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Removal of Copper from Aqueous Amminecopper(II) Solution by Foam Flotation

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ABSTRACT

Copper is removed from aqueous amminecopper(II) solution by adsorbing colloid flotation. Iron(III) hydroxide is used as the adsorbing carrier floc, and an anionic surfactant sodium dodecyl sulfate is used as the collector. Optimal flotations are achieved at the pH of maximum adsorption of copper on the resultant flocs. Adsorption of copper on the flocs enhances their floatability. Rapid and efficient removal of copper can be obtained by a batch operation under controlled dosing of iron(III) for samples in various concentrations of total ammonia. A two-step batch method has the advantages of higher efficiency and lower copper residue when dealing with samples of high copper concentration (>200 ppm) and low total ammonia (<0.15 M).

INTRODUCTION

Numerous techniques exist for the removal of metal ions from aqueous solutions. These include chemical precipitation as an insoluble salt or hydroxide, ion exchange, solvent extraction, reverse osmosis, and foam flotation. In the electroplating industry, many bath solutions contain metal complexing agents (1–3) so that conventional neutralization and the formation of hydroxide precipitates is infeasible due to high solubility of the metal ions in complexed forms.

Foam flotation for the removal of metal ions from solution has been developed to achieve rapid operation and low space requirement (4–10). Wastewater containing dilute metal ions in large volume has been treated successfully on a pilot-plant scale (11–14). The flotation techniques com-

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monly employed for the removal of heavy metals are ion flotation (15–19), precipitate flotation (20–23), and adsorbing colloid flotation (24–29).

In the absence of complexing agents, metal ions in the simple hydrated form can be readily precipitated as metal hydroxides. Subsequent flotation of the precipitates, after the addition of a collector, can result in a low level of residue in the effluent (15, 23). Alternatively, the method of adsorbing colloid flotation can be used by introducing a floc to adsorb or coprecipitate the metal solutes from solution and then floating the resulting floc. Adsorbing colloid flotation has been used to attain the advantages of lower operation basicity and the need for a smaller amount of surfactant in comparison with the method of precipitate flotation (23).

The use of foam fractionation and ion flotation in the presence of complexing agents have been reported to remove a metal complex from a solution (30–34). The proper surfactant with the ionic charge opposite to that of the metal complex is added in order to bind the metal-bearing species and make it surface active. In such cases, amounts of surfactant greater than stoichiometric are required to achieve the associating reaction and to act as a frother. Other approaches to precipitate flotation and adsorbing colloid flotation to remove complexed cyanides have also been reported (35, 36), but only partial removal of metal cyanides complexes has been achieved.

Certain kinds of spent etchants in the printed circuit-board manufacturing process contain amminecopper(II) (3). The concentration of soluble copper in these basic ammonia solutions depends on the solution pH and the total ammonia concentration. The concentrations of total copper and ammonia of the original spent liquids may be as great as 100 g Cu/L and 1.3 M, respectively. Preliminary treatment for the removal of copper by the method of acid neutralization and precipitation as an insoluble hydroxide can result in a residual soluble copper concentration of 50–1400 mg/L depending on the concentration of total ammonia in the etchants. Thus, further treatment is required to reduce the copper content. In this report, experiments to test the effectiveness of removing copper from this amminecopper(II) solution by adsorbing colloid flotation using iron(III) hydroxide as the adsorbing floc and sodium dodecyl sulfate (SDS) as the collector are described. Factors which may influence the results of the flotation, such as solution pH, concentration of total ammonia, iron(III) dosage, and copper density of the floc, are examined.

EXPERIMENTAL

The foam flotation equipment used in this study was described in detail in earlier reports (37, 38). The foam flotation column was 60–90 cm in length with an inside diameter of 3.0 cm. The air flow rate was adjusted to 22.5 mL/min. An atomic-absorption spectrophotometer (Varian model AA-20) was used to determine the copper and iron content of the solution.

