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Removal of Heavy Metals from a Chelated Solution with Electrolytic Foam Separation

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ABSTRACT

An experimental study was conducted on the chelation and electrolytic foam separation of trace amounts of copper, nickel, zinc, and cadmium from a synthetic chelated metal wastewater. Sodium ethylenediaminetetraacetate (EDTA), citrate, sodium diethyldithiocarbamate (NDDTC), and potassium ethyl xanthate (KEtX) were used with sodium dodecylsulfate (NaDS) as a foam-producing agent. Experimental results from an electrolytic foam separation process showed that chelating agents NDDTC and KEtX, due to their higher chelating strength and hydrophobic property, can efficiently separate Cu and Ni from chelated compounds (Cu, Ni/EDTA, and Cu, Ni/citrate). In a Cu–EDTA–NDDTC system with a chelating agent/metal ratio of 4, the residual Cu(II) concentration is 0.7 mg/L. The effects of chelating agent types and different chelating agents concentrations on the removal of metal ions were studied. The effect of NaDS dosage on flotation behavior and the efficiency of metal removal were also investigated.

INTRODUCTION

Industrial wastewater generated in the metal finishing and electroplating industries typically contains toxic heavy metals (Cu, Cd, Ni, Zn, etc.). Since continuing discharge of such metals into receiving water may result in a pollution problem, their removal from wastewater is essential to environmental protection. Numerous techniques have been studied and developed to remove metal ions from aqueous solutions (1, 2). The most com-

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mon method is chemical precipitation (typically by hydroxide, carbonate, or sulfide compounds), but this often produces troublesome amounts of bulky sludge. Other available techniques include ion exchange, reverse osmosis, and adsorption on activated carbon, but these methods are usually relatively expensive.

Depending on the origin of metal-contaminated wastewater, chelating agents such as EDTA, citrate, NTA, and tartrate may also be present. The presence of chelating agents severely inhibits the removal of heavy metals by conventional precipitation techniques (3). Several approaches have been proposed by previous workers to remove metal complexes from a solution (4–7). Peters and Ku (5) studied the effect of various chelating agents (EDTA, citrate, tartrate, etc.) on the removal of heavy metals (Cu, Ni, Zn, and Cd) by sulfide precipitation. Their results showed that EDTA formed very strong metal chelates which interfered with the precipitation of zinc sulfide; on the other hand, weaker chelating agents such as citrate and tartrate formed weak metal chelates which did not significantly inhibit precipitation of the metal sulfide. Wing et al. (6) and Spearot et al. (4) conducted extensive studies on the treatment of copper in the presence of EDTA with ferrous sulfate and calcium sulfate, and Argumagan (7) investigated the effects of EDTA on the removal of nickel with Fe(III). However, most of the methods proposed to deal with heavy metals in the presence of chelating agents require increased treatment time and also generate hazardous sludge which requires disposal.

Foam separation techniques have attracted considerable interest in recent years as a potential means of removing toxic heavy metals from industrial effluents (8–11). When dealing with dilute wastewater, foam separation has several advantages, including rapid operation, low space requirements, and low cost. Foam separation techniques are based on the fact that a surface-active material tends to concentrate at the gas–liquid interface of foam or of bubbles rising through a liquid pool. There are many kinds of methods which generate suitably small bubbles (12, 13). A very promising method, which improves the probability of fine particle collision during the foam separation process, is electroflotation. During electrolysis, fine bubbles of oxygen and hydrogen are produced at the anode and cathode, respectively, and carry the metal surfactant complex to the surface of the liquid. The advantages of an electroflotation cell are its high degree of gas saturation and the dimensional uniformity of generated bubbles, factors which lead to high metal removal in a short time span.

A recently studied alternative for the removal of metals from wastewater involves the use of thio compounds as chelating agents to form complexes with metal ions in solution, and the subsequent separation of the complexes from the bulk liquid by foaming (13–16). Various thio-chelating agents such as NDDTC (sodium diethyl dithiocarbamate), *O*-alkyl dithiocarbonate (usually termed xanthate), and dodecyl dithiocarbamic acid have been applied with the foam separation method (12, 14, 15); the results have shown that these thio-chelating agents are efficient in removing metals from a solution. However, few investigators have studied the effectiveness of thio-chelating agents in relation to the removal of metal complexes. How such agents will be affected by a wastewater stream already containing other chelating agents such EDTA or citrate is therefore a topic of vital interest.

This study investigates the metal-removing efficiency of the thio-chelating agents NDDTC and KEtX (potassium ethyl xanthate) on a metal-chelated solution in an electrolytic foam separation process. The competitive behavior between metals and multiple chelating agents during the electrolytic foam separation process and the effect of such variables as the type of chelating agent, the chelating agent dosage, and the metal ion types are also discussed.

EXPERIMENTAL

Reagents and Samples

In this study, chelated metal solutions were simulated with analytical reagent-grade chemicals. The metal compounds $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, and $CdSO_4 \cdot 8H_2O$ were selected for study with the following chelating agents: EDTA, citrate, potassium ethyl xanthate (KEtX), and sodium diethyl dithiocarbamate (NDDTC). Sodium dodecyl sulfate (NaDS) was applied as a frother and Na_2SO_4 was used as a supporting electrolyte.

