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TECHNICAL NOTE

# Separation of Cadmium(II) from Aqueous Solutions by the Precipitate Flotation Technique

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## ABSTRACT

The separation of cadmium(II) from aqueous solutions by a precipitate flotation technique using sodium sulfide as a precipitant and oleic acid (HOL) as a surfactant has been investigated. The effects of HOL and sodium sulfide concentrations, pH, addition of some ions, ionic strength, temperature, and order of reagents addition on flotation efficiency have been studied. A 100% floatability of Cd(II) was obtained at pH 5.5–6.5. It was found that the order of reagents addition markedly affects the flotation of Cd(II).

## INTRODUCTION

The study of metal pollution in aqueous solutions has gained importance because metals exhibit various biological effects on living organisms in aquatic media (1). A number of studies involving the precipitate flotation technique have been carried out (2–10). Heavy metal ions may be removed from aqueous solutions as metal sulfides (11). A typical example of a coagulant is sodium sulfide. The precipitated metal sulfides, however, are often colloidal and do not grow large enough to allow easy filtration. Therefore, in this paper cadmium is precipitated as its sulfide followed by flotation without the precipitate adhering on such coagulants as $Al(OH)_3$ (12) and $In(OH)_3$ (13).

Inakazu et al. (14) removed Cd from aqueous solutions at pH 11.3 by adsorption on bentonite and flotation with cationic surfactant. Further, El-

Tanbouly and Ghazy (15) separated Cd by adsorption on active charcoal at pH 11.3 and flotation with an oleic acid surfactant. In this investigation, Cd is separated as a metal sulfide in acidic medium, which may be a means for separating Cd from other metal ions.

## EXPERIMENTAL

### Apparatus

The flotation cell was a test tube of 12 mm inner diameter and 290 mm length with a stopcock at the bottom. All glassware was soaked overnight in 50% nitric acid and rinsed thoroughly with double-distilled water.

A Perkin-Elmer Atomic Absorption Spectrophotometer 2380 was used for Cd determination at wavelength 228.8 nm. The pH measurements were carried out with a Hanna Instruments 8519 digital pH-meter.

### Reagents

Unless otherwise stated, all reagents used were of analytical grades. The aqueous solutions were prepared in double-distilled water. For the cadmium stock solution ($35.6 \times 10^{-3}$ mol·L$^{-1}$), 7.1637 g $CdCl_2 \cdot H_2O$ was dissolved in 1 L water. For the sodium sulfide stock solution (0.05 mol·L$^{-1}$), 4.8 g $Na_2S \cdot H_2O$ was dissolved in 1 L water. Oleic acid, HOL, stock solution ($12.72 \times 10^{-2}$ mol·L$^{-1}$) consisted of 40 mL HOL dispersed in 1 L kerosene.

### Procedure

To carry out the flotation measurements, 20 cm$^3$ of an aqueous solution containing cadmium ions, sodium sulfide, oleic acid surfactant, and HCl or NaOH (for controlling the pH) was introduced into the flotation cell. The flotation cell was turned upside down 20 times by hand.

The concentration of Cd(II) ions in the background solution was determined by an atomic absorption spectrophotometer at wavelength 228.8 nm. The floatability ($F\%$) was calculated by

$$F = [(C_i - C_f)/C_i] \times 100\%$$

where $C_i$ and $C_f$ denote the concentration of Cd(II) ions before and after flotation, respectively, as described previously (16).

To study the effect of temperature, the Cd(II), HOL, and sodium sulfide solutions were either cooled or heated to the same temperature. The sodium sulfide and HOL were quickly poured into the Cd(II) solution at time zero. The solution was introduced into the flotation test tube jacketed with a 1-cm thick fiberglass insulator. The same flotation procedure mentioned above was followed. Most flotation occurred in the first few minutes. The fact that the test tube was insulated and that only a small change in the solution temperature occurred after 10 minutes shows that temperature has a minimal effect on the flotation response.

Other measurements were carried out at room temperature, about 25°C.

