Removal of trace Cu^{2+} from aqueous solution by foam fractionation

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ARTICLE INFO

ABSTRACT

A system for removal of Cu^{2+} from aqueous solution by foam fractionation is proposed. The effects of pH, gas flow rate, surfactant concentration and froth/solution ratio on the removal rate and the enrichment ratio were studied to optimize the conditions. The results show that the removal rate increased with gas flow rate decreased, surfactant concentration increased and the froth/solution ratio increased, and was higher at pH4.0–5.0 than at other pH value. The optimum separation conditions were pH5.0, 200 mL/min of gas flow rate, 0.15 g/L of surfactant concentration and 1.1 of froth/solution ratio. Under the optimum conditions, the removal rate was 97.2% and the enrichment was 53.0.

1. Introduction

Water pollution is nowadays a matter of deep apprehension. Many industrial wastewaters contain numerous toxic metals, such as chromium, mercury, cadmium, lead, copper, which must be removed before reuse of the water or its discharge to the environment. And as environmental regulations tighten, there is an increasing concern about the removal of metal in the effluent streams. Therefore, intense scientific research is being directed towards the implementation of novel approaches dealing with the efficient removal of toxic metals from wastewater [1,2].

Copper is an essential element but can cause adverse health effects. Copper deficiency is associated with anaemia, neutropenia and bone abnormalities but clinically evident deficiency is relatively infrequent in humans [3]. These facts have motivated some physicochemical methods for copper removal from the stream. One of the commonly used methods is precipitation [4,5]. However, a serious problem on how to remove the precipitate from the solution occurs. And when the metal concentration is low, the precipitate can't be easily formed and the metal still remain in the solution. Other commonly used processes for the removal of copper were ion exchange, chemical oxidation and reduction, filtration, and electrochemical treatment. Numbers of methods have appeared recently to deal with copper in aqueous solution by something cheap [6–11], chemical materials [12], or some microorganism [13], but the process is more complex and trace metals can't be removed.

Foam fractionation, a process in which solute species adsorbs at the gas–liquid interfaces between the dispersed phase (gas bubble) and the continuous phase (bulk liquid), is generally preferred to apply for purification of industrial solutions from traces metals due to its high efficiency, easy handling, availability of different adsorbents and low cost.

It appears from review of the source publications and monographic papers that, so far, few papers dealing with the application of foam fractionation, in order to remove copper from aqueous solution, have been reported. And the residual metal concentration was determined by the atomic adsorption spectrometry (AAS) or spectrophotometry. However, the former is of higher expense and the latter is more complex and less accurate [14].

In this study, foam fractionation of copper separation from the aqueous solution was investigated and an ion activity meter with copper electrode was used, replacing the two apparatus mentioned previously, to determine the copper concentration in the residual solution.

2. Materials and methods

2.1. Reagents

$Cu(NO_3)_2$ and Dodecyl Benzenesulfonic acid (the anionic surfactant used in this study) were of analytical grade reagent and obtained from Tianjin Wenda Chemical Co. and Tianjin Letai Chemical Co., Ltd, respectively. The feed solution of Cu^{2+} was prepared by dissolving the $Cu(NO_3)_2$ in double distilled water at the concentration of 0.05 g/L in all the experiments, with the surfactant concentration of 0.15 g/L except for the experiments on the effect of surfactant concentration.

2.2. Apparatuses

A PHS-25 pH meter, obtained from Shanghai Precision & Scientific Instrument Co., Ltd. China, was used to measure the pH values of the feed solution. An ion activity meter of PXS-215 with PCu-I copper electrode, obtained from Tianjin Shengbang Scientific Co., was used to measure the trace Cu^{2+} concentration.

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2.3. Fractionation procedure

The bubble column is composed of a cylindrical glass tube (50 mm in an inner diameter) with a sintered glass filter (porosity of 20–26 μm) mounted at the bottom of the column as a gas distributor, according to a generally used method [15–17].

Air was used as carrier gas, introduced through the distributor at 200 mL/min except for the experiments on the effect of gas flow rate, and allowed to pass through the column until foam bubbles ceased to form. Then, the residual solution in the column was collected and analyzed for the copper concentration.

The copper removal efficiency was estimated at the end of each experiment by measuring residual Cu^{2+} concentration of the residual solution in the column. Effects of several parameters on the separation efficiency of trace Cu^{2+} were studied and evaluated using the removal rate and the enrichment ratio as shown below:

$$Removal\ rate\ R = \frac{m_i - m_e}{m_i}$$

$$Enrichment\ ratio\ \beta = \frac{C_f}{C_i}$$

where m_i and m_e are the mass of copper nitrate (g) in the influent and effluent streams, respectively; C_f is the copper concentration (mol/L) in the collapsed foam, which is calculated under the assumption of the mass balance, and C_i is the original copper concentration (mol/L).

2.4. Experimental design and statistical analysis

2.4.1. Single factor experiments design

Four factors, pH, gas flow rate, surfactant concentration and froth/solution ratio, were tested for the effect of them on the removal rate and enrichment ratio and were fixed at 4.0, 200 mL/min, and 0.15 g/L, 1.1, respectively, except for the study on its effect.