Apparatus

A schematic diagram of the electrolytic foam separation apparatus employed in this study is shown in Fig. 1. The flotation cell consisted of a cylindrical Pyrex glass tube 370 mm in height, with an inner diameter of 30 mm, and with two circular electrodes arranged vertically in the bottom. The total volume of the solution in the foam separation column was 290 mL. The cathode was made of a stainless steel wire, and the anode was a DSA (dimensionally stable anode) wire. The total surface area of each electrode was 42 cm^2.

Procedure

Prior to electrolytic foam separation, a metal solution containing 10^{-3} M of the selected metal (Cu, Ni, Zn, and Cd) was mixed with a stoichiometric equivalent solution of chelating agent (EDTA, citrate, KEtX, or NDDTC

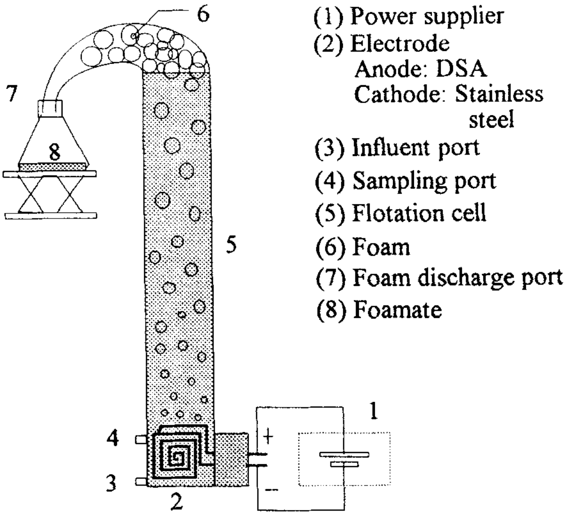

FIG. 1 A schematic diagram of the electrolytic foam separation apparatus.

solution) in a series of separate tests, and then it was placed into the electrolytic flotation cell. For electrolytic foam separation, NaDS was added as a frother; during separation, the electrical conductivity was maintained at 8000 μmhos/cm, and the pH of the solution was adjusted to 4.0 using a 0.1 M sulfuric acid solution. The chelated metal solution was continuously stirred with a magnetic stirrer in order to avoid settling of materials. During the electrolytic foam separation experiment, bubbles of oxygen and hydrogen were generated at the anode and cathode under a current density of 2.4 A/dm^2. Samples of about 10 mL were withdrawn from the sampling outlet of the column at selected time intervals, and the residual concentrations of metal ions were analyzed after acidification with a few drops of concentrated nitric acid with a Perkins-Elmer 5100 atomic absorption spectrophotometer. The arithmetic mean bubble size was determined by a Marvern 2600 laser particle-size analyser.

An additional experiment was designed to investigate the solubility of the complexes, metal–NDDTC, and metal–KEtX. The concentration of each metal ion (Cu, Ni, Zn, and Cd) was 10^{-3} M. These four metal ions were mixed together and then an equivalent amount of one of the two chelating agents, NDDTC and KEtX, was added to the metal solution in two separate tests. The total volume of 100 mL was magnetically stirred. The entire solution was filtered by vacuum pump through a 0.45-μm membrane filter. The metal contents of both the filtered residue, following digestion with nitric acid, and filtrate were analyzed by an atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Metal Removal from a Chelated Solution

In this experiment, the capability of the electrolytic foam separation process to remove metals from a chelated solution was investigated. Residual metal concentration and efficiency of metal removal by solutions of the various chelating agents (EDTA, citrate, KEtX, and NDDTC) are shown for Cu(II) and Ni(II) in Figs. 2 and 3, respectively. As shown in Fig. 2, Cu(II) is more efficiently removed by the chelating agents NDDTC and KEtX than by EDTA and citrate during electrolytic foam separation, especially in the initial period. The efficiency of Cu(II) removal by the four chelating agents after 30 minutes of flotation is approximately NDDTC (85%) > KEtX (81%) > citrate (26%) > EDTA (14%). Figure 3

