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Removal of Cu(II) from Aqueous Solutions by the Foam Separation Techniques of Precipitate and Adsorbing Colloid Flotation

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Abstract

Experimental investigations on the removal of Cu(II) from aqueous solution were carried out through two foam separation techniques: precipitate flotation and adsorbing colloid flotation with Fe(III). The optimum pH for good removal was found to be about 9 for the former and about 7 for the latter. The effects of surfactant (sodium lauryl sulfate), foreign ions (Na^+, Ca^{2+}, NO_3^-, and SO_4^{2-}), and Al(III) addition on the efficiency of Cu(II) removal are discussed.

INTRODUCTION

Foam separation is generally used in separating or concentrating soluble and/or insoluble materials from aqueous solution. When one deals with dilute wastes, foam separation has several advantages: low residual metal concentration, rapid operation, low space requirements, and low cost. A number of excellent reviews on foam separation are available (*1–4*), and the application of flotation techniques to wastewater treatment has been an important issue in the field of separation science (*5–8*).

Foam separation techniques are based on the fact that a surface-active material tends to concentrate at a gas–liquid interface. By bubbling the air through the solution, the surface-active material can be adsorbed on

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the surface of the rising bubbles and then be separated from the solution. The substance to be removed, if not surface active, can be made surface active through union with other surface-active materials. For instance, adsorbing colloid flotation involves the addition of a flocculant (alum or ferric chloride) to produce a floc. The dissolved metal is adsorbed onto the floc particle and/or coprecipitated with the floc particle. A surfactant is then added, attaches to the floc particle, renders it hydrophobic, and the floc is removed by flotation.

Foam separation of copper(II) has been investigated by many workers. Rubin et al. (*9*, *10*) and other workers (*11–13*) have carried out the ion and/or precipitate flotation of copper(II). It was found that both ion and precipitate flotation depend on the pH of the solution, and that copper(II) removal by precipitate flotation is more efficient than by ion flotation. Ion flotation was found very sensitive to the concentration of ions, but precipitate flotation was not. Kim and Zeitlin (*14*) carried out adsorbing colloid flotation of seawater with $Fe(OH)_3$ and dodecylamine at pH 7.6. Wilson and coworkers (*15–17*) investigated the adsorbing colloid flotation of Cu(II) from aqueous solution with $Fe(OH)_3$ and sodium lauryl sulfate. It was found that the flotation efficiency was maximum at about pH 7.0 and was inhibited by the presence of foreign ions.

In the present work the performances of two foam separation techniques, precipitate flotation and adsorbing colloid flotation with $Fe(OH)_3$, are compared by showing the relative effects of pH, initial surfactant (or collector) concentration, and concentration of foreign ions on the removal efficiency of copper(II) from aqueous solution. The effect of the addition of Al(III) on adsorbing colloid flotation with $Fe(OH)_3$ was also investigated.

EXPERIMENTAL

Chemicals

Laboratory-grade surfactant sodium lauryl sulfate (NLS) was used as the collector for the removal of Cu(II) by foam separation. Aqueous solutions of Cu(II) were prepared by dissolving $Cu(NO_3)_2 \cdot 6H_2O$ in distilled and deionized water. $NaNO_3$, Na_2SO_4, and $Ca(NO_3)_2$ were used as sources of foreign ions, and $Fe(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)S_3 \cdot 9H_2O$ were used to generate adsorbing colloids.

Apparatus and Procedure

A schematic diagram of the foam separation apparatus is shown in Fig. 1. The flotation column was made of Pyrex tubing of 3.5 cm in diameter and 90 cm in length, and foams were generated by bubbling a nitrogen stream into an aqueous solution through a coarse fritted glass sparger. The arithmetic mean bubble size of the foam was about 0.06 cm and the column was operated at 25°C.

