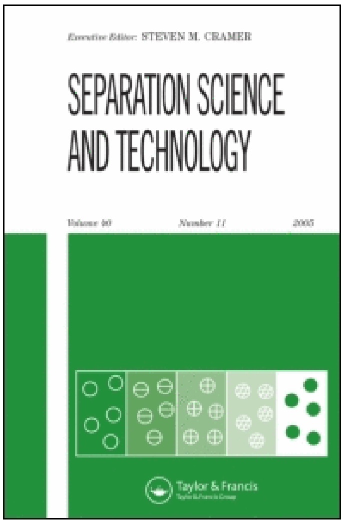

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Electroflotation Studies on Cu, Ni, Zn, and Cd with Ammonium Dodecyl Dithiocarbamate

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NOTE

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Abstract

The concentration of Cu, Ni, Zn, and Cd ions by electroflotation using the ammonium salt of dodecyl dithiocarbamic acid as an anionic collector is examined. Quantitative studies reveal better separation efficiency by this method as compared to column flotation using dodecyl dithiocarbamic acid ligand as a chelating surfactant.

INTRODUCTION

Foam separation techniques have proven useful for separating many materials, particularly when their bulk concentration is very small (*1*). The main advantage of flotation techniques is the medium, water, which is a universal solvent in wet analysis and commercial operations (*2*).

The use of precipitating and chelating agents such as xanthates (*3*), phosphate (*4*), oximes (*5*), and dimethyl dithiocarbamate (*6*) has been reported. Diethyl dithiocarbamate was used as an anionic collector to separate metal ions like Cu, Ni, Zn, and Mn from deep seawater samples by adsorbing colloid flotation (*5*), and dodecyl dithiocarbamate has been employed for the recovery of copper by precipitate flotation (*4*). The use of a collector like dodecyl dithiocarbamate, with its long hydrocarbon chain, is advantageous because of its ability to function as a chelating agent as well as a surfactant.

In order to exploit the usefulness of such collectors, the present investigation was carried out to study the electroflotation behavior of metal ions such as Cu, Ni, Zn, and Cd, using dodecyl dithiocarbamic acid ligand as the chelating surfactant.

EXPERIMENTAL

Reagents and Solutions

Analytical reagent-grade sulfate salts of copper, nickel, zinc, and cadmium were used to prepare stock solutions (1 mg/mL). Dodecyl amine (Fluka), carbon disulfide (AR), ammonia, EDTA (AR), sodium sulfate (AR), ethanol (AR), and acetone (AR) were also used in the study.

Dithiocarbamate

Ammonium dodecyl dithiocarbamate was prepared as reported earlier (*7*). To an ethanolic solution of amine, an ethanolic solution of carbon disulfide and ammonia was added dropwise with constant stirring. The white product formed was washed with ether and recrystallized from chloroform.

Apparatus

The flotation cell employed for the present study was based on Elmore's model (*8*). The cell consisted of a cylindrical glass tank of 1-L capacity with two circular gauze electrodes arranged horizontally (10 cm diameter, 100 mesh size, and 0.5 mm thickness). The upper electrode (cathode) was made of stainless steel, and the lower electrode (anode) was made of copper coated with nickel. The electrodes were placed at a distance of about 1 cm from each other and were separated by a PVC ring, and positioned 1 cm above from the bottom of the cell. Both the electrodes were soldered to 3 × 20 copper wires and connected to the dc supply. During electrolysis, fine bubbles of oxygen and hydrogen were produced at the anode and cathode, respectively, which carried the precipitated metal surfactant complex to the surface of the liquid.

Procedure

The metal ion solution containing 5–20 mg of the desired metal was placed in the flotation cell and diluted with water to about 600 mL. The total electrolyte concentration was maintained at 0.001 *M* with respect to sodium sulfate by adding 6 mL of 0.1 *M* sodium sulfate. The pH of the solution was adjusted to the appropriate value (pH 3–7) with dilute sodium hydroxide or sulfuric acid with the aid of a pH meter. The solution was continuously stirred using a magnetic stirrer in order to avoid settling of materials which would interrupt the free flow of gas bubbles from the electrodes to the surface. About 5 to 10 mL of freshly prepared 0.1 *M* ammonium dodecyl dithiocarbamate (ligand excess) in ethanol was injected into the flotation cell.

The electrolysis was carried out by maintaining a current density of 2.5 A/cm^2 and 12.5 V for a fixed length of time, 3 to 5 min. The floated material was separated quantitatively and then decomposed by digesting it with a minimum volume of concentrated nitric acid. The metal ion in solution was estimated by EDTA (*9*).

RESULTS AND DISCUSSION

Role of the Dodecyl Dithiocarbamate Ion

Flotation processes require primarily the use of (a) a frother to form a stable froth and (b) a collector to impart hydrophobicity to the solid particles to be floated.