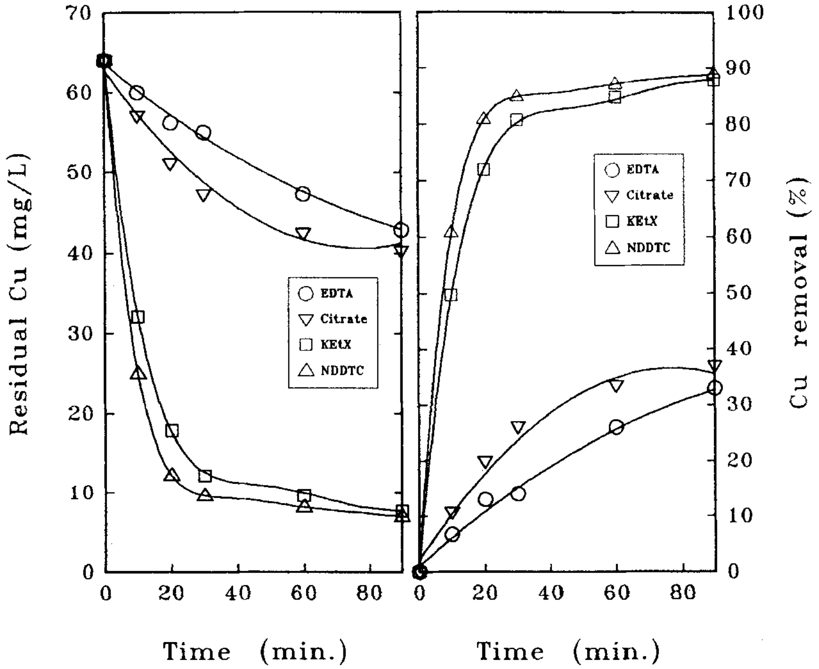

FIG. 2 The effect of chelating agents on Cu removal during the electrolytic foam separation process. [Cu(II)] = 10^{-3} M (64 mg/L). [Citrate] = [KEtX] = [NDDTC] = 2 × 10^{-3} M. [EDTA] = 10^{-3} M. Equivalent C/M ratio is 1.0. [NaDS] = 10^{-3} M. pH 4.

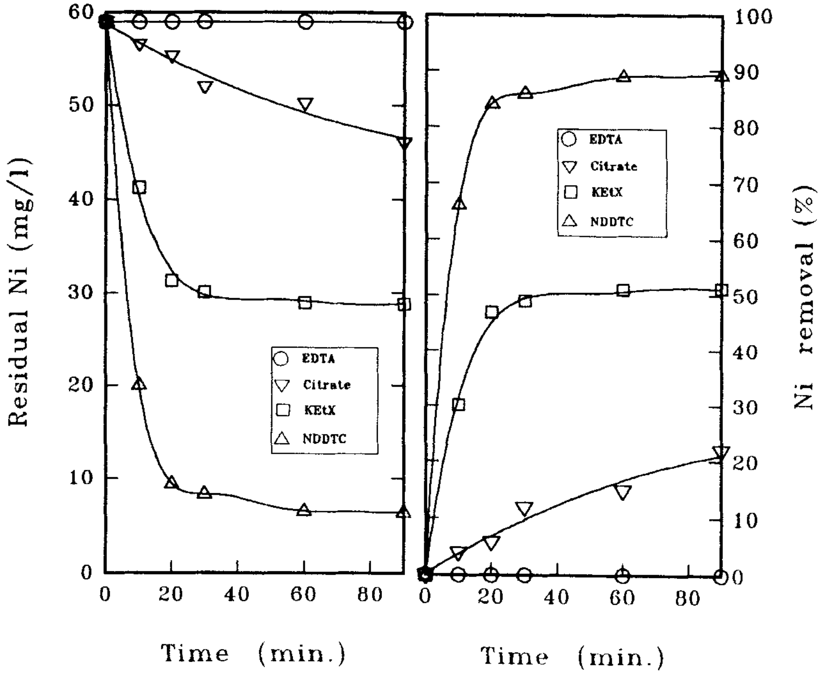

FIG. 3 The effect of chelating agents on Ni removal during the electrolytic foam separation process. [Ni(II)] = 10^{-3} M (64 mg/L). [Citrate] = [KEtX] = [NDDTC] = 2 × 10^{-3} M. [EDTA] = 10^{-3} M. Equivalent C/M ratio is 1.0. [NaDS] = 10^{-3} M. pH 4.

shows a similar pattern for the four chelating agents acting on the Ni(II) solution, except that Ni(II) could not be removed from an EDTA–Ni(II) chelated solution by the electrolytic foam separation process. Table 1 summarizes the efficiency of metal removal and the residual concentrations of Cu(II), Ni(II), Zn(II), and Cd(II) with the different chelating agents EDTA, citrate, KEtX, and NDDTC after 30 minutes of flotation. As seen in Table 1, the relative efficiency of the various chelating agents is the same for all four metals, namely, NDDTC > KEtX > citrate > EDTA. The chelating agents NDDTC and KEtX form relatively strong complexes with metal ions by means of their thio groups and most of these complexes are generally hydrophobic, migrating quickly to and concentrating at the gas–liquid interface (15, 17). EDTA forms strongly bound complexes with metal ions by means of amino groups, while citrate forms soluble, weakly bound complexes with metal ions, presumably by means of its hydroxyl groups (14). In addition, the metal–NDDTC and metal–KEtX complexes formed hydrophobic floc, while the metal–EDTA and metal–citrate com-

TABLE 1
The Effect of Various Chelating Agents on Concentration of Metal in Residue and Percent of Metal Removed Following Electrolytic Foam Separation Process[a]

Metal	Initial conc. (mg/L)	Chelating agent	Residue (mg/L)	Removal (%)
Cu	64	EDTA	55.0	14.1
		Citrate	47.2	26.3
		KEtX	12.2	81.0
		NDDTC	9.6	85.0
		NaDS[b]	39.0	39.0
Ni	59	EDTA	59.0	0.0
		Citrate	50.2	15.0
		KEtX	30.1	49.0
		NDDTC	8.8	85.1
		NaDS[b]	49.0	17.0
Zn	65	EDTA	65.0	0.0
		Citrate	36.4	44.0
		KEtX	20.2	69.0
		NDDTC	13.5	79.2
		NaDS[b]	31.9	51.0
Cd	112	EDTA	96.3	13.1
		Citrate	94.1	16.0
		KEtX	26.9	76.0
		NDDTC	20.2	82.0
		NaDS[b]	93.0	17.0

[a] [Metal] = 10^{-3} M. [Citrate] = [KEtX] = [NDDTC] = 2×10^{-3} M. [EDTA] = 10^{-3} M. Equivalent C/M ratio = 1.0. [NaDS] = 10^{-3} M. pH 4. Flotation duration time = 30 minutes.