An iron(III) solution was prepared from iron(III) nitrate at a concentration of 11.1 g Fe/L to which concentrated sulfuric acid (40 mL) was added for each liter of stock solution. The eventual concentration of iron in the stock solution was further determined by atomic-absorption spectrometry (AAS) after appropriate dilutions. A copper(II) solution with a concentration 12.9 g Cu/L was obtained by dissolving copper(II) sulfate anhydrous in distilled water to which concentrated nitric acid (20 mL) was added for each liter of copper(II) solution. The copper content of this solution was also measured by AAS. An ammonia solution was made by dissolving ammonium chloride (40.12 g) and adding 50 mL of concentrated ammonia water (25%, 0.91 kg/L) for each 500 mL of solution. The concentration of total ammonia in this solution was 2.836 M. Amminecopper(II) solutions were made by mixing the copper(II) solution with an appropriate amount of ammonia solution. The final amminecopper(II) solutions for the test contained total copper and total ammonia in concentration ranges of 0.014–0.60 g Cu/L and 0.14–0.57 M, respectively. The solution of sodium dodecyl sulfate was prepared from the laboratory grade reagent without further purification. The total volumes of the solutions in the foam separation column were 200–500 mL.

Prior to foam separation, SDS was mixed with an appropriate amount of iron(III) solution, and the resulting solution was introduced into the amminecopper(II) solution with magnetic stirring. The pH of the sols was adjusted by adding concentrated nitric acid or NaOH (0.5 M) dropwise. Before the sols were poured into the foam separation column, 10 mL aliquots of the sols were collected with Whatman GF/F filter paper for analysis. The copper contents of the filtrates were determined in order to obtain the copper density of the floc.

During the foam flotation, samples of about 15 mL were withdrawn from the bottom of the column at intervals and analyzed for their copper and iron content by AAS after acidification with a few drops of concentrated nitric acid.

RESULTS AND DISCUSSION

The Optimal pH for Flotation

Absorbing colloid flotations in solutions of different pH values and concentrations of total ammonia of 0.14 and 0.57 M, respectively, were carried out. The results for metal residues after flotations are shown in Table 1. The correlated copper densities of the flocs are also shown. In solutions

TABLE 1
The Effect of pH on the Flotation of Copper fromAmminecopper(II) Solutions

Total ammonia (M)	pH	Residue after flotation (ppm) Copper	Residue after flotation (ppm) Iron	Copper density of carrier flocs (g Cu/g Fe)
0.14[a]	6.0	9.1	8.1	0.301
	6.5	2.8	1.1	0.346
	7.0	1.6	0.6	0.354
	7.5	1.8	0.9	0.354
	8.0	3.2	0.1	0.342
	9.0	33.5	106	0.298
0.57[b]	5.4	70	42	0.253
	5.9	58	19	0.369
	6.4	48	1.3	0.450
	6.9	58	20	0.409
	7.4	62	29	0.326

[a] Sample: Cu 51.6 ppm, total ammonia 0.14 M; dose of iron(III) 142 ppm, SDS 192 ppm; flotation duration 20 minutes.

[b] Sample: Cu 77.4 ppm, total ammonia 0.57 M; dose of iron(III) 68 ppm, SDS 96 ppm; flotation duration 20 minutes.

with 0.14 M total ammonia, an optimum at pH 7.0 is observed. A copper residue of less than 3.0 ppm was achieved in the pH range of 6.5 to 7.5 after 20 minutes of flotation. Flotation at pH 8.0 gives a somewhat greater copper residue than that at pH 7.0 due to the smaller extent of copper adsorption on the carrier flocs. At pH higher than 8.0 or lower than 6.5, incomplete removal of the floc from solution is observed. At a total ammonia concentration of 0.57 M, an optimum at pH 6.4 is observed. Incomplete removal of the resultant flocs due to a slower flotation rate at pH values other than 6.4 are seen in Fig. 1. From the effects of pH and the concentration of total ammonia on the adsorbing colloid flotation of copper with iron(III) hydroxide, as shown in Table 1, it can be concluded that the optimum pH for flotation in various concentrations of total ammonia is at the point of maximum adsorption of copper species on the resultant floc. At these pHs, the adsorption efficiency of the adsorbent is higher and thus results in a lower copper residue after removal of the floc by flotation. Furthermore, the flotation of copper at the optimum pH is accompanied by faster flotation of the resultant carrier floc. Both the extent of copper removal and the rate of removal are favorable at the pH of maximum adsorption of copper on the floc.