When dispersed in water, ammonium dodecyl dithiocarbamate, having a polar $-CSSNH_4$ group and a nonpolar hydrocarbon chain $CH_3(CH_2)_{10}CH_2NH-$, acts in the same way as any surfactant and forms a stable foam on the surface of the water. Since it contains sulfur donor atoms in its ionic head, it forms stable chelates with transition metal ions which are neutral and insoluble in water. All the metal ions under study form bis chelates with the ligand (*10*) and are precipitated.

$$CH_3(CH_2)_{10}CH_2NH{-}C{\left\langle{S^- \atop S}\right.} + M^{2+} \rightarrow \left(CH_3(CH_2)_{10}CH_2NH{-}C{\left\langle{S \atop S}\right\rangle}\right)_2 M$$

The Cd and Zn chelates are colorless, whereas Cu and Ni form brown and greenish yellow chelates, respectively. The precipitated metal chelates are transported by the electrogenerated gas bubbles to the surface of the solution, where the metal ion can be collected and concentrated. Thus the three effective functions, viz., 1) foaming, 2) chelation-cum-precipitation of the metal ions, and 3) flotation, are achieved by using this chelating surfactant.

ELECTROFLOTATION OF METAL IONS

The advantages of an electroflotation cell are its high degree of gas saturation and the dimensional uniformity of the generated bubbles; these lead to the highest recovery in a short time span. Apart from these, electroflotation also overcomes the difficulties arising from the unstable nature of the ligand under extreme conditions of high acidity (*4*). The results of the flotation of different cations as functions of pH are presented in Table 1. In the case of Cu, the recovery of metal ions was only about 85% at pH 3; this gradually rose with increasing pH and reached a maximum value of 90% at pH 7. For other ions, recoveries varied from 94 to 96% for Ni, 93 to 96% for Zn, and 95 to 97% for Cd, showing almost constant values. When compared with the earlier report (*4*), the present study showed higher recoveries of metal ions.

Table 2 indicates the recovery of metal ions at initial concentrations of 5, 10, 15, and 20 mg in a volume of 600 mL at pH 6 to 7 (the optimal range, based on the earlier study). It can be seen from the results that electroflotation with dodecyl dithiocarbamate can be effectively used to concentrate metal ions from large volumes of solutions.

The study indicates that in general the flotation of Cu, Ni, Zn, and Cd with ammonium dodecyl dithiocarbamate is not influenced by pH in the range 3 to 7. This is because, in general, metal dithiocarbamate complexes are formed under neutral or slightly acidic conditions, and the reaction is not specific (*11*). The maximum recovery is as high as 95% except for Cu for which it varied from 85 to 90%. Since all the metal ions show a recovery value close to 100% without any selectivity, separation of these ions from one another is not possible by the flotation process. However, it can be employed as a preconcentration process for the total recovery of metal ions present in very high dilution. At higher pH values

TABLE 1. Effect of pH on the Recovery of Metal Ions by Electroflotation Using Ammonium Dodecyl Dithiocarbamate

Metal ion	pH	Amount in feed solution (mg)	Amount recovered (mg)	Percent recovery[a]
Cu	3	10	8.51	85.1
	4	10	8.64	86.4
	5	10	8.64	86.4
	6	10	8.77	87.7
	7	10	9.02	90.2
Ni	3	10	9.51	95.1
	4	10	9.63	96.3
	5	10	9.45	94.5
	6	10	9.54	95.4
	7	10	9.29	92.9
Zn	3	10	9.36	93.6
	4	10	9.42	94.2
	5	10	9.55	95.5
	6	10	9.42	94.2
	7	10	9.29	92.9
Cd	3	10	9.62	96.2
	4	10	9.67	96.7
	5	10	9.52	95.2
	6	10	9.57	95.7
	7	10	9.57	95.7

[a]Average of 5 to 6 determinations. Error ≈ ±1%.

TABLE 2
Recovery of Metal Ions of Various Concentrations at pH 6–7

Metal	Amount taken (mg)	Found (mg)	Percent recovery	Standard deviation[a]
Cu	5	4.54	90.8	0.32
	10	8.84	88.4	0.51
	15	13.36	89.1	0.45
	20	17.49	87.4	0.39
Ni	5	4.76	95.2	0.50
	10	9.51	95.1	0.23
	15	14.41	96.1	0.24
	20	19.14	95.7	0.50
Zn	5	4.73	94.6	0.23
	10	9.42	94.2	0.50
	15	14.36	95.7	0.62
	20	19.26	96.3	0.32
Cd	5	4.81	96.2	0.25
	10	9.57	95.7	0.43
	15	14.54	96.9	0.74
	20	19.26	96.3	0.50

[a]Average of 5 to 6 determinations.

(>8), precipitation of metal hydroxides predominates and no ion flotation is possible when using ammonium dodecyl dithiocarbamate as the collector. At lower pH values (<3), the ligand was found to be unstable and to decompose.

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