end{aligned} \tag{16}$$

These expressions will be used to interpret the results obtained in the experimental work.

DESCRIPTION OF EXPERIMENTAL WORK

Both batch and continuous foam separation runs were performed in small-scale foam columns consisting of a Buchner glass cylinder of 50 mm i.d. with a volume of 210 mL (see Fig. 2). The lower section of the Buchner funnel has a fritted glass bottom of porosity size C (ASTM 40-60). The upper section of the funnel converged to a ground glass joint of 14.4 mm i.d. A 20-mm i.d. by 250 mm long vertical glass tube was used to drain and convey the foam to a round bottom flask in which the foam coalesced. The liquid pool depth in the column was about 5–7 cm. The foam height was about 25 cm.

Filtered, metered, and humidified compressed air was passed through the sparger section to generate the foam in the column. The foam was coalesced by rising ethanol fumes produced by a small amount of ethanol in the round bottom receiver flask.

Batch runs were performed by charging the column with 50 mL solution containing the metal, 25 mL chelating agent solution, and 1 mL surfactant solution. Cadmium chloride, lead nitrate, and zinc chloride were used to prepare the metal ion solutions. Chelating agents included EDTA, citric acid, and NDDTC. The surfactant used was SDS. One milliliter of a 1% solution of SDS was added to the contents of the foam column. The resulting concentration of surfactant was about 130 ppm for all runs, compared to the reported critical micelle concentration of 2300 ppm (*6*). Foam was generated by an air flow of 10–40 mL/min. The foam was collected in the round bottom flask until no more was produced, at which time another milliliter of SDS solution was added and the second

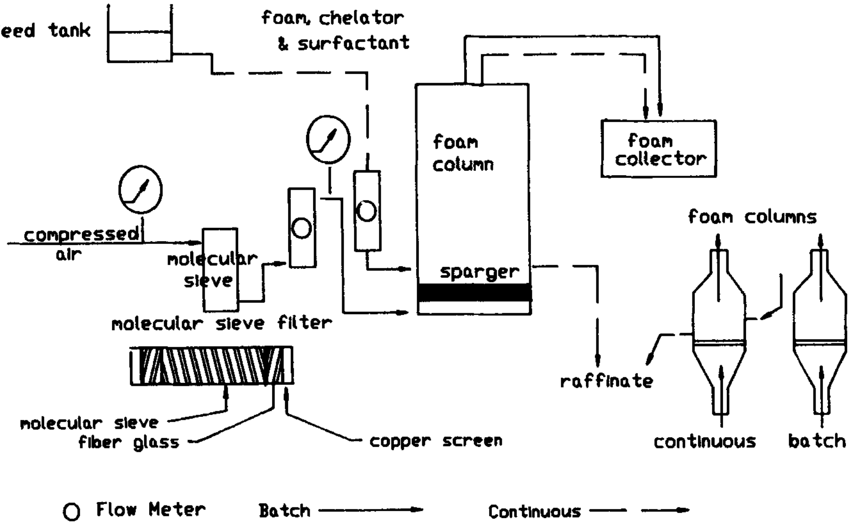

FIG. 2. Flow diagram.

foam sample collected. Samples of the feed solution and of the liquid pool and foam after addition of the first and second milliliter of surfactant were analyzed for metals.

The continuous runs were performed in an apparatus similar to that described for the batch studies. The liquid was injected through a port in the glass tube section at a depth of about half of the liquid pool depth. The liquid was delivered by a gravity feed system at a flow rate of 60 mL/h. The pool discharge was located just above the fritted glass section of the foam column and the pool height maintained by means of a U-tube overflow line. Air was delivered at a flow rate of 20 mL/min. Foam was coalesced by discharge into the round bottom flask containing ethanol. Three periodic samples (after about 1, 3, and 5–7 h of operation) of the pool overflow were taken. The foam was collected in one batch. Sample analysis was performed by diluting the samples and analyzing them for metals by means of atomic absorption. An instrumentation Laboratories Model 1L 353 atomic absorption spectrophotometer was used for the analysis.