Aqueous solutions of Cu(II) having a concentration of 50 ppm (0.78 m*M*) were prepared in the precipitating tank, and Fe(III) and/or Al(III) were added for adsorbing colloid flotation runs. Foreign ions, if needed, were also introduced. The precipitations were achieved at a given pH which was controlled continuously by adding small amounts of NaOH. The Cu(II) concentration remaining after precipitation was determined

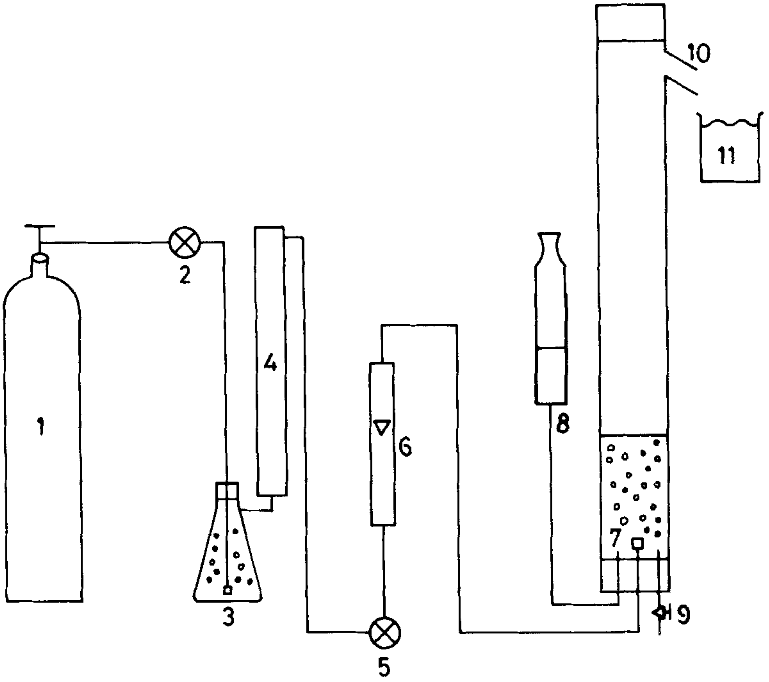

FIG. 1. Schematic diagram of experimental system. 1) Nitrogen supply; 2) valve; 3) humidifier; 4) glass wool column; 5) needle valve; 6) rotameter; 7) fritted glass sparger; 8) reagent syringe; 9) drain and sampling; 10) foam discharge port; 11) discharge foam.

in the residual solution after the precipitates had been removed by filtering through 0.45μ Millipore filter paper.

The aqueous solution of NLS was introduced from the bottom of the column to make the volume of the solution 200 mL. Flotation was started by passing the nitrogen stream through the fritted glass at 80 cm^3/min.

A 5-mL sample was taken every 5 min and the concentrations of Cu(II), Fe(III), and Al(III) were analyzed by an atomic absorption spectrophotometer (Shimadzu AA-610S). The concentration of NLS in the residual solution was determined by the methylene blue-chloroform extraction technique (*18*).

In order to recover NLS, the discharged foam was treated with 0.25 *M* NaOH solution.

RESULTS AND DISCUSSION

Effect of pH on the Removal

The effects of pH on the removal of Cu(II) from aqueous solution are plotted in Fig. 2, where Curve A is for precipitate flotation and Curve B is for adsorbing colloid flotation. The removal efficiency is represented by the lowness of the residual Cu(II) concentration. Adsorbing colloid flotation shows better removal efficiency than precipitate flotation over the ranges of pH less than 8. For the foam separations there exists an optimum value of pH, which in the present study is about 9 for precipitate flotation and about 7 for adsorbing colloid flotation. To determine the effects of other variables, these values of pH were taken as experimental conditions in the following discussions.

The optimum pH value of adsorbing colloid flotation with Fe(III) was less than that of precipitate flotation due to the coprecipitation of $Cu(OH)_2$ with $Fe(OH)_3$. $Cu(OH)_2$ is easily coprecipitated with $Fe(OH)_3$, which is precipitated at much lower pH (about 2 to 3).