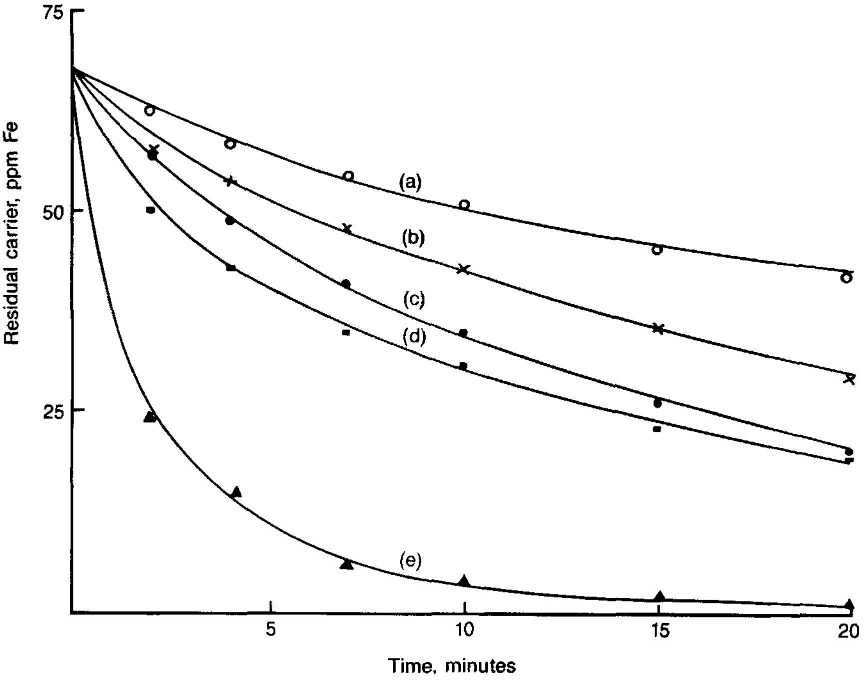

FIG. 1 Flocs removal vs flotation time from solution of total ammonia 0.57 M at pH (a) 5.4, (b) 7.4, (c) 6.9, (d) 5.9, (e) 6.4. Initial conditions: Cu 77.4 ppm, Fe 68 ppm, SDS 96 ppm.

As evidence of the influence of copper adsorption on the enhancement of floatability of the adsorbing colloid, the comparative tests in Fig. 2 show the flotation curves for sample solutions initially in the presence [Fig. 2a(Cu) and 2a(Fe)] or absence of copper ions [Fig. 2b(Fe)]. A much faster rate of floc removal is observed in solutions initially containing copper ions. Copper and its carrier floc with an adsorption density of 0.35 g Cu/g Fe were readily floated to give residual copper of 1.6 ppm and residual iron of 0.6 ppm for a run of 20 minutes, whereas the floc bearing no copper gave residual iron of 122 ppm.

At the optimum pH for the adsorption of copper (which is also the optimum pH for flotation), the floc adsorbs the copper species $Cu(NH_3)_x^{2+}$, $x = 1–3$, as found in a previous study (39). Adsorption of cationic metal species on the particle surface can increase the zeta potential of the solid (40, 41). Because of this the floatability of the resultant floc is increased when an anionic collector is used. Huang et al. (37) reported a similar effective activation on adsorbing colloid flotation from solutions

