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Floatation-Atomic Absorption Spectrophotometric Separation and Determination of Copper

S.E. GHAZY* and M.A. KABIL
Chemistry Department, Faculty of Science, Mansoura University, Mansoura, P.O. Box 66, Egypt.

An experimental investigation is presented for the colloidal floatation of copper (II) ions, as sulfide, from aqueous solutions using sodium sulfide and oleic acid (HOL). The effects of pH, the concentrations of sodium sulfide and HOL, the reagent's order, the interference from different ions and the ionic strength have been studied. The maximum floatation efficiency of Cu^{2+} (*ca.* 100%) was obtained in a wide pH (1–8.7) range. It was found that, the order of the additive reagents, markedly affects the floatability. Both of foreign ions and ionic strength have no appreciable effect on the floatation efficiency.

INTRODUCTION

The separation of substances from aqueous solutions has drawn increasing attention due to problems of water pollution[1]. Numerous techniques exist to remove metal ions from aqueous solutions[2,3]. These techniques may involve: chemical precipitation, ion exhange, reverse osmosis, adsorption on active carbon, solvent extraction and/of floatation separation processes. Of these, the floatation separation techniques have been of considerable interest in recent years due in large part, to their ready adaptability for removing traces of toxic heavy metals from industrial effluents[4,5], their preconcentrating and analysis of trace substances[6–8]and to the fact that these floatation techniques are most effective and less expensive[9]. The use of a surfactant with or without a polyelectrolyte has been confirmed to be effective for the floatation of anions, cations and particles[10].

Cu^{2+} is important metal ion in aqueous and natural waters, because it is the most toxic species of dissolved copper to fish, plants and other aquatic organisms[11–15]. Therefore, in this investigation our attention is focused towards the removal of Cu^{2+} ions from aqueous solutions by the colloidal floatation technique with the use of sodium sulfide and oleic acid as a surfactant.

EXPERIMENTAL

All glassware was soaked overnight in 50% nitric acid, rinsed throughly before use with double distilled water. The floatatation cell was a test tube of 12 mm

inner diameter and 290 mm long with a stopcock at the bottom. Perkin-Elmer 2380 Atomic Absorption Spectrophotometer was used for Cu determination at wavelength 324.7 nm. The pH measurements were carried out with HANNA Instruments 8519, digital pH–meter.

Unless otherwise stated, all reagents used were of analaR and BDH grades. The aqueous solutions were prepared in double distilled water. Copper stock solution (17.6×10^{-2} mol l^{-1}). 26.83 gm. of $CuCl_2 \cdot 2H_2O$ was dissolved in one liter of water. Sodium sulfide stock solution (0.1 mol l^{-1}). 9.6 gm. of $Na_2S \cdot H_2O$ was dissolved in one liter of water. Oleic acid (HOL) stock solution (6.36×10^{-2} mol l^{-1}). 20 ml of HOL, food grade (d 0.895) were dispersed in one liter of kerosene.

Procedure for the floatation step

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

Concentration of Cu^{2+} ions in the underlying solution was determined by Atomic Absorption Spectrophotometer at wavelength 324.7 nm. The floatability (F%) was calculated by the following equation:

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

where C_i and C_f express the concentration of Cu^{2+} ions before and after floatation as has been described[16,17]. The measurements were carried out at room temperature, about 25°C. Each point in the results is the average of three experiments.

RESULTS AND DISCUSSION

Effect of HOL concentration

Figure 1 shows the results of flotability of Cu^{2+} plotted against HOL concentration at pH 7 without (curve a) and with (curve b) the addition of sodium sulfide. The floatability reaches its maximum value at HOL concentration ranges from 1.0×10^{-3} to 4.13×10^{-3} mol l^{-1}. The concentration of HOL in our measurements has been taken at 4.13×10^{-3} mol l^{-1}. The floatation efficiency of Cu^{2+} decreases at higher concentration 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 floatation to redispersion with an increase in the amount of the surfactant[18]. Further, the effect of additon of sodium sulfide is evident from comparison of (curve b), where the floatability of copper, ions reaches nearly 100%, with (curve a), where the floatability does not exceed 38%.