The residual concentration after filtration (indicated by dashed lines in Fig. 2), which represents the precipitation effect only, decreases very sharply and remains almost constant over the pH range higher than the optimum value. The residual concentration after flotation (indicated by solid lines), which represent the effect of flotation after precipitation, also decreased very sharply but beyond the optimum pH tends to increase with increasing pH.

During flotation, the precipitates of the metal hydroxides are adsorbed on the surfaces of foam bubbles. This adsorption is facilitated by the

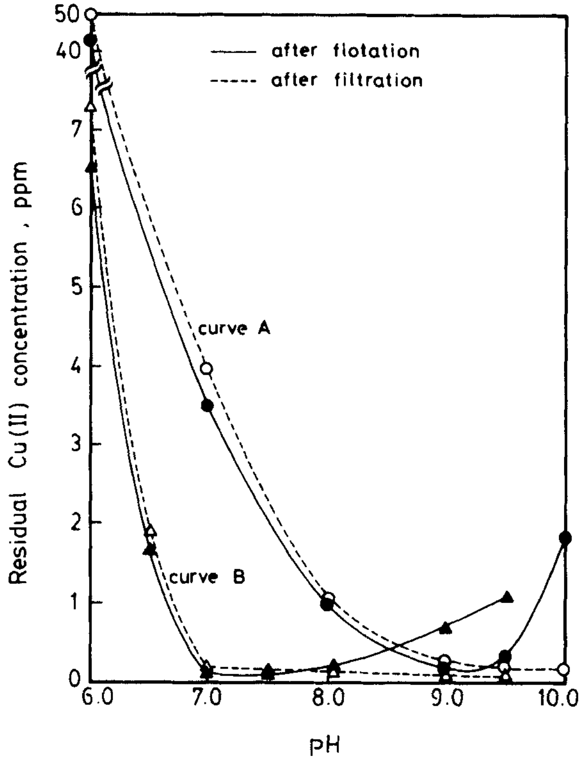

FIG. 2. Effect of pH on Cu(II) removal. Curve A is for precipitate flotation and Curve B for adsorbing colloid flotation with 100 ppm of Fe(III). Initial Cu(II) concentration was 50 ppm (0.78 m*M*), gas flow rate 80 mL/min, and NLS concentration 100 ppm.

nature of the surfactant. Since NLS is an anionic surfactant, it is desirable that the metal precipitates have some positive charges (i.e., that they be below the isoelectric points). It was reported that in water the isoelectric point of $Cu(OH)_2$ is about 9.4 (*19*) and that of $Fe(OH)_3$ is about 7.1 (*20*). The optimum efficiency of Cu(II) removal was attained at a pH near the isoelectric points. Above the optimum pH, the charges of metal precipitates tend to become less positive. Therefore, adsorption of the anionic surfactant (NLS) becomes weaker and the removal efficiency decreases with pH.

Effect of Initial Surfactant (or Collector) Concentration

Tables 1 and 2 show the effects of the initial surfactant concentration on Cu(II) removal by precipitate and adsorbing colloid flotation, respectively.

When the concentration of surfactant NLS is less than 100 ppm for precipitate flotation, the removal efficiency is very low. This seems to be due to unstable, collapsing foam at low surfactant concentrations, thereby resulting in the redispersion of the precipitated $Cu(OH)_2$. Sufficient collector is required to induce stable foams.

In contrast to precipitate flotation, adsorbing colloid flotation requires less surfactant for the favorable removal of Cu(II), and a certain optimum surfactant concentration exists. When $Fe(OH)_3$ is used as the adsorbing colloid, it acts as a flocculating material which prevents the precipitates from redispersion. A surfactant concentration of 50 ppm was found to be the most desirable for the production of stable and efficient foam during batch operation.

The NLS concentration was taken as 100 ppm for precipitate flotation and as 50 ppm for adsorbing colloid flotation in the remaining parts of this work.

