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Ion Flotation of Copper Using Ethylhexadecyldimethylammonium Bromide

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Abstract

Studies have been undertaken to determine the effect of variables such as pH, flow rate, collector: copper ratio, and chemical interferences in order to develop optimum conditions to remove copper ions from aqueous solutions by ion flotation using ethylhexadecyldimethylammonium bromide (EHDABr). Copper can be removed quantitatively from 6×10^{-5} *M* solutions containing tartrate using EHDABr over a pH range of 6 to 11. A number of foreign metallic ions supress the flotation of copper. No foreign ion studied supressed the flotation 10%.

INTRODUCTION

Adsorptive bubble separational techniques are becoming increasingly more important for separating a wide variety of substances in aqueous solutions (*1*, *2*). Generally, in these techniques the desired substance is adsorbed (often selectively) at the surface of air bubbles rising through the liquid, thereby separating it from other species in solution. Ion flotation is one of the adsorptive bubble separational techniques in which a surfactant ion of opposite charge to that to be floated serves as a collector. By bubbling a nonreactive gas (usually air) through the solution by use

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of a fine gas distributor, an extended air–solution interface is produced. The collector reacts chemically with the metal ion to produce a metal complex which adsorbs at the air–liquid interface or flocculate to form aggregates that subsequently attach to air bubbles passing through the aqueous solution.

Ion flotation foam separational techniques are currently drawing considerable attention as possible methods or processes to remove certain metal ions from aqueous solutions. Of particular concern has been the utilization of these versatile techniques for removing various toxic metal ions from polluted wastewater. Copper is one of the metals which has received research interest recently. Sebba reported that copper can be floated as a cation from aqueous and ammoniacal solutions (*3*). Koichi screened a series of collectors to ascertain their utility for floating copper (*4*). These included sodium α-sulfolaurate, sodium laurate, and dodecylsulfate. Of the ones studied, sodium α-sulfolaurate appeared to be superior. It removed 95% of the copper over a pH range of 7 to 11. Rubin reported flotation methods for the removal of copper from aqueous solutions using lauryl sulfate and stearylamine (*5*).

This paper describes a study of the removal of copper ions from aqueous solutions by ion flotation using ethylhexadecyldimethylammonium bromide (EHDABr).

EXPERIMENTAL

Apparatus

A Perkin-Elmer Model 360 atomic absorption spectrophotometer was used to analyze the solutions for copper. The accessories included a standard copper hollow cathode lamp and a Houston Instruments Model 5110 recorder. An ion-flotation apparatus was constructed consisting of an air filter assembly capable of removing particulate matter of 0.6 μm or less in the laboratory compressed air line, a Pyrex glass flotation column (3.8 × 122 cm), a medium porosity Pyrex dispersion tube, and a Roger Gilmont Flow Meter Assembly. With slight modifications, the apparatus is similar to that described by Ferguson and co-workers (*6*). A Corning Model 119 pH meter with digital display was used for pH measurements.

Reagents

EHDABr was obtained from the Eastman Kodak Co. and used without further purification. A 2.0×10^{-2} *M* stock solution was prepared by dissolving the appropriate quantity of the reagent in deionized water. Aqueous standard copper solutions (1000 ppm) for atomic spectrophotometric use were obtained from the Curtin Matheson Co., Houston, Texas. Reagent grade potassium tartrate was obtained from the J. T. Baker Co. A 2.0×10^{-2} M potassium tartrate stock solution was prepared by dissolving the appropriate quantity of the salt in deionized water. All other chemicals used were of reagent grade. Deionized water was used in preparing all the aqueous solutions.

Evaluation Procedure

A typical ion-flotation procedure involves mixing 1.0 ml of 1000 ppm copper solution with 2.0 ml of 2×10^{-2} M potassium tartrate, adjusting the solution to the desired pH with HCl or NaOH, and diluting to 250 ml with deionized water. The air flow rate is adjusted to the desired value prior to transferring the aqueous copper solution to the flotation column. The surfactant (collector) is injected into the solution to initiate the metal removal process. The copper content of the solution in the column is measured with an atomic absorption spectrophotometer after the process has proceeded the desired time span.

RESULTS

Several parameters which affect the efficiency with which copper ions are floated using EHDABr were studied by use of the evaluation procedure described in the proceding section. The efficiency of the copper removal can be expressed by

$$F = \frac{C_i - C_f}{C_i} \times 100$$

where F is the percent metal floated, C_i is the concentration of the metal before flotation, and C_f is the concentration of the metal after flotation.

A study was undertaken to determine the flotation efficiency of copper as a function of pH. The results shown in Table 1 indicate a sharp increase in flotation at a pH of about 6 with a continued gradual increase to a pH of about 11. Above 11, the flotation decreases gradually. Below 6, the flotation decreases rapidly.