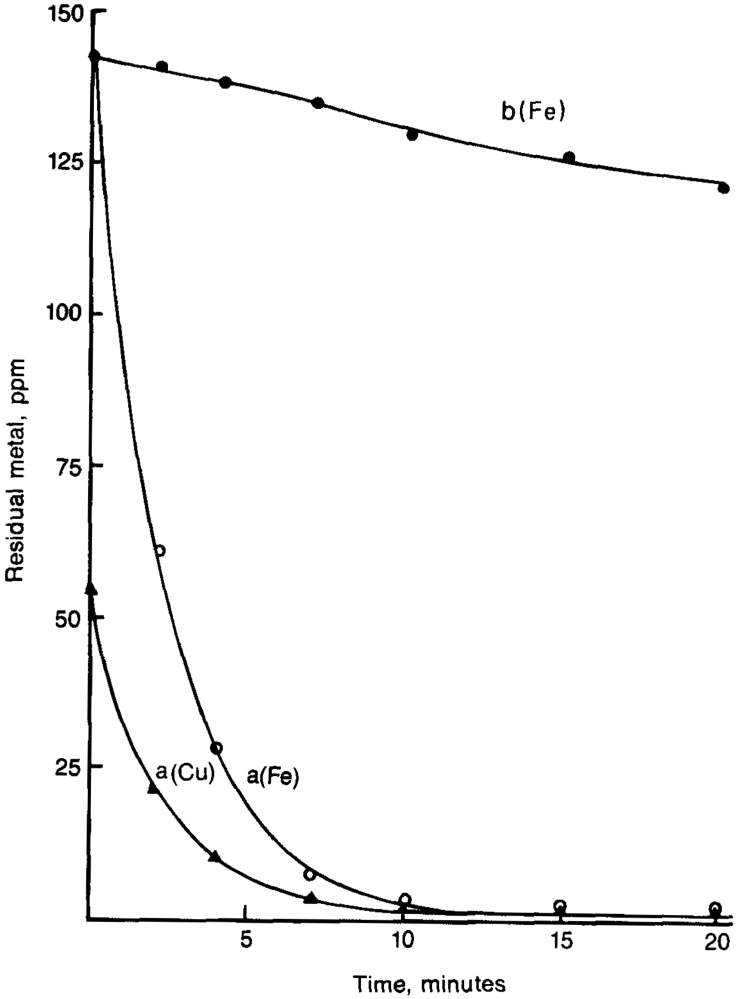

FIG. 2 Metal removal vs flotation time from solution of total ammonia 0.14 M at pH 7.0. (a) Initial: Fe 142 ppm, Cu 51.6 ppm. (b) Initial: Fe 142 ppm, no copper. a(Fe) and b(Fe) indicate iron residues, a(Cu) indicates copper residues.

of high electrolyte concentrations by the use of the sorptions of some cationic metal ion species on the resultant iron(III) hydroxide.

The Dosage of Iron(III)

A series of experiments was performed to study the effect of iron(III) dosage on the removal of copper from ammonia solutions by flotation.

TABLE 2
The Amount of Iron(III) Required to Result in Residual Copper 3.0 ppm by Adsorption at pH 7.0 for Samples in Total Ammonia 0.14 M

Initial copper in sample (ppm)	Iron required (ppm)	Fe/Cu (g/g)
10	19.4	1.94
20	47.2	2.36
30	74.9	2.50
40	103	2.58
50	130	2.60

The optimum pH of flotation, as mentioned previously, was used in this work. From the adsorption isotherm of amminecopper(II) species on ferric hydroxide floc (39), an estimate of the amount of iron dose needed to reduce the residual copper levels to less than 3.0 ppm after removing the floc can be made, as shown in Table 2 for samples in 0.14 M total ammonia at pH 7.0 [the optimum pH for amminecopper(II) species adsorption]. Removal of floc by flotation was carried out by adding an iron(III) dose somewhat greater than the corresponding value listed in Table 2 for samples with initial copper concentrations of 23, 30, and 52 ppm, respectively, as shown in Table 3. The copper densities of flocs are approximately 0.35 g Cu/g Fe. It was found that the removals of flocs are rapid and complete,

TABLE 3
Flotations of Copper from Solutions with Total Ammonia of 0.14 M[a]