## RESULTS AND DISCUSSION

### Effect of HOL Concentration

Several experiments were conducted to find the most suitable concentration of HOL surfactant for removing Cd(II) ions from aqueous solutions without (Curve a) and with (Curve b) $Na_2S$, 25 × $10^{-4}$ mol·$L^{-1}$ at pH 5.8. The results are shown in Fig. 1. It can be seen that the floatability of Cd(II) ions reaches its maximum value at a HOL concentration of 63.6 × $10^{-4}$ mol·$L^{-1}$. Therefore, this concentration was used for all measurements. The flotation efficiency decreases at higher concentrations of HOL, which may be attributed to the fact that the surfactant changes the state of suspension of the particles from coagulation precipitation through coagulation flotation to redispersion with an increase in the amount of surfactant added (17). Further, the effect of addition of $Na_2S$ is evident from comparison of Curve b, where the flotation efficiency of Cd(II) ions reaches 100%, with Curve a, where the floatability does not exceed 92%.

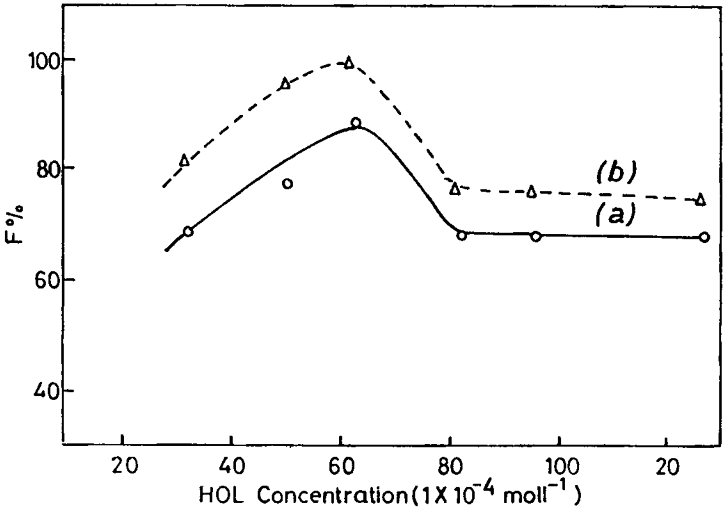

FIG. 1 Floatability of Cd(II) vs HOL concentration. Cd(II), 35.6 × $10^{-5}$ mol·$L^{-1}$; pH 5.8; (a) without $Na_2S$; (b) with $Na_2S$, 25 × $10^{-4}$ mol·$L^{-1}$.

### Effect of Sodium Sulfide Concentration

The effect of $Na_2S$ concentration on the floatability of Cd(II) ions ($35.6 \times 10^{-5}$ mol·L$^{-1}$) with HOL ($63.6 \times 10^{-4}$ mol·L$^{-1}$) was investigated in the $5 \times 10^{-4}$ to $40 \times 10^{-4}$ mol·L$^{-1}$ range. The flotation efficiency of Cd(II) ions (100%) was obtained at a sulfide concentration of $20 \times 10^{-4}$ to $25 \times 10^{-4}$ mol·L$^{-1}$. Therefore, the concentration of $Na_2S$ was fixed at $25 \times 10^{-4}$ mol·L$^{-1}$ for this work. At higher sulfide concentrations the flotation of Cd(II) ions decreases, which is in agreement with the literature data (18) that the sulfides of the metal cations, e.g., Cu(I), Cd(II), Pb(II), and Zn(II), should show solubility increases with increasing sulfide concentration. Moreover, Cd(II) may form the species $Cd(HS)_2$, $Cd(HS)_3^-$, and $Cd(HS)_4^{2-}$ (19) which are incapable of flotation with oleate ions formed at pH $\geq 5.2$ (20).

### Effect of pH

Figure 2 shows the flotation efficiency of Cd(II) ions as a function of pH under the optimum conditions specified in the figure. It can be seen

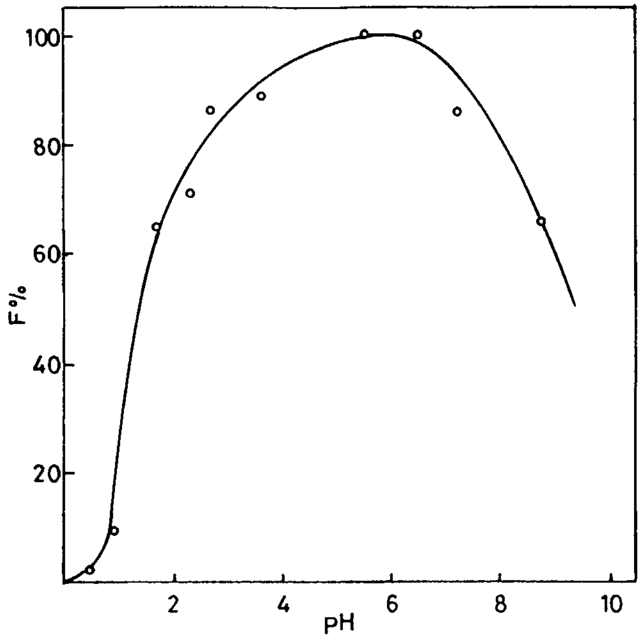

FIG. 2 Floatability of Cd(II) vs pH. Cd(II), $35.6 \times 10^{-5}$ mol·L$^{-1}$; $Na_2S$, $25 \times 10^{-4}$ mol·L$^{-1}$; HOL, $63.6 \times 10^{-4}$ mol·L$^{-1}$.