[b] NaDS only.

plexes did not. For this reason, the chelating agents NDDTC and KEtX were more efficient at metal removal than EDTA and citrate. Because the stability constant of the metal–citrate chelate is lower than that of metal–EDTA (18), the citrate solution allows NaDS to form complexes with the metal ions, thus raising the overall metal removal efficiency well above that of the EDTA solution. Although NaDS was used as a foam-producing agent in the experiment, it also acted as a chelating agent; in background trials, NaDS by itself also exhibited some capability to remove metals (see Table 1).

The efficiency of metal removal by NDDTC and KEtX during selective foam separation relative to the different metallic species can also be inferred from Table 1. For the chelating agent NDDTC, the efficiency in removing the different metals was found to have the following order: Cu(II) = Ni(II) > Cd(II) > Zn(II); for KEtX, the order was Cu(II) > Cd(II) > Zn(II) > Ni(II). Figures 4 and 5 show the results of the simple experiments carried out to compare the solubility of the complexes metal–NDDTC and metal–KEtX in an attempt to explain the order of removal efficiencies for the different metals, as described above. When KEtX was added to the metals solution to form a solution with a ratio of chelating agent to metal (C/M ratio) of 0.5, the metal–KEtX complex showing the highest molar fraction in the residue (following passage through a 0.45-μm membrane filter) was Cu–KEtX followed by Cd–KEtX, Zn–KEtX, and Ni–KEtX (Fig. 4). When the C/M ratio was increased to 1.0, it was found that Ni–KEtX advanced to third place and Zn–KEtX was last. This means that the chelating stability constant for the metal–KEtX complexes has the order Cu(II) > Cd(II) > Ni(II) > Zn(II). Similarly, as shown in Fig. 5, the order of chelating stability constant for the metal–NDDTC complexes is Cu(II) > Ni(II) > Cd(II) > Zn(II). The same results have been described in a review by Leja (17). As Table 1 shows, there is generally a good relationship between the chelating stability constant and the efficiency of metal removal during

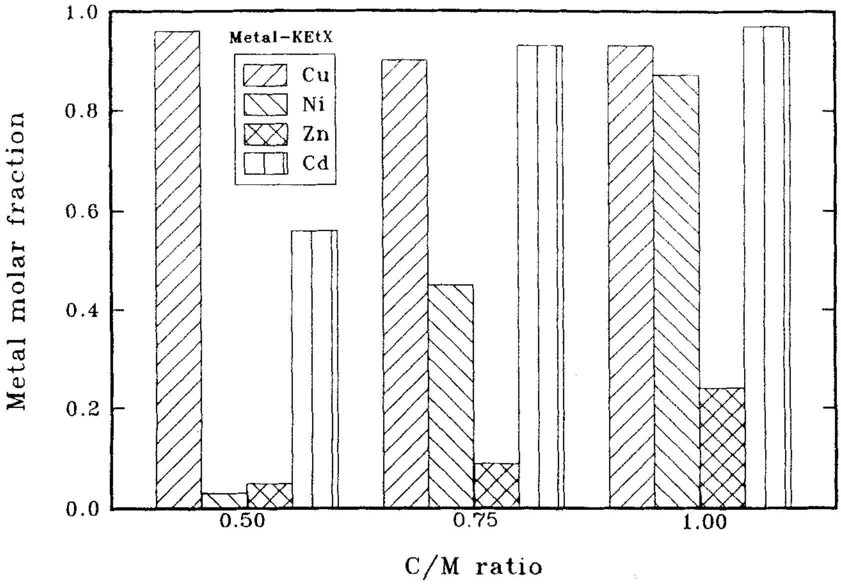

FIG. 4 The effect of C/M ratio on the molar fraction of metal in filtered residue from a metal-KEtX chelated solution. $[Cu(II)] = [Ni(II)] = [Zn(II)] = [Cd(II)] = 10^{-3}$ M. [KEtX] $= 4 \times 10^{-3}$ M, 6×10^{-3} M, 8×10^{-3} M.