2.4.2. Orthogonal experiment design

The four variable factors and the coded levels used to optimize the fractional process were shown in Table 1.

3. Results and discussion

3.1. Effect of pH on removal of trace Cu^{2+}

The effect of pH on the removal rate of trace Cu^{2+} under the conditions of pH3.0, 3.5, 4.0, 4.5, 5.0, 5.5 and 6.0 was studied and the results were shown in Fig. 1. The results show that the removal of trace Cu^{2+} was remarkably affected by pH value. As the pH value increased from 3.0 to 4.0, the removal rate and enrichment ratio sharply increased and the removal rate reached the maximum of 91.75% at pH4.0. As the pH value increased from 4.0 to 5.0, the removal rate and enrichment ratio were approximately constant. As the pH value was increased from 5.0 to 6.0, the removal rate sharply drop, however, the enrichment ratio increased and reached the maximum of 27.58 at pH6.0. In the aqueous solution the surfactant

Table 1
Orthogonal test factors and their coded levels.

Factor	Level		
	1	2	3
A. pH	3	4	5
B. Gas flow rate/(mL/min)	150	200	250
C. Surfactant concentration/ (g/L)	0.10	0.15	0.20
D. Froth/solution ratio	0.80	1.10	1.40

Every experiment was replicated three times and the mean values were reported.
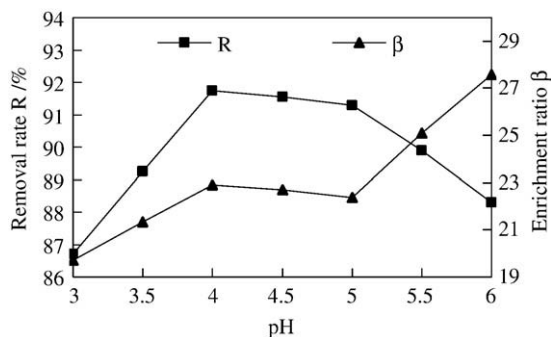
Fig. 1. Effect of pH on the removal of trace Cu^{2+}. Gas flow rate was 200 mL/min; surfactant concentration was 0.15 g/L; froth/solution ratio was 1.1.

dissolved can ionize into H^+ and R^-. It was expected that the chelates resulting from reactions between H^+ and R^- would compete with reactions between Cu^{2+} and R^-. So it is less effectively for the separation at pH3.0 due to the higher concentration of H^+, leading to the low removal rate and the low enrichment ratio. Fig. 1 can also indicate that the pH range of Point of Zero Charge (PZC) of the chelates formed by Cu^{2+} and R^- is from 4.0 to 5.0, at the pH of which the chelates can precipitate and be taken out of the column by the foam more easily. As the pH increased to 6.0, some Cu^{2+} may attach to OH^- mainly because Cu^{2+} can be best precipitated as hydroxides at pH6.5 [18], leading to a lower removal rate. Additionally, we observed that the stability of the foam in the column was declining dramatically with pH increasing, and above pH 6.0 the foam would collapse more easily, which resulted in worse separation. It was difficult to get a good separation so that the results were not reported in this paper. We also suggested that the separation should be carried out at acidic conditions.

3.1.1. Effect of gas flow rate on removal of trace Cu^{2+}

The effect of the gas flow rate on the removal of trace Cu^{2+} under the conditions of gas flow rate 150, 175, 200, 225, 250, 275 and 300 mL/min was investigated and the results were shown in Fig. 2. The data presented in Fig. 2 indicate that the removal rate and enrichment ratio were highly affected by the gas flow rate. As gas flow rate decreased, both the removal and enrichment ratio increased, because low gas flow rate can increase the stability of foam that could contribute to the removal rate [19]. Whereas when gas flow was below 200 mL/min, the increase in the removal rate was not significant, and the operation time will increase. Therefore, the suitable gas flow rate was proposed at 200 mL/min.

3.1.2. Effect of surfactant concentration on removal of trace Cu^{2+}

The results obtained for the effect of the surfactant concentration on the removal of trace Cu^{2+} with surfactant concentration of 0.050,
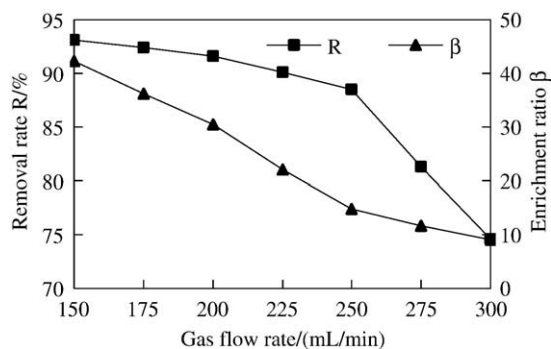
Fig. 2. Effect of gas flow rate on the removal of trace Cu^{2+}. pH4.0; surfactant concentration was 0.15 g/L; froth/solution ratio was 1.1.