Effect of Foreign Anions

Figure 3 shows the effects of foreign anions on the removal of Cu(II) by precipitate flotation. Anions (NO_3^- and SO_4^{2-}) were introduced as sodium salts ($NaNO_3$ and Na_2SO_4). Sulfate anions were found to reduce the

TABLE 1

Effect of Initial Surfactant Concentration on Cu(II) Removal by Precipitate Flotation[a]

pH	Initial surfactant concentration (ppm)	Residual Cu(II) concentration (ppm)
9.0	25	19.7
	50	16.3
	75	7.5
	100	0.22
	150	0.22
	200	0.32

[a] All runs were made at an initial Cu(II) concentration of 50 ppm (0.78 m*M*), an air flow rate of 80 mL/min, and a flotation time of 30 min.

TABLE 2
Effect of Initial Surfactant Concentration on Cu(II) Removal by Adsorbing Colloid Flotation with $Fe(OH)_3$[a]

pH	Initial surfactant concentration (ppm)	Residual Cu(II) concentration (ppm)
7.0	25	0.41
	50	0.12
	75	0.12
	100	0.13
	150	0.21

[a] All runs were made at an initial Cu(II) concentration of 50 ppm (0.78 m*M*), an air flow rate of 80 mL/min, a Fe(III) concentration of 100 ppm, and a flotation time of 30 min.

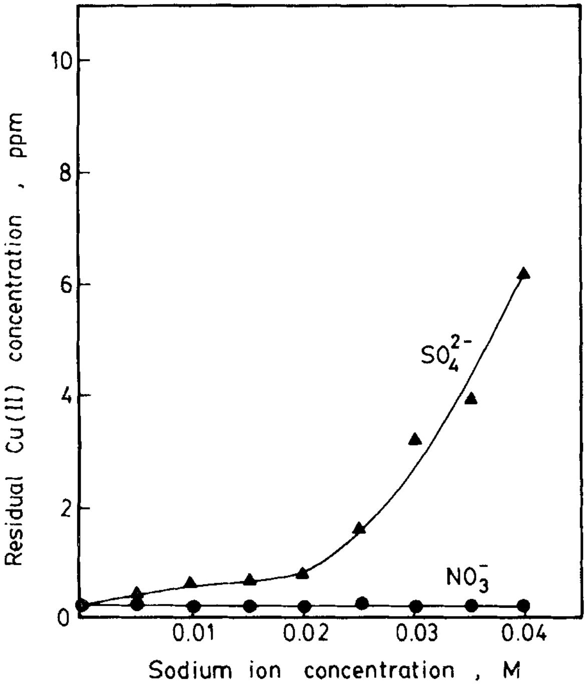

FIG. 3. Effects of foreign anions on Cu(II) removal by precipitate flotation at a pH of 9.0. Initial copper(II) concentration was 50 ppm (0.78 m*M*), flotation time 30 min, gas flow rate 80 mL/min, and NLS concentration 100 ppm.

Cu(II) removal efficiency greatly, and this is also true for adsorbing colloid flotation with $Fe(OH)_3$ (Fig. 4).

Significant reduction in Cu(II) removal efficiency by sulfate anions is thought to be due to the stronger adsorption of the divalent sulfate anion than of the monovalent nitrate anion on the positively charged metal precipitates, resulting in the reduction of the zeta potential of the particles. The attraction between the positively charged precipitates of Cu(II) and the anionic surfactant will then weaken, and the removal efficiency decreases sharply.

Effect of Foreign Cations

Figures 5 and 6 show the effects of foreign cations on the removal of Cu(II) by precipitate and adsorbing colloid flotation, respectively. Cations (Na^+ and Ca^{2+}) were introduced as nitrates.

Divalent calcium cations inhibit the removal of Cu(II) more significantly. The presence of Ca(II) enhances the competition with the positively charged precipitates for the anionic surfactant. The Cu(II) removal efficiency then decreases.

The inhibition of Cu(II) removal due to calcium cation appears to be more significant for adsorbing colloid flotation than for precipitate flotation. Calcium cations are believed to deprive $Fe(OH)_3$ of its flocculating role. The particle size of the coprecipitates will then become small due to reduced floc formation. With a fixed amount of surfactant, precipitate particles smaller than an optimum size are entrained with air flotation less easily than the larger ones (*21*).