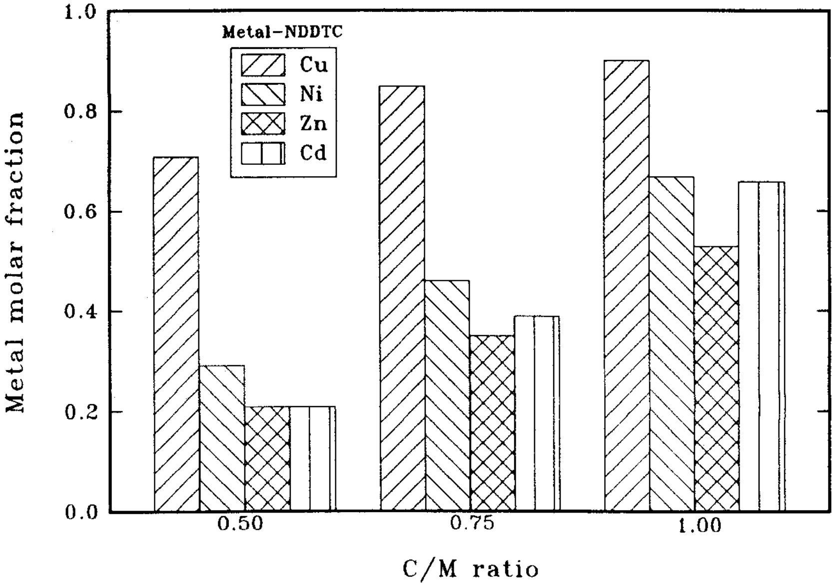

FIG. 5 The effect of C/M ratio on the molar fraction of metal in filtered residue from a metal-NDDTC chelated solution. [Cu(II)] = [Ni(II)] = [Zn(II)] = [Cd(II)] = 10^{-3} M. [NDDTC] = 4×10^{-3} M, 6×10^{-3} M, 8×10^{-3} M.

selective foam separation, except for the Zn–KEtX system. As seen in Table 1, NaDS is much more efficient in removing Zn(II) (with a removal efficiency of 51%) than in removing the other metals (efficiency less than 39%). The low stability constant of the Zn–KEtX complex allows the formation of the Zn–NaDS complex, and both these complexes can then be removed much more efficiently than the Ni–KEtX complexes.

Metal Removal in Multiple Chelating Agents System

The preceding experimental results indicate that low metal removal efficiency by electrolytic foam separation in metal–EDTA and metal–citrate systems is due to the solubility of the complexes formed by EDTA and citrate with metal ions. However, NDDTC and KEtX exhibit more efficient metal removal because of their high chelating strength and hydrophobic property. In actual experience, chelating agents EDTA and citrate are often found dissolved in the wastewaters from electroplating plants and form stable complexes with heavy metal ions which severely inhibit the removal of heavy metal ions by conventional precipitation techniques. Therefore, this experiment was designed to test the feasibility of using the chelating agents NDDTC and KEtX to separate heavy metal ions from solutions containing either EDTA or citrate by a competitive displacement mechanism.

As seen by the low residual copper concentration after 90 minutes of flotation (Fig. 6), the chelating agents NDDTC and KEtX are capable of efficiently separating Cu(II) from either an EDTA- or a citrate-chelated solution. It can also be seen that after 90 minutes flotation the order of Cu(II) removal is citrate–KEtX > citrate–NDDTC = EDTA–NDDTC > EDTA–KEtX. Figure 6 also shows the different trends of Cu(II) removal during flotation. The initial Cu(II) flotation efficiencies are low in the Cu–EDTA–NDDTC and Cu–citrate–NDDTC systems, and high in the Cu–EDTA–KEtX and Cu–citrate–KEtX systems. It is possible that Cu(II) removal efficiency is influenced by the proportional relationship between particle size and bubble size. NaDS concentration decreases with time in a batch system, resulting in a concurrent increase of surface tension. This condition inhibits gas bubbles from leaving the electrode inter-

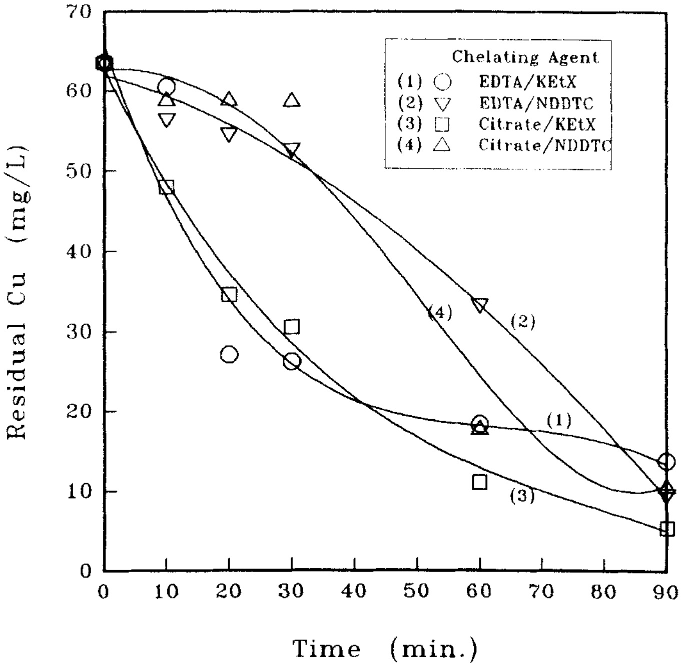

FIG. 6 The effect of multiple chelating agents on Cu removal in the electrolytic foam separation process. [Cu(II)] = 10^{-3} M (64 mg/L). [Citrate] = [KEtX] = [NDDTC] = 2 × 10^{-3} M. [EDTA] = 10^{-3} M. [NaDS] = 10^{-3} M. pH 7.

face, causing an increase in both bubble lifetime and size. Therefore, as NaDS concentration decreases, the size distribution of gas bubbles generated by electrolysis increases at the same time. According to experimental observation, the particles in Cu–EDTA–NDDTC and Cu–citrate–NDDTC systems are larger and appear denser than those in the Cu–EDTA–KEtX and Cu–citrate–KEtX systems. The average gas bubble size at the initiation of flotation, after 30 minutes of flotation, and after 60 minutes was measured to be 40, 60, and 78 μm, respectively. As shown in Fig. 6, the metal removal rate in the KEtX systems, which have a small particle size, is higher during the initial period of flotation when the average bubble size is small (40 μm), while the NDDTC systems, which are characterized by a larger particle size, are more effective in metal removal during the later phase of flotation when the bubble size is larger (78 μm). These results are consistent with the reports of Matis (11) and Yoon (19). They demonstrate that the probability and selectivity of flotation depend on the proportion of particle size to bubble size.