	Initial concentration (ppm)			Residue after flotation (ppm)		Flotation duration (minutes)	Copper density of carrier flocs (g Cu/g Fe)
	Copper	Iron	SDS	Copper	Iron		
	23	60	80	1.9	1.4	10	0.36
	30	84	80	1.8	0.8	10	0.34
	52	142	192	1.6	0.6	20	0.35
	155	142	192	23	0.3	7	0.94
	155	200	192	12	0.3	14	0.71
	155	270	192	4.6	3.4	40	0.56
Twostep (1)	155	142	192	23	0.3	7	0.94
(2)	23	58	—	1.9	1.4	10	0.37
(1)	300	50	200	30	0.1	20	5.4
(2)	30	84	—	1.8	0.8	10	0.34

[a] pH = 7.0.

and the residual copper levels are less than 3.0 ppm, as expected. However, when the sample solution initially contains 155 ppm copper, a large amount of iron(III) is required. It takes a long time to remove the floc by single-step foam flotation, and the residual copper level is high [with a residual copper level of 4.6 ppm for a run of 40 minutes with an iron(III) dose of 270 ppm, as shown in Table 3]. The separation can be improved by using

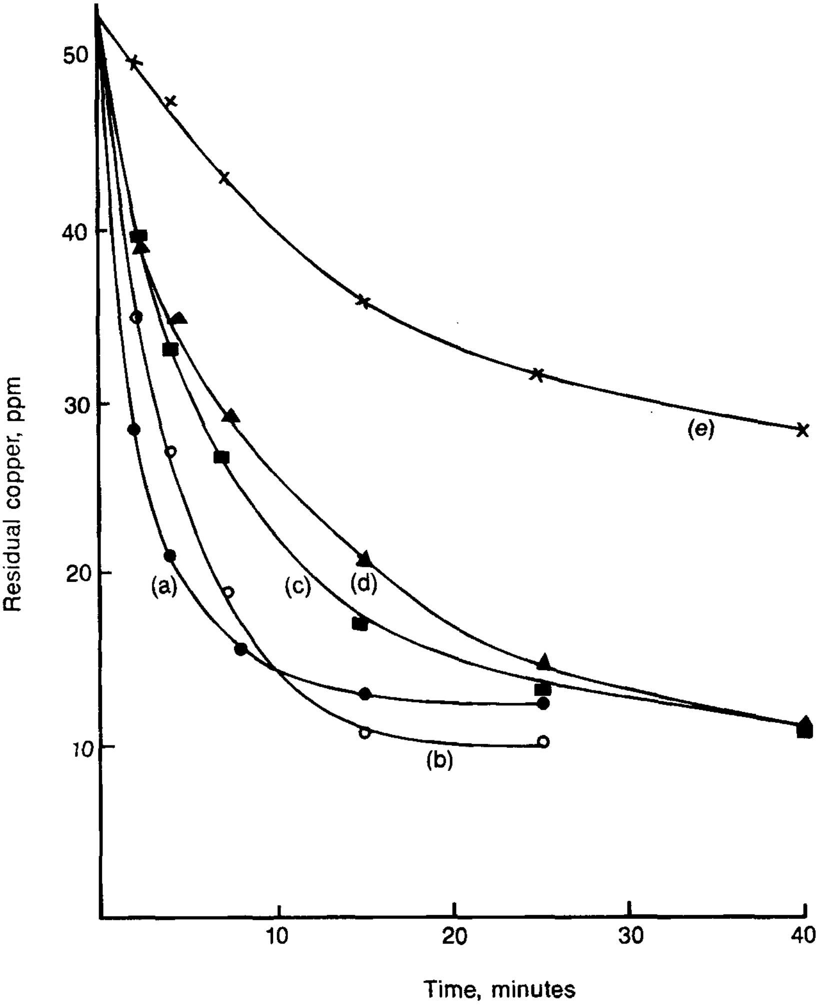

FIG. 3 Copper removal vs flotation time from solution of total ammonia 0.31 M at pH 6.7. Initial conditions: Cu (a)–(e) 52 ppm; Fe (a) 113 ppm, (b) 131 ppm, (c) 147 ppm, (d) 170 ppm, (e) 226 ppm; SDS (a)–(e) 100 ppm.