RESULTS AND DISCUSSION

The results of the batch runs are summarized in Table 1. The results in the table indicate that the use of chelating agents EDTA and NDDTC

TABLE 1
Batch System Results

Metal	Initial concentration range (ppm)	Chelation agent	Agent/metal concentration (*M*)	Foamate concentration (ppm)	Pool concentration (ppm)
Cd	5–50	EDTA	50–500	5–70	5–48
Cd	5–50	NDDTC	5–50	5–70	5–10
Cd	2–25	CA	0.6–650	10–260	0.2–10
Zn	1–100	CA	10–130	10–300	0.5–30
Pb	70	EDTA	110	70	70
Pb	70	NDDTC	10	70	70
Pb	4–220	CA	100–5400	2–260	2–90

did not result in any appreciable removal of the metals cadmium or lead. These chelating agents form relatively strong complexes with metal ions [p*K* 16.4 and 18.2 for EDTA complexes with cadmium and lead (*3*); p*K* of 18.3–17.7 for NDDTC complex with lead (*7*)]. However, it appears that the complex is not very hydrophobic, based upon the low separation. Indeed, Martell and Plumb (*2*) indicate that metal ion chelated compounds with EDTA are quite soluble. Even though the concentration of chelate compound is high, the surface concentration is low and these chelating agents should not be used for foam separation in the manner studied.

The use of citric acid, on the other hand, appears to result in a significant separation of cadmium, lead, and zinc. Figure 3 shows the results for the removal efficiency of zinc {[(initial amount of zinc in pool) − (final amount in pool divided by initial amount in pool)] × 100} as a function of the initial zinc metal concentration and the concentration of citric acid, 3300 and 1650 ppm. As the initial zinc concentration rises above 2 ppm, the removal efficiency rises. As the concentration continues to rise above 20 ppm, the removal efficiency drops. Somewhat better removal efficiencies are seen for higher citric acid concentrations.

The decrease in the removal efficiency with moderate initial zinc ion concentration is predicted by the simple model presented above. As the zinc concentration rises, the surface concentration remains constant and

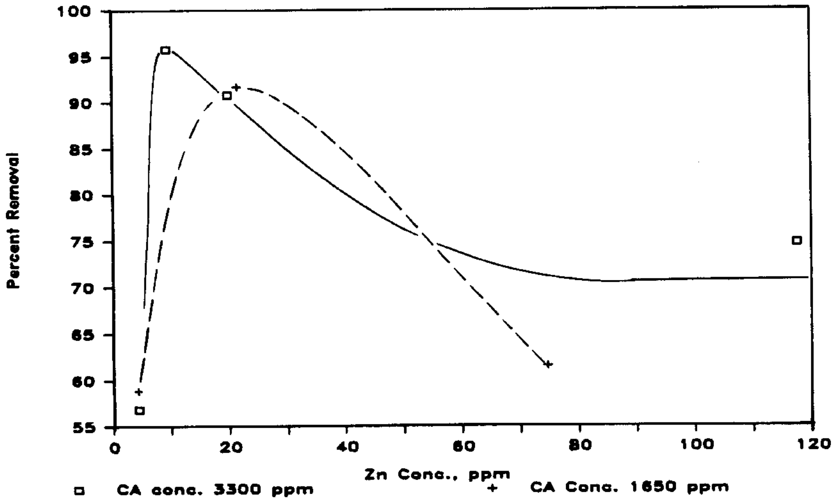

FIG. 3. Batch study of Zn removal. Surfactant concentration: 130 ppm.

the ratio of foam concentration to pool concentration decreases to unity. Similarly, the foam concentration approaches the initial concentration so the removal efficiency will drop to zero. This is a consequence of the saturation of the interface at moderate to high concentrations of the metal ion complex. At very low concentrations, less than around 3 ppm, Fig. 3 shows a decrease in removal efficiency as the metal ion concentration decreases. There are two possible explanations for this behavior. At these low concentrations there may be insufficient metal complex to saturate the interface. The surface concentration becomes a function of the bulk phase concentration and decreases with decreasing bulk phase concentration. The other explanation is that there may not be enough of the metal ion complex to compete with the surface-active agent for sites at the gas-liquid interface.