Figure 7 shows the different trends observed for Ni(II) removal during flotation. Ni(II) flotation efficiencies for the Ni–EDTA–KEtX and Ni–citrate–KEtX systems are very low, and are higher in the Ni–EDTA–NDDTC and Ni–citrate–NDDTC systems. It appears that complexes in the Ni–EDTA–KEtX and Ni–citrate–KEtX systems have lower stability constants and less hydrophobic properties than complexes in the Ni–EDTA–NDDTC and Ni–citrate–NDDTC systems. Furthermore, Ni(II) is more efficiently removed in the Ni–citrate–NDDTC system than in the Ni–EDTA–NDDTC system. Because the chelating constant of Ni–EDTA is greater than that of Ni–citrate, the chelating agent NDDTC can efficiently cause competitive displacement in the Ni–citrate–NDDTC system. The flotation trends in the Ni–citrate–NDDTC system are similar to those for the Cu–EDTA–NDDTC and Cu–citrate–NDDTC systems described in the discussion of Fig. 6.

Effect of Dosage on the Foam Separation Process

In the previously described experiments, the addition of a stoichiometrically equivalent amount of the chelating agents NDDTC and KEtX (with a resulting C/M ratio of 1:1) was insufficient to reduce residual metals concentration to meet effluent standards. The use of an excess stoichiometric dosage of chelating agent was therefore expected to further improve the flotation results. The following series of experiments was performed to study the effect of dosage on the removal of metals from chelated solutions by electrolytic foam separation.

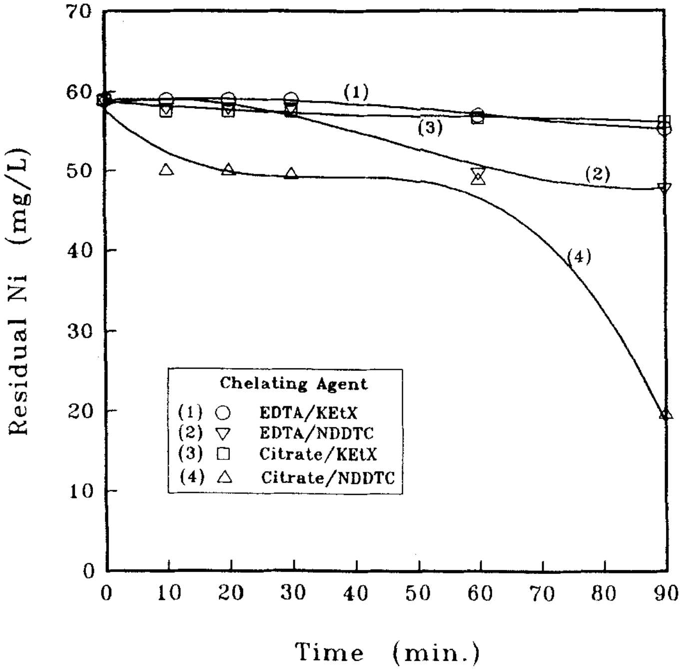

FIG. 7 The effect of multiple chelating agent on Ni removal in the electrolytic foam separation process. [Ni(II)] = 10^{-3} M (59 mg/L). [Citrate] = [KEtX] = [NDDTC] = 2×10^{-3} M. [EDTA] = 10^{-3} M. [NaDS] = 10^{-3} M. pH 7.

Single Chelating Agent System

The effects of different dosages of the chelating agents NDDTC and KEtX on metal removal by electrolytic foam separation were studied for Cu(II), Ni(II), Zn(II), and Cd(II), first by doubling the C/M ratio from 1 to 2. As Table 2 reveals, the efficiency of metal removal following 30 minutes of flotation increased with the C/M ratio doubled. For example, in the Ni–KEtX system, when the C/M ratio was 1, the residual Ni(II) concentration after 30 minutes of flotation was 30.1 mg/L, but when the C/M ratio was increased to 2, the residual Ni(II) concentration decreased to 13.1 mg/L. In other words, the use of a 100% excess dosage of KEtX may improve the flotation results for the removal of Cu(II), Ni(II), Zn(II), and Cd(II). Further experiments for a number of C/M ratios were then carried out to more thoroughly investigate the effect of dosage of the chelating agent on the foam separation process. As Fig. 8 shows, the effects are very similar in the Cu–KEtX and the Cu–NDDTC systems. It is also seen that some increase of copper removal in the

TABLE 2
The Effect of KEtX on Residue Concentration of Metal in Residue and Percent of Metal Removed Following Electrolytic Foam Separation Process[a]

Metal	Initial concentration (mg/l)	Chelating agent	C/M ratio	Residue (mg/L)	Removal (%)
Cu	64	KEtX	1	12.2	81.0
			2	5.8	91.0
Ni	59	KEtX	1	30.1	49.0
			2	13.1	78.0
Zn	65	KEtX	1	20.2	69.0
			2	10.4	84.0
Cd	112	KEtX	1	26.9	76.0
			2	7.8	93.0

[a] [Metal] = 10^{-3} M. [KEtX] = 2×10^{-3} M, 4×10^{-3} M. C/M = chelating agent (KEtX)/metal equivalent ratio. [NaDS] = 10^{-3} M. pH 4. Flotation duration time = 30 minutes.