Effect of Al(III)

The results of Fig. 4 show that Cu(II) removal by adsorbing colloid flotation was extremely poor in the presence of the sulfate ions. Improvement of Cu(II) removal from aqueous solution with a high sulfate level was attempted by adding Al(III) as an activator, and the results are shown in Table 3. By adding small amounts of Al(III) to Fe(III), Cu(II) could be removed from the solution more effectively.

Al(III) has been known to increase the zeta potential of the coprecipitates (*22–24*), which presumably increases the affinity between the coprecipitates and the anionic surfactant. The removal efficiency seems to increase significantly, in agreement with this.

Calcium cations also inhibit Cu(II) removal by adsorbing colloid

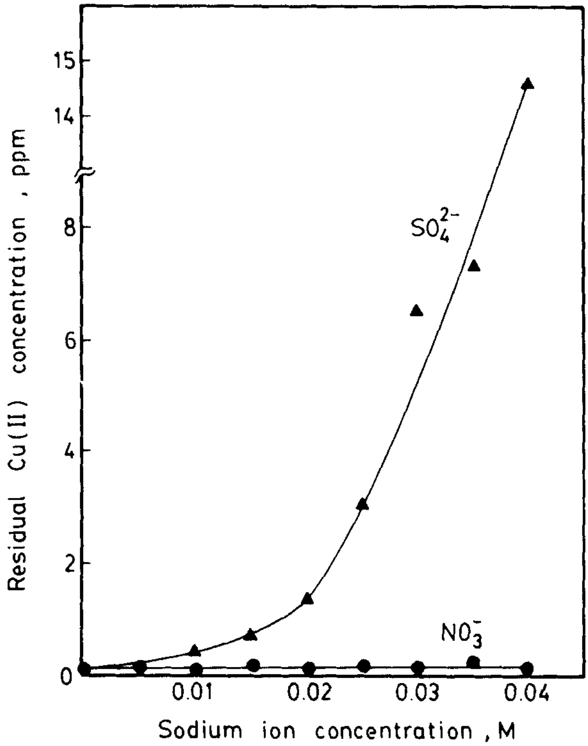

FIG. 4. Effects of foreign anions on Cu(II) removal by adsorbing colloid flotation with $Fe(OH)_3$ at a pH of 7.0. Initial copper(II) concentration was 50 ppm (0.78 m*M*), 100 ppm of Fe(III), flotation time 30 min, gas flow rate 80 mL/min, and NLS concentration 50 ppm.

flotation as shown in Fig. 6. It was observed in our experiment that the addition of Al(III) did not overcome inhibition of flotation by calcium cations.

CONCLUSIONS

Copper(II) has been removed from aqueous solution by the foam separation techniques of precipitate and adsorbing colloid flotation.

Efficient removal of copper(II) could be achieved by coprecipitation and adsorbing colloid flotation at lower pH than by precipitate flotation.