Further investigation of the system indicated that the EHDABr–copper molar ratio influenced the flotation efficiency. Table 2 shows that at a pH of 6, a large EHDABr–copper ratio of 11 to 1 is necessary to remove more than 99% of the copper. Nevertheless, more than 93% removal

TABLE 1

Effect of pH on the Flotation of Copper[a]

pH	Copper removed (%)
5	35.8
6	93.7
7	96.2
8	97.5
9	98.3
10	98.9
11	99.0
12	98.8
13	98.4

[a] Cu^{2+}, 6.0 × 10^{-5} *M*; EHDABr, 2.4 × 10^{-4} *M*; flow rate, 40 ml/min; time, 60 min.

TABLE 2

Molar Ratio Studies[a]

EHDABr–Cu^{2+} ratio	Copper removed (%)
4.0	93.7
4.9	94.2
6.1	95.7
8.7	95.9
9.9	96.0
11.1	99.0
14.4	93.9
18.4	87.5

[a] pH, 6; flow rate, 40 ml/min; time, 60 min.

is achieved from molar ratios of 4 to 1 to 14 to 1. The optimum EHDABr–copper ratio was found to be a function of the pH of the solution. The results shown in Table 3 indicate that the optimum collector–copper ratio decreases as pH increases. At a pH of 6, an 11 to 1 ratio is required to remove greater than 99% of the copper from solution. At a pH of 9, the optimum ratio is decreased to 4 to 1.

A study was carried out to determine the effect of ionic strength on the flotation efficiency. Sodium chloride was used to adjust the aqueous solutions to the desired ionic strengths. The results shown in Table 4 indicate that there is an increase in flotation efficiency for ionic strengths from 1.5 × 10^{-3} to 2.2 × 10^{-3} *M*. Above 2.2 × 10^{-3} *M*, the efficiency decreases.

TABLE 3

Effect of pH on Optimum EHDABr–Cu^{2+} Ratio[a]

pH	EHDABr–Cu^{2+} ratio
6	11.1
7	6.4
8	5.1
9	4.0

[a] Flow rate, 60 ml/min; time, 60 min; >99% copper removed in all four cases.

TABLE 4

Effect of Ionic Strength on Flotation[a]

Ionic strength × 10^3 (*M*)	Copper removed (%)
1.5	96.1
1.7	96.2
1.8	96.3
1.9	96.5
2.0	97.0
2.2	97.2
2.3	97.1
2.5	96.4
2.8	94.1

[a] pH, 6; flow rate, 40 ml/min; time, 60 min; EHDABr, 2.4×10^{-4} *M*; Cu^{2+}, 6×10^{-5} *M*; tartrate, 1.6×10^{-4} *M* (NaCl used to adjust the ionic strengths).

An interference study was carried out to determine the effect which a number of metallic ions commonly found with copper in solution would have on the flotation efficiency. The results, shown in Table 5, indicate that the ions studied suppressed the removal of copper. However, there was no case in which the interference was greater than 10%. The concentrations of the interfering ions were in the same general concentration range as copper. Zinc had very little effect on the removal of copper.

DISCUSSION

The pH of the solutions appears to have the greatest effect on the flotation rate. The pH dependence is associated with its effect on the structures of the copper tartrate complexes. Beck and Cisiszar studied the composition of copper tartrate complexes as a function of pH using polarimetric and other techniques (*7*). They postulated the formation of dinuclear copper tartrate complexes with Cu–OH–Cu bridging. The nature

TABLE 5

Effect of Foreign Ions on Copper Flotation[a]

Foreign ion	Foreign ion concentration ($M \times 10^5$)	Foreign ion removed (%)	Copper removed (%)
None	—	—	>99.9
Cd^{2+}	3.2	1.7	96.2
Cr^{3+}	15.0	76.0	91.3
Pb^{2+}	2.1	42.5	95.6
Ni^{2+}	5.9	13.6	91.4
Zn^{2+}	5.9	0.3	99.7

[a] pH, 7; flow rate, 60 ml/min; time, 60 min; Cu^{2+}, 6.6×10^{-5} *M*; EHDABr, 4×10^{-4} *M*; tartrate, 3.3×10^{-4} *M*.

of this bridging varies with pH, which results in changes in the charge on the complexes. According to Beck and Cisiszar, the charge on a copper tartrate complex is zero at a pH of 5, at a pH of 9 the charge is −2, and at a pH of 12 the charge is −3. Based on these findings, different reaction mechanisms can be written depending on the pH of this solution. The inability to float a significant amount of copper at pH values below 6 can be attributed to the copper tartrate complex existing in the neutral or perhaps positively charged state.

The effect of collector concentration is also influenced by pH. It is possible to achieve a complete removal of copper at any pH between 6 and 11, providing the appropriate collector–copper molar ratio is used. It is observed that ratios larger than the optimum ratios caused a decrease in flotation. This can probably be attributed to the competition between the sublate and the collector ions for sites on the surfaces of the bubbles.

The study shows that the ion-flotation technique is very effective for removing copper ions from extremely dilute solutions using EHDABr. The interference study indicates that EHDABr floats both chromium and lead substantially from tartrate solutions. These and perhaps other collector–metal ion systems should be studied due to the simplicity of the ion-flotation techniques.

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