a two-step flotation procedure, as is also shown in Table 3. The flotation was run for 7 minutes with a 142 ppm dose of iron as the first step of flotation, and a 58 ppm dose of iron was used for the 10 minute run as the second step of flotation. The residual copper level is 1.9 ppm, and the total dose of iron(III) is only 200 ppm. The two-step flotation procedure is also very effective for copper removal from a sample solution initially containing copper as high as 300 ppm. The rate of removal of the floc is faster during the first flotation step of the two-step flotation procedure compared with that of the single-step flotation procedure. The copper density of the floc

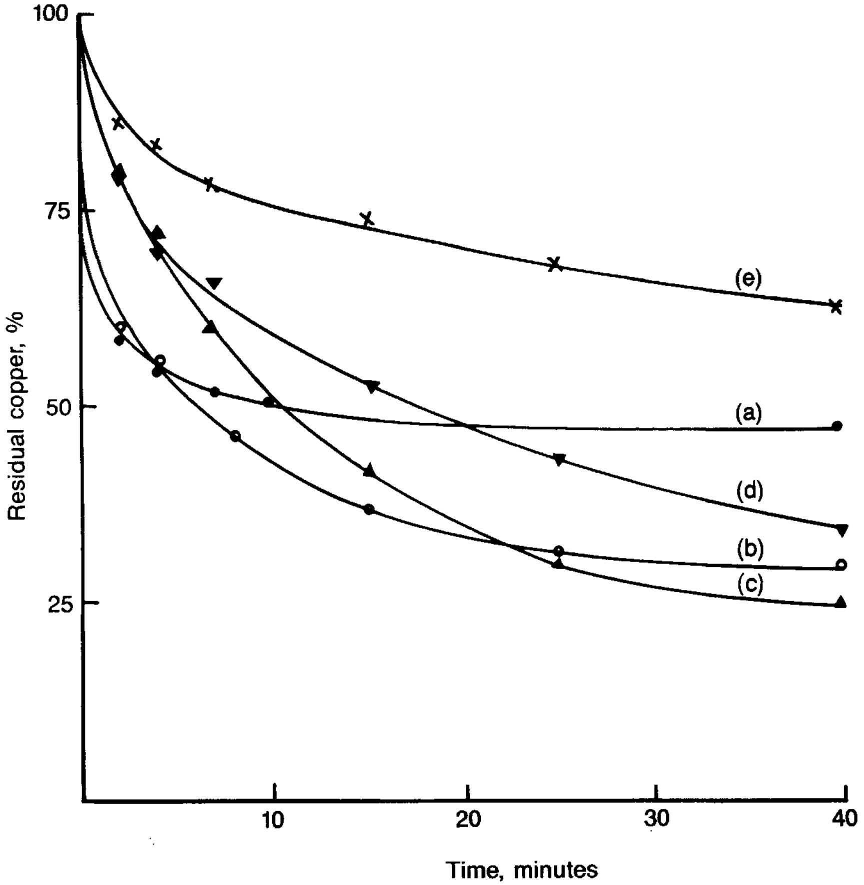

FIG. 4 Copper removal vs flotation time from solution of total ammonia 0.57 M at pH 6.4. Initial conditions: ppm Cu/Fe (a) 155/136, (b) 103/189, (c) 103/215, (d) 103/236, (e) 39/113; SDS (a)-(d) 96 ppm, (e) 48 ppm.

of the first flotation step was larger so that the floatability of the floc was higher, and the efficiency of copper removal by the ferric hydroxide floc was also greater compared with the single-step flotation procedure. The second flotation step was required to reduce the residual copper level closer to the desired value.

The effects of iron(III) dosage on adsorbing colloid flotation of copper from solutions containing 52 ppm of copper and 0.31 M total ammonia are shown in Fig. 3. Optimum separation was achieved with a 131-ppm dose of iron, and the residual copper level was 9.2 ppm. The copper density of the floc was 0.33 g Cu/g Fe. The residual copper level was higher with a smaller dose of iron due to incomplete adsorption of the copper species.

