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Cascade sulfidation and separation of copper and arsenic from acidic wastewater via gas−liquid reaction

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Abstract: Copper and arsenic in acidic wastewater were separated by cascade sulfidation followed by replacement of arsenic in the precipitates by copper in the solution which was realized by recycling precipitates obtained in the first stage into the initial solution. The effects of reaction time, temperature and H_2S dosage on copper and arsenic removal efficiencies as well as the effects of solid-to-liquid ratio, time and temperature on the replacement of arsenic by copper were investigated. With 20 mmol/L H_2S at 50 °C within 0.5 min, more than 80% copper and nearly 20% arsenic were precipitated. The separation efficiencies of copper and arsenic were higher than 99% by the replacement reaction between arsenic and copper ions when solid-to-liquid ratio was more than 10% at 20 °C within 10 min. CuS was the main phases in precipitate in which copper content was 63.38% in mass fraction.
Key words: acidic wastewater; copper; arsenic; cascade sulfidation; separation

1 Introduction

Many industrial processes, especially in the mining and metallurgical processing industry, discharge acidic effluents contain significant amounts of metals such as copper, nickel, zinc, lead and arsenic [1−4]. Copper is often associated with arsenic in mixed sulphide minerals such as enargite (Cu_3AsS_4) and tennantite ($Cu_{12}As_4S_{13}$) [5], therefore, among theses heavy metals, Cu and As are found to behave similarly and exist simultaneously in the wastewater [6]. Arsenic contamination has greatly threatened water safety due to its high toxicity and carcinogenicity [7,8]. However, copper in the wastewater is still valuable product that can be recovered from the residual water, which is beneficial to the reuse of the purified water to the production process [9].

The undesirable effects of copper and arsenic can be avoided after treatment prior to discharge [10], by which the recovery of copper can be also achieved. While the first challenge is the effective removal and separation of copper and arsenic [11,12]. In the case of liquid effluents, there are many methods available for the removal of heavy metals: chemical precipitation, adsorption, coagulation, ion-exchange, microbial reduction, and so on [13−21]. On the other hand, dissolved-air flotation was used to recover and separate heavy metals. STALIDIS et al [22] separated copper, zinc and arsenic ions from dilute aqueous solutions by using the dissolved-air technique for the production of fine gas bubbles. It seems to be complex and expensive for the treatment of acidic wastewater. Sulfide precipitation is indeed an effective process for the treatment of toxic heavy metals ions [23,24]. One of the primary advantages of using sulfides is that sulfide precipitation process can achieve a high degree of metal removal over a broad pH range. Metal sulfide sludge also exhibits better thickening and dewatering characteristics than the corresponding metal hydroxide sludge [25]. BHATTACHARYYA et al [26] separated arsenic and

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other heavy metals by using sodium sulphide. The removals of Cd, Zn and Cu from the actual wastewaters are greater than 99%, and those of As and Se are 98% and >92%, respectively. However, it is H_2S that reacts with heavy metals by gas−liquid reaction as sulfur exists almost in the form of H_2S rather than S^{2-} and HS^- in acid conditions. It takes 5−10 times excess of theoretical amount of sodium sulphide, moreover, a lot of hydrogen sulfide gas escapes, which leads to serious secondary pollution [27].

Gas−liquid sulfidation reaction was proposed in this work to constantly break the balance between hydrogen sulfide and sulfur ions and intensify dynamics process, achieving the high sulfidation efficiency with low cost. H_2S was controlled and recycled in a closed system. The objective of this work is to separate copper and arsenic from wastewater by sulfide precipitation and replacement of arsenic in the precipitates by copper in the solution, from which copper is concentrated in the precipitate and recovered. The feasibility of sulfidation and separation of copper and arsenic was analyzed by thermodynamic calculation first. Secondly, the effects of time, temperature and sulfide dosage on copper and arsenic removal efficiencies were investigated, followed by influence of solid-to-liquid ratio, time and temperature on the replacement of arsenic by copper.