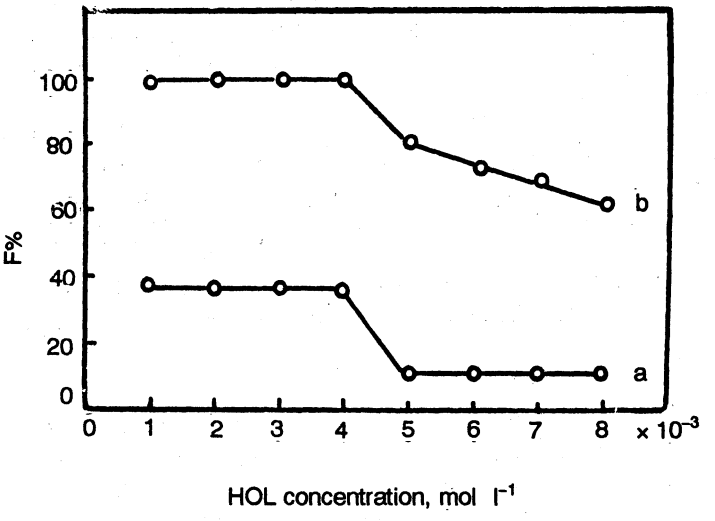

Fig. 1 Floatability of Cu^{2+} vs HOL concentrations. Cu, 1.57×10^{-5} mol l^{-1}; pH 7; (a) without Na_2S; (b) with Na_2S; 20×10^{-5} mol l^{-1}

Effect of sodium sulfide concentration

A series of experiments was performed to study the effect of Na_2S concentration on the floatability of Cu^{2+} ions at constant concentration of HOL (4.13×10^{-3} mol l^{-1}) and pH 7. The results are presents in Fig. 2. As may be seen, a floatation

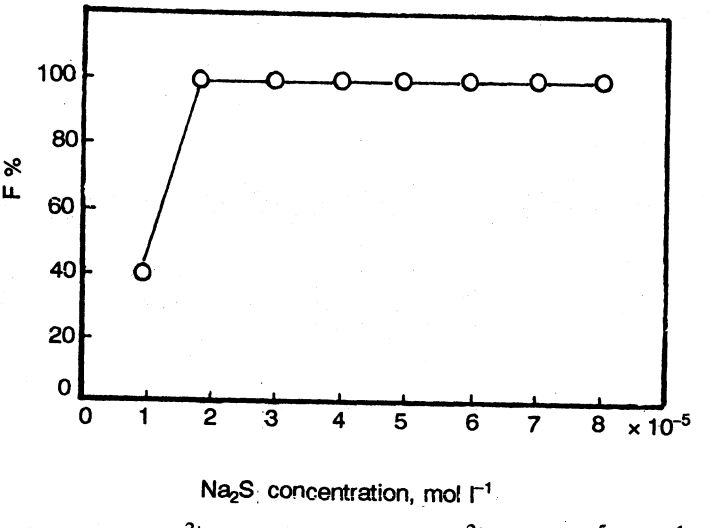

Fig. 2 Floatability of Cu^{2+} vs Na_2S concentration. Cu^{2+}, 1.57×10^{-5} mol l^{-1}, HOL 4.13

of nearly 100% is obtained at a molar ratio of sulfide: copper ion 1 : 1. This is in agreement with the formation of the colloidal precipitate of copper sulfide. During our experiments the concentration of Na_2S is fixed at 2.0×10^{-5} mol l^{-1}.

Effect of pH

It was attempted to study the effect of pH on the floatation of Cu^{2+} ions from aqueous solutions in the presence of HOL without (curve a) and with (curve b) the addition of Na_2S. The results are shown in Fig. 3.