that the floatability of Cd(II) ions begins to increase at pH > 1. This may be due to the fact that in strongly acidic solutions, CdS either will not be precipitated at all or will be incompletely precipitated owing to the reversibility of the reaction (21)

$$Cd^{2+} + S^{2-} \rightleftharpoons CdS$$

The maximum flotation of 100% was observed in the pH 5.5–6.5 range. Flotation decreases in the alkaline region due to the formation of excessive foams and the dispersed emulsion in the flotation medium.

## Effect of Reagent Addition (order)

An extensive series of experiments was carried out to study the effect of order of reagent addition on the floatability of Cd(II). This effect seems to be an important factor affecting the flotation efficiency of Cd(II). The following orders were attempted under the optimum conditions:

1. Cd(II) ions + HOL + $Na_2S$ and HCl or NaOH
2. Cd(II) ions + HOL + HCl or NaOH and $Na_2S$
3. Cd(II) ions + $Na_2S$ + HOL + HCl or NaOH
4. HOL + $Na_2S$ + Cd(II) ions + HCl or NaOH

The order which gave complete separation of Cd(II) ions was number 3. The other orders give very low separation of Cd(II) ions, sometimes nearly zero, due to the formation of excessive foaming, evolution of hydrogen sulfide gas, dispersion of CdS precipitate, and formation of white emulsion in the flotation pulp.

## Effect of Some Foreign Cations

The effect of such added cations as Cu(II), Co(II), Ni(II), Mn(II), Pb(II), Hg(II), and Bi(III) on the flotation efficiency of Cd(II) ions was investigated under the optimum conditions. These foreign cations did not affect the flotation efficiency of Cd(II) if they were added in the following sequence: Cd(II) ions + $Na_2S$ + foreign cation(s) + HOL. Other sequences of reagent addition e.g., Cd(II) + foreign cation(s) + $Na_2S$ + HOL, should markedly decrease the floatability of Cd(II), sometimes reaching zero. This may be because these metal cations and Cd(II) are in competition for the sulfide ions. Metal sulfides having a lower solubility product should precipitate first and float with the HOL surfactant.

## Effect of Ionic Strength and Temperature

Table 1 shows the effect of varying ionic strength and temperature on the floatability of Cd(II) ions. As may be seen, the floatability of Cd(II)

TABLE 1

Effect of Ionic Strength and Temperature on the Floatability (*F%*) of Cd(II) ($35.6 \times 10^{-5}$ mol·L$^{-1}$) with $Na_2S$ ($25 \times 10^{-4}$ mol·L$^{-1}$) and HOL ($63.6 \times 10^{-4}$ mol·L$^{-1}$) at pH 5.8

| | | *F%* at a temperature (°C) of | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Ionic strength (M) | Salt | 10 | 25 | 30 | 40 | 50 | 70 | 80 |
| 0.1 | NaCl | 91 | 95 | 96 | 98 | 98.2 | 100 | 100 |
| | KCl | 98 | 100 | 100 | 100 | 100 | 100 | 100 |
| | $CaCl_2$ | 96 | 97 | 97.5 | 98 | 98.6 | 100 | 100 |
| 0.5 | NaCl | 89 | 93 | 95 | 96 | 98 | 100 | 100 |
| | KCl | 97.8 | 100 | 100 | 100 | 100 | 100 | 100 |
| | $CaCl_2$ | 96 | 97 | 97.3 | 99 | 99.1 | 100 | 100 |
| 1.0 | NaCl | 89 | 93 | 95 | 96 | 98 | 100 | 100 |
| | KCl | 97 | 100 | 100 | 100 | 100 | 100 | 100 |
| | $CaCl_2$ | 95 | 96 | 97.2 | 98 | 99 | 100 | 100 |

ions is only affected by NaCl and $CaCl_2$, which may be due to the formation of sodium oleate and calcium oleate, a white precipitate. This effect was overcome by raising the temperature to about 80°C. KCl has no effect on the flotation efficiency of Cd(II).