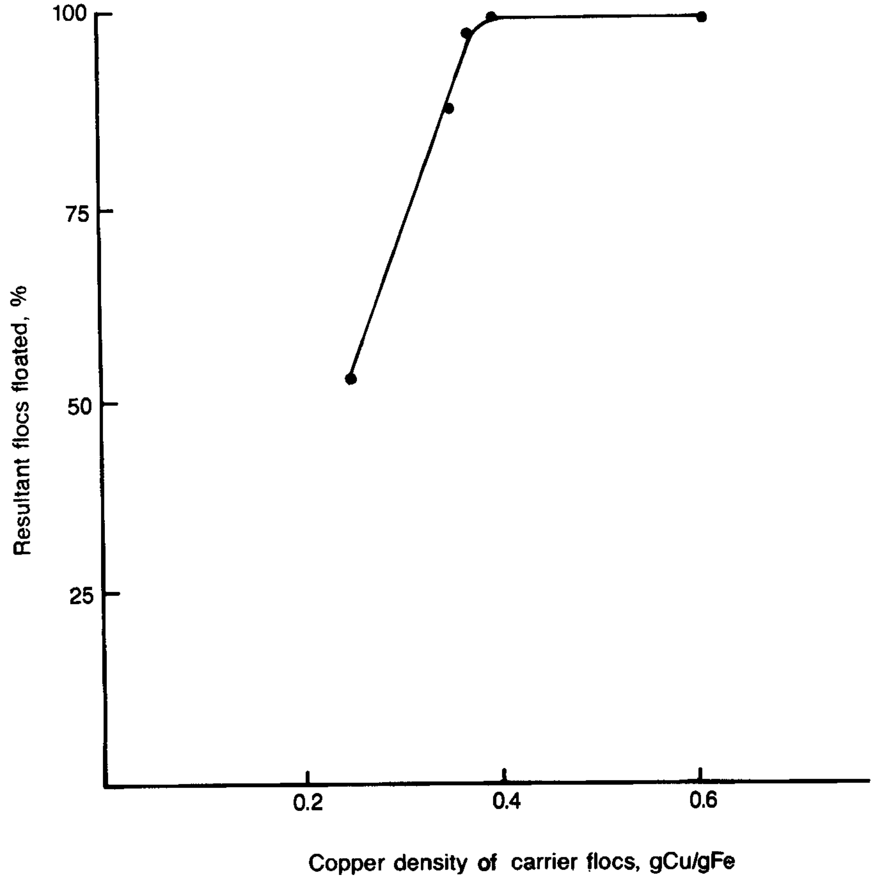

FIG. 5 Floatability of the resultant flocs at total ammonia 0.57 M, pH = 6.4. Initially: Cu 39–115 ppm, Fe 113–236 ppm, SDS 48–96 ppm.