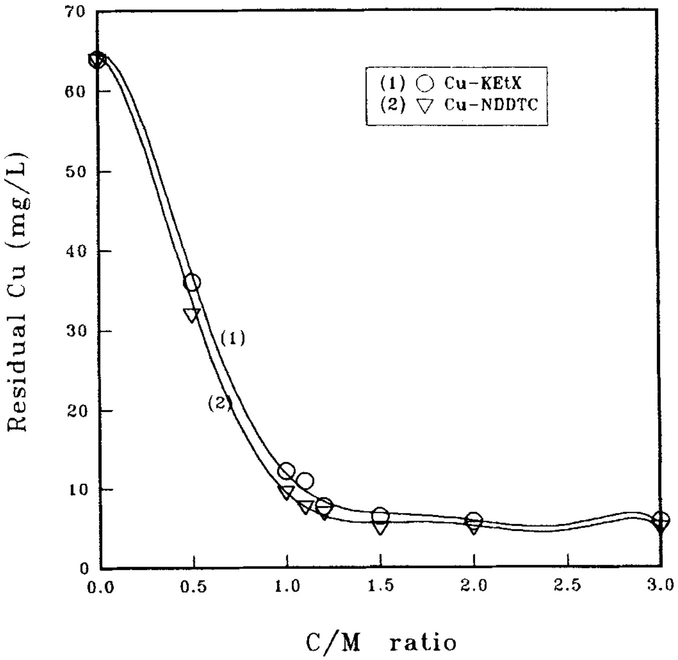

FIG. 8 The effect of dosage of chelating agents on Cu removal in electrolytic foam separation process. [Cu(II)] = 10^{-3} M (64 mg/L). C/M = Chelating agent (KEtX or NDDTC) / Metal (Cu). [NaDS] = 10^{-3} M. pH 4.

Cu–KEtX(NDDTC) system occurs when the C/M ratio is increased above 1.0, but additional increases above 1.5 result in little change in the residual Cu(II) concentration. Stalidis et al. (15) reported that the use of a 10% excess of xanthate improves the efficiency of copper recovery. The results indicate that there is some excess dosage of chelating agent at which optimum metal removal is achieved (C/M ratio = 1.2), above which little improvement occurs.

Multiple Chelating Agents System

In order to anticipate how chelating agents would operate in wastewater already containing EDTA or citrate, it is also necessary to study the effect of dosages of chelating agents in a multiple agent system. Thus experiments were carried out to investigate the effect of dosage of the chelating agents KEtX and NDDTC on the removal of Cu(II) and Ni(II) in the Cu(Ni)–EDTA and Cu(Ni)–citrate systems by electrolytic foam separation. As Table 3 shows, even when the C/M ratio is increased to 4, the

TABLE 3

The Effect of Multiple Chelating Agents on Concentration of Metal in Residue and Percent of Metal Removed Following Electrolytic Foam Separation Process[a]

		Cu		Ni	
Chelating agent	C/M ratio	Residue (mg/L)	Removal (%)	Residue (mg/L)	Removal (%)
KEtX/EDTA	1	13.8	78.3	55.2	6.4
	2	5.5	91.3	53.1	10.0
	4	33.0	48.0	53.7	9.0
KEtX/citrate	1	5.4	91.5	56.1	4.9
	2	13.6	78.6	53.7	9.0
	4	10.2	83.4	40.1	32.0
NDDTC/EDTA	1	9.5	85.0	47.7	19.2
	2	1.3	98.0	20.7	64.9
	4	0.7	98.8	41.3	30.0
NDDTC/citrate	1	10.5	83.5	19.6	66.8
	2	0.6	99.1	1.2	98.0
	4	13.3	79.1	2.4	95.9

[a] [Cu(II)] = 10^{-3} M (64 mg/L). [Ni(II)] = 10^{-3} M (59 mg/L). C/M = chelating agent (NDDTC and KEtX)/metal equivalent ratio. [NaDS] = 10^{-3} M. pH 7. Flotation duration time = 90 minutes.