The change in temperature has no appreciable effect on the flotation of Cd(II). At low temperatures the floatability decreases slightly, probably because the particles aggregate poorly. An increase in temperature promotes collection by speeding up the thinning of the hydration layers between particles and bubbles, thereby increasing the probability of attachment, which leads to a high flotation efficiency.

## Selective Separation of Cd(II) from Hg(II) in Admixture

It was attempted to separate selectively Cd(II) from a mixture containing Cd(II) and Hg(II) ions. The separation was completely successful when the pH of the floating medium was controlled with $HNO_3$ to pH $\leq 1$. The Hg(II) ions were completely floated with $Na_2S$ and HOL at this pH, while Cd(II) ions were not. This may be because CdS is completely floated at pH 5.5–6.5 and is highly soluble in strongly acidic solutions, especially nitric acid (21).

## Mechanism of Flotation

Colloidal systems have an ion-exchange capacity (22), and the presence of ionic points on their surfaces originates from the solvation of counter groups of the electrical double layer (23). Oleate ions obtained from the dissociation of HOL at pH $\geq 5.2$ (20) combine electrostatically with colloidal CdS precipitate, and the hydrophobic aggregate floats on air bubbles to the surface of the solution.

## REFERENCES

1. P. Pakains and Y. J. Farrar, *J. Water Res.*, *11*, 145 (1977).
2. R. L. Cardozo and P. Dejonphe, *Nature*, *199*, 687 (1963).
3. L. D. Skaryler, G. S. Kranova, and S. G. Morkushin, *Kolloid Z.*, *30*, 134 (1968).
4. E. J. Mahne and T. A. Pinfold, *Chem. Ind.*, p. 1299 (1966).
5. E. J. Mahne, *J. Appl. Chem.*, *18*, 52 (1968).
6. E. J. Mahne, *Chem. Ind.*, p. 1917 (1967).
7. I. Sheiham and T. A. Pinfold, *J. Appl. Chem.*, *18*, 217 (1968).
8. A. J. Rubin, *J. Am. Water Works Assoc.*, *60*, 832 (1968).
9. A. J. Rubin and J. D. Johnson, *Anal. Chem.*, *39*, 298 (1968).
10. A. J. Rubin, J. D. Johnson, and J. C. Lamb III, *Ind. Eng. Chem., Process Des. Dev.*, *5*, 368 (1966).
11. K. Yahikozawa, T. Aratani, R. Ito, T. Sudo, and T. Yano, *Bull. Chem. Soc. Jpn.*, *51*, 613 (1978).
12. M. Hiraide, Y. Yoshida, and A. Mizuike, *Anal. Chim. Acta*, *81*, 185 (1976).
13. M. Hiraide, T. Ito, M. Baba, H. Kawagushi, and A. Mizuike, *Anal. Chem.*, *52*, 804 (1980).
14. T. Inakazu, K. Kobayashi, and T. Sasaki, *Bull. Chem. Soc. Jpn.*, *48*, 3008 (1975).
15. M. A. El-Tanbouly and S. E. Ghazy, *Analusis*, *18*, 89 (1990).
16. S. E. Ghazy, *Anal. Sci.*, *6*, 20 (1990).
17. R. Lemlich, *Adsorptive Bubble Separation Techniques*, Academic Press, New York, 1972, p. 276.
18. W. Stumm and J. J. Morgan, *Aquatic Chemistry*, Wiley-Interscience, New York, 1981, p. 780.
19. S. Emerson, L. Jacobs, and B. Tebo, in *Trace Metals in Seawater* (Wong, Boyle, Bruland, Burton and Edberg, Eds.), Plenum Press, 1983, p. 579.
20. S. I. Bolkin and G. S. Berger, *Izvestya Vechix Ytchebenex Zavedenia Tsvetnia Metallurgia*, No. 3 (1968).
21. A. I. Vogel, *Macro and Semimicro Qualitative Analysis*, 4th ed., Orient Longman, Bombay, 1977, pp. 41, 230.
22. T. Sasaki, K. Mochizuki, and S. Ishiwata, *Bull. Chem. Soc. Jpn.*, *55*, 3717 (1988).
23. S. Voyutsky, *Colloid Chemistry*, Mir, Moscow, 1978.

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