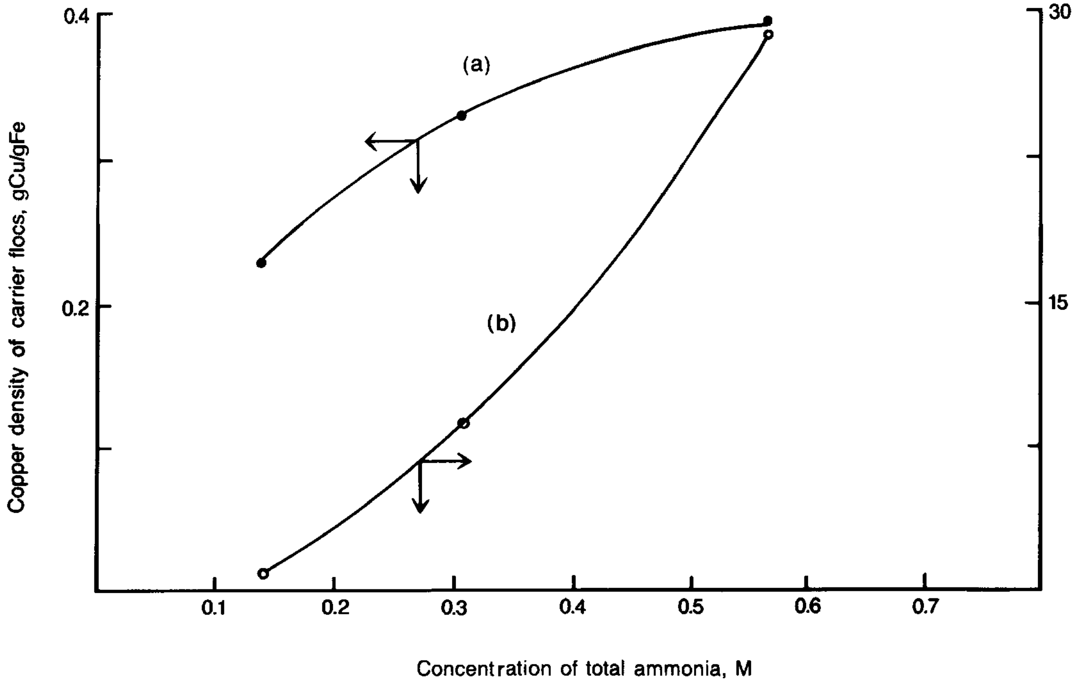

FIG. 6 (a) The optimum dosage of iron in terms of copper density of carrier floc against the concentration of total ammonia. (b) The corresponding equilibrium concentration of copper in the solution.

Addition of a quantity of iron(III) greater than this optimum dosage reduced the floatability of the floc due to the lower copper density of the floc. The flotation of such a floc leads to slow and incomplete removal during a reasonable time period (e.g., 40 minutes).

The effects of iron(III) dosage on the flotation of copper from a 0.57 M total ammonia solution are shown in Fig. 4. Floatability as a function of the copper density of the floc is shown in Fig. 5. It was found that effective removal of the floc by flotation from a solution containing 0.57 M total ammonia could be achieved provided that the copper density of the floc was no less than 0.4 g Cu/g Fe. Optimal removal of copper was achieved (Curve c in Fig. 4) with a copper density of the floc of this value. Further experiments showed that the removal of copper by adsorbing colloid flotation from ammonia solutions initially containing 103, 155, and 200 ppm copper are optimal when the dose of iron produces a floc with a copper density of 0.40 ± 0.1 g Cu/g Fe. Thus, the copper density of the floc can be used as an important parameter toward choosing the optimal iron dose for an effective separation of copper from ammonia solution.

Figure 6 presents the maximum dosing of iron(III) in terms of the minimum copper density of the resultant floc which is floatable at various concentrations of total ammonia. The residual copper in equilibrium with such a floc in the sol solution is also shown. The efficient dose of iron(III) for batch flotation can thus be estimated once the copper concentration of the sample solution is known. Sample solutions with a total ammonia concentration as high as 0.57 M and initial copper concentrations up to 300 ppm can be treated as indicated by Fig. 6 for the rapid recovery of most copper by flotation.

CONCLUSIONS

Copper can be removed from aqueous amminecopper(II) solution by adsorption colloid flotation. The optimum pH for flotation is the point of maximum adsorption of copper on the resultant floc. A greater extent of copper removal and faster rate are achieved at the optimum pH. Flotations for sample solutions in various concentrations of total ammonia require controlled dosing of iron(III) for efficient single batch operation. The copper density of the floc can be used as an important parameter toward choosing the optimal iron dose. In some cases, when the copper concentration of the sample is high (>200 ppm) and the concentration of total ammonia is low (<0.15 M), a two-batch operation gives better results. Such a mode can result in high efficiency in the first batch and more complete separation at the end. With samples containing a high concentration of total ammonia, a higher copper residue remains after a batch operation. Under this condition, the method can be used for the recovery of copper from a concentrated amminecopper(II) solution since it places little limitation on the load capacity as compared with other separation techniques such as ion exchange.

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