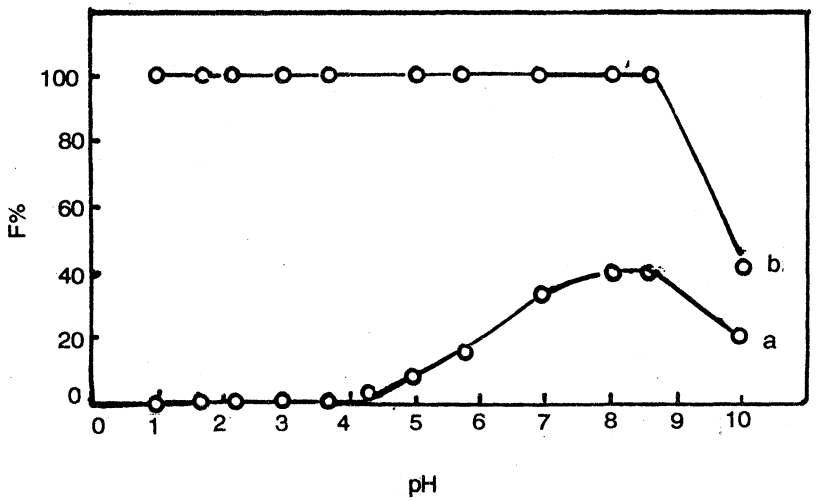

Fig. 3 Floatability of Cu^{2+} vs pH. Cu^{2+}, 1.57×10^{-5} mol l^{-1}; Na_2S, 2.0×10^{-5} mol l^{-1}; HOL, 4.13×10^{-3} mol l^{-1}.

From curve a, it is evident that Cu^{2+} ions are not floated by HOL at pH lower than 5, due to the fact that HOL begins to dissociate at pH ≥ 25.2[19]. At pH range from 5 to 7 Cu^{2+} ions may float as copper oleate. At pH around 8.7 Cu^{2+} ions may float with oleate ions as polynuclear species[20,21] according, for instance, to

$$nCu^{2+} + (n-1)H_2O \rightarrow Cu^{+}(OCu)_{n-2}OCu^{+} + 2(n-1)H^{+}$$

This may also explain the fact that large amounts of Cu^{2+} ions are removed by a small amount of surfactant. Above pH 8.7, the floatation decreases due to the formation of white precipitate and excessive foams from the HOL surfactant.

Curve b, shows that the flotation efficiency of Cu^{2+} ions is nearly 100% at a wide pH range from 1 to 8.7. this may due to the fact that Cu–S system is markedly complex[22], having colloidal properties[23] and capable of floatation with dissociated and undissociated molecules of HOL surfactant.

Effect of some foreign ions

It was attempted to float copper ions from aqueous solutions containing the following combinations: (1) Cu (II) and Pb (II); (2) Cu (II) and Hg (II); (3) Cu (II) and Cd (II); (4) Cu (II) and Mn (II); (5) Cu (II) and Zn (II); (6) Cu (II) and Co (II); (7) Cu (II) and Ni (II); (8) Cu (II) and Bi (III); (9) Mixture of all the above cations. The experiments were carried out at pH ranges from 1 to 7 with HOL in the presence of Na_2S. It was noted that the floatation efficiency of Cu (II), nearly 100%, was not affected by any of the investigated various coimbinations.

Effect of order of reagents addition

The order of addition of reagents has markedly affects the floatation of copper (II) ions. The addition of the reagents in the order: copper ions + sulfide solution + HOL surfactant is the optimum one. In the case of adding the sulfide solution as the last reagent gives a white precipitate, foaming and dispersion of the HOL surfactant with very low flotation of Cu^{+2} ions. This may due to an interaction between sulfide ions and HOL surfactant.

Effect of ionic strength

A series of experiments were conducted to study the effect of ionic strength on the floatation efficiency of Cu^{2+} ions with HOL surfactant in the presence of Na_2S. The test solutions are that of KCl, NaCl, $CaSO_4$, and $NaNO_3$. All the studied compounds have no effect on floatability of copper at different concentrations. Only $CaSO_4$ decreases slightly the flotation efficiency of Cu^{2+} ions which may due to the formation of insoluble calcium oleate and to further modifications in surface area of the precipitate[24].

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