NLS as a collector has an optimum concentration to give stable foams

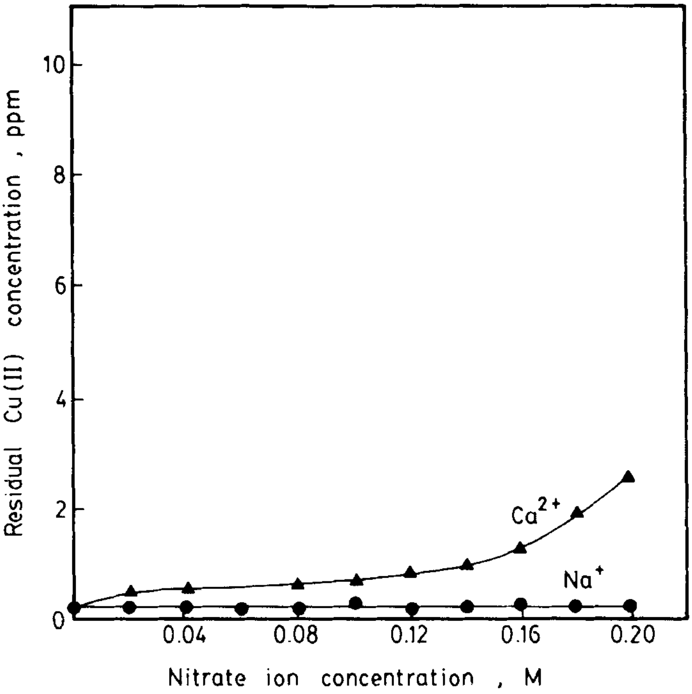

FIG. 5. Effects of foreign cations on Cu(II) removal by precipitate flotation at a pH of 9.0. All the other conditions are the same as in Fig. 3.

which can transport the metal precipitates effectively. In adsorbing colloid flotation, a lower concentration of NLS was needed because of the flocculating role of $Fe(OH)_3$. In precipitate flotation, more collector was needed due to the redispersion of metal precipitates.

Foreign ions inhibit the separation efficiency. The extent of inhibition by the divalent ions Ca^{2+} and SO_4^{2-} was found to be more serious than that by the monovalent ions Na^+ and NO_3^-.

It was suggested that Al(III) added as an activator could improve removal efficiency, especially when sulfate ions inhibit the performance of adsorbing colloid flotation with $Fe(OH)_3$.

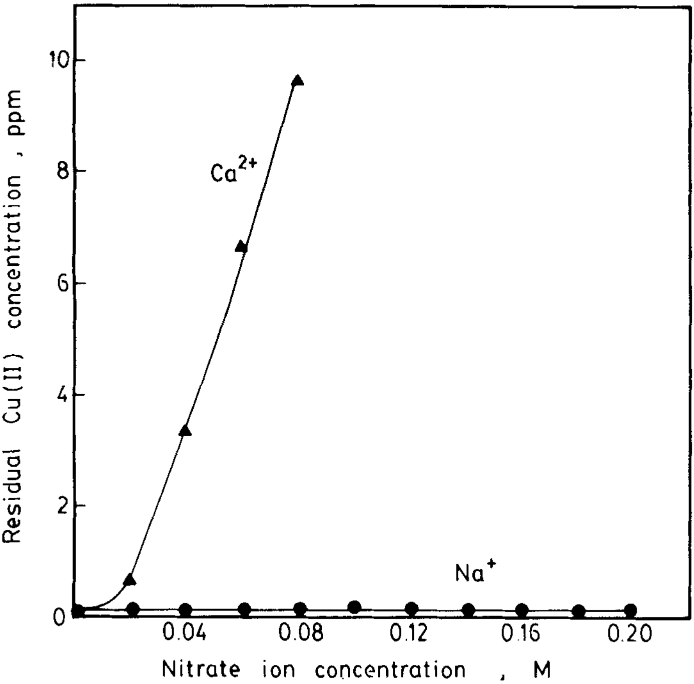

FIG. 6. Effects of foreign cations on Cu(II) removal by adsorbing colloid flotation with $Fe(OH)_3$ at a pH of 7.0. All the other conditions are the same as in Fig. 4.

TABLE 3

Effect of Al(III) on Cu(II) Removal by Adsorbing Colloid Flotation with $Fe(OH)_3$[a]

Na_2SO_4 (*M*)	Fe(III) (ppm)	Al(III) (ppm)	pH	Residual Cu(II) concentration (ppm)
0	100	0	7.0	0.12
0.015	100	0	7.0	6.6
0.02	100	0	7.0	14.7
0.03	100	0	7.0	No removal
0.05	100	0	7.0	No removal
0.015	100	30	7.0	0.14
0.02	100	30	7.0	0.41
0.03	100	30	7.0	0.82
0.05	100	30	7.0	2.23

[a] All runs were made at an initial Cu(II) concentration of 50 ppm (0.78 m*M*), an air flow rate of 80 mL/min, a NLS concentration of 50 ppm, and a flotation time of 30 min.

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