The decrease in removal efficiency with citric acid concentration is indicated by the results depicted in Fig. 4. A sudden decrease in removal efficiency with the ratio of citric acid/zinc initial concentration is seen at a CA/Zn ratio of 400. Based upon this, one would conclude that citric acid is not needed and that the surfactant forms a sufficiently surface-active complex with the metal ion to produce good separation. The citric acid p*K* value for zinc is about 4.5 (*8*). This is fairly low and results in enough free metal ion to complex with the surfactant to form a stronger complex and high removals. Similar low chelate metal ion stability

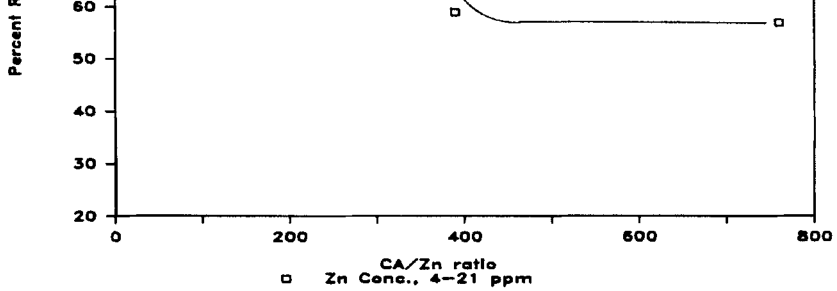

FIG. 4. Batch study of Zn removal. Surfactant concentration: 130 ppm.

complexes are reported for cadmium and lead with citric acid which explains the higher removal efficiencies reported in Table 1 for chelation of these metals with citric acid and surfactant. The surfactant SDS is actually producing the metal ion complex that is adsorbed and removed by the foam. The low stability constants for citric acid chelates allows SDS to complex and remove these much better than for the chelating agents EDTA and NDDTC which form stronger complexes, have higher p*K* values.

Figure 5, which summarizes the continuous column results for cadmium, further illustrates this. As the citric acid concentration increases, the removal efficiency drops. The continuous runs indicate very high removals would be obtained in the presence of low amounts of citric acid for initial cadmium concentrations of 0.5 ppm and surfactant concentrations of 100 ppm. Lower surfactant concentrations were attempted, but at 50 ppm the foam production decreased radically.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be made based upon the experimental results:

(1) The use of chelating agents EDTA and NDDTC results in a

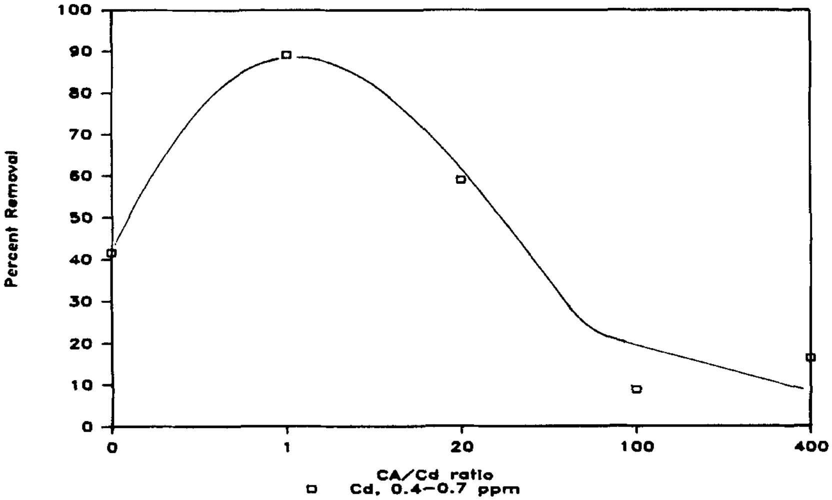

FIG. 5. Continuous study of Cd removal. Surfactant concentration: 100 ppm.

strong metal ion chelate that is fairly soluble. These complexes are not very hydrophobic and result in little surface adsorption and consequently little foam separation. For this reason, the chelating agents sodium ethylenediaminetetraacetate and sodium diethyldithiocarbamate are not good choices for the foam separation of metals.

(2) The use of citric acid as a chelating agent results in a weak metal ion chelate. The low value of the stability constant allows the formation of stronger complexes with the surface-active agent SDS. Consequently, citric acid is also not a good choice for the foam separation of metals.

(3) The surface-active agent SDS forms a complex with metal ions that can result in high removals of the ions from solution at low concentrations of the surfactant and metal ions.

(4) Foam separation is an efficient process for removing relatively low concentrations of metal ions, below about 10–20 ppm cadmium, lead, and zinc, provided that there is sufficient metal ion to form a complex, above about 2 ppm. Recommendations for further work include the determination of the stability constant for the surface-active agent SDS and the metal ion, determination of the surface concentration from surface tension measurements as a function of metal ion concentration at a series of surfactant concentrations, determination of the stability constant and surface concentration as a function of pH in order to determine the possibility of recycling the surfactant in a process, evaluation of the operating parameters of gas flow rate, liquid flow rate, bubble size, pool depth, and foam column height upon the removal efficiencies.

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