efficiency of Ni(II) removal still remains very low in the Ni–EDTA-(citrate)–KEtX and Ni–EDTA–NDDTC systems. This is because competitive replacement by the chelating agents KEtX and NDDTC cannot proceed in these systems due to the fact that the difference between the chelating strengths of Ni–KEtX and Ni–EDTA(citrate) is not large enough [p*K* of 12.5 for KEtX complex with nickel (17); p*K* 18.6 and 3.3 for EDTA and citrate complexes with nickel (18)]. However, increasing the C/M ratio dose, in general, results in efficient metal removal in the Cu–EDTA-(citrate)–KEtX(NDDTC) and Ni–citrate–NDDTC systems. For example, in the Cu–EDTA–NDDTC system with a C/M ratio of 1, the residual Cu concentration is 9.5 mg/L; when the C/M ratio is increased to 4, the residual Cu concentration drops to 0.7 mg/L. In the Ni–citrate–NDDTC system, it also appears that the residual Ni(II) concentration can be decreased to 1.2–2.4 mg/L by increasing the C/M ratio. However, it is also evident in Table 3 that Cu(II) removal efficiencies decrease in the Cu–EDTA-(citrate)–KEtX(NDDTC) system when they are treated with an overdose of the chelating agents NDDTC and KEtX. In Cu–EDTA–KEtX systems, residual Cu(II) concentrations are 13.8, 5.5, and 33.0 mg/L with C/M ratios of 1, 2, and 4, respectively. From these results we may conclude that it is possible to overdose a system with a Cu-adsorbable species (chelating agents such as NDDTC or KEtX) and cause restabilization as a result of a reversal of charge on the colloidal particle. In some systems of multiple chelating agents, there exits an optimum dosage of chelating agent which must be applied in order to obtain the most efficient metal removal.

The Effects of NaDS Dosage

As the results shown in Fig. 6 indicate, the probability and selectivity of flotation probably depend on the proportion between particle size and bubble size and, in turn, the size distribution of gas bubbles generated by electrolysis depends on surface tension and NaDS concentration. In order to evaluate the reproducibility of the results shown in Fig. 6, a confirmation experiment was performed. The results, shown in Fig. 9, indicate that at three dosage levels of NaDS (288, 144, and 96 mg/L) in a Cu–citrate–NDDTC system, there are three distinct trends for Cu(II) removal. At a dose of 96 mg/L of NaDS, the Cu(II) removal trend in the initial 10 minutes of flotation is much steeper than for NaDS = 144 or 288 mg/L. The average bubble size at the onset of the experiment was 40 μm for NaDS = 288 mg/L, 61 μm for NaDS = 144 mg/L, and 80 μm for NaDS = 96 mg/L. The residual Cu(II) concentrations were 13.8, 6.7, and 0.2 mg/L, respectively. These results clearly show that NaDS dosage (or surface tension) affects flotation behavior and its efficiency.

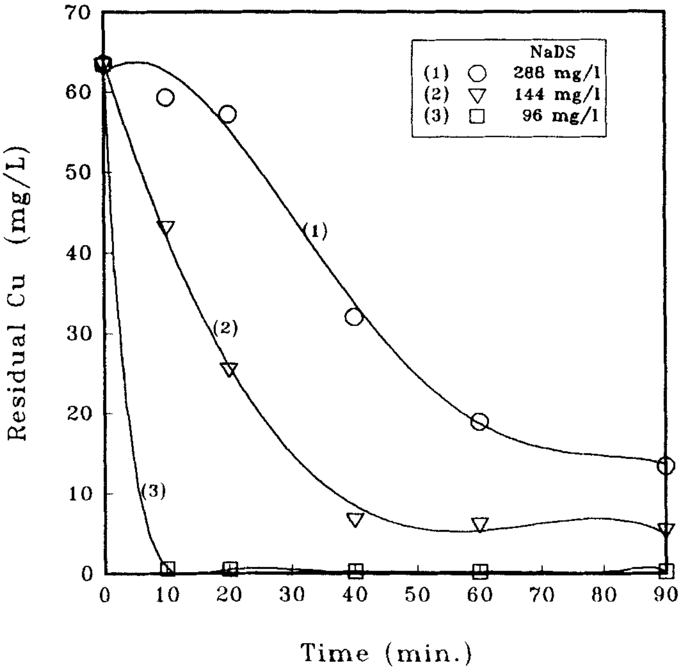

FIG. 9 The effect of NaDS dosage on Cu removal in the citrate–NDDTC system by the electrolytic foam separation process. [Cu(II)] = 10^{-3} M (64 mg/L). [Citrate] = [NDDTC] = 2×10^{-3} M. pH 7.

CONCLUSIONS

Based upon the experimental results, the following conclusions can be made.

(1) The chelating agents NDDTC and KEtX efficiently separate metals (Cu, Ni) from metals chelated solutions (Cu/Ni–EDTA/citrate). These agents succeed in competitive displacement of heavy metal ions because of their higher chelating ability and their hydrophobic property. Thus, NDDTC and KEtX appear to have potential in the separation of wastewater containing contaminants from the electroplating industry, such as EDTA and citrate.

(2) It is important to determine the optimum dosage of the chelating agents NDDTC and KEtX because an overdose of chelating agents may actually decrease the efficiency of metal removal in some systems [Cu–EDTA(citrate)–KEtX(NDDTC)].

(3) NaDS dosage affects flotation behavior and its efficiency. This is because the surface tension of the solution is dependent on the concentration of NaDS.

(4) Except for the Zn–KEtX system, there is a good relationship between the chelating stability constant and the efficiency of metal removal during selective foam separation. The behavior of the Zn–KEtX system may be explained by the fact that NaDS also act as a chelating agent which involves and improves the overall Zn(II) removal efficiency. For the chelating agent NDDTC, the order of metal removal efficiency is found to be Cu(II) = Ni(II) > Cd(II) > Zn(II), and for the chelating agent KEtX, the order of metal removal efficiency is Cu(II) > Cd(II) > Zn(II) > Ni(II).

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