2 Experimental

2.1 Reagents

Experiments were carried out with simulated solution. Analytical grade reagents were used in experiments. $CuSO_4·5H_2O$ and $Na_2HAsO_4·12H_2O$ were used for preparing certain concentrations of the solutions. pH value was adjusted by 0.05 mol/L H_2SO_4 and 0.1 mol/L NaOH solution. Gaseous sulphide source (H_2S) was generated by reaction of FeS and HCl.

2.2 Experimental design

The experimental program was divided into two stages. In the first stage, copper and arsenic were primarily separated by sulfide precipitation. The schematic diagram of the experimental apparatus is shown in Fig. 1.

All experiments were operated at time of 0.5−4 min, temperature of 24−60 °C, and sulfide dosage of 0−75 mmol/L in order to investigate the effect of time, temperature and sulfide dosage on removal efficiencies of arsenic and copper, respectively. In the second stage, precipitates obtained in the first stage were recycled to the initial solution to improve the grade of copper in the precipitates through the replacement of arsenic by copper. Investigations on the effect of liquid-to-solid ratio, time and temperature on the removal efficiency were conducted. The removal efficiency was defined by

$$\eta = \frac{C_{i0} - C_i}{C_{i0}} \times 100\% \quad (1)$$

where η is the removal efficiency, C_{i0} is the copper or arsenic concentration in the initial solution, C_i is the copper or arsenic concentration in the solution after reaction under certain conditions.

2.3 Experimental procedures

Gaseous sulfide source (H_2S) generated was collected by displacement of water. Two-way valve was turn off at first. The gas tank was filled with the saturated H_2S solution and sealed with paraffin. Gaseous sulfide generated in three-necked flask was then introduced into the tank. Solution in the gasholder was pushed into the fluid reservoir when the two-way valve was opened. A certain volume fraction of H_2S gas was obtained by introducing nitrogen into the gasholder when the pressure gauge of cylinder was adjusted to the specified pressure with nitrogen cylinder open. The

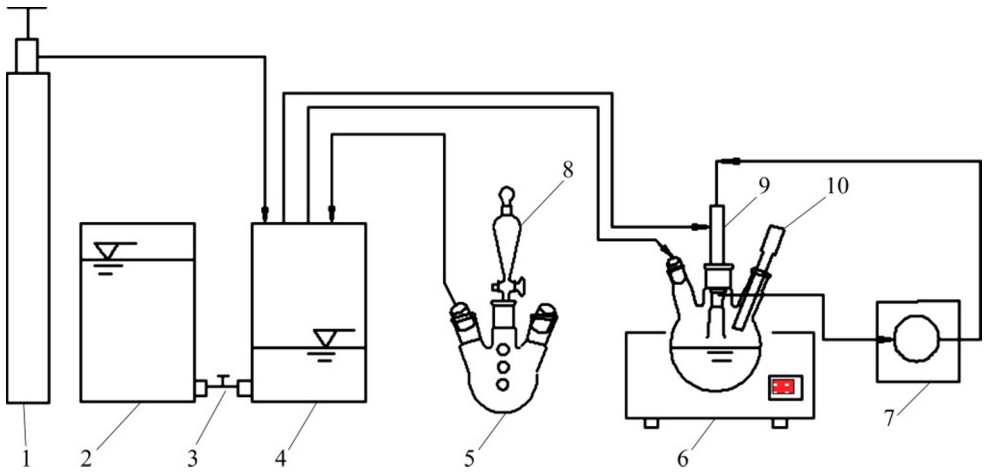

Fig. 1 Schematic diagram of experimental apparatus (1—Nitrogen cylinder; 2—Fluid reservoir; 3—Two-way valve; 4—Gasholder; 5—Gas generating bottle; 6—Temperature controller; 7—Peristaltic pump; 8—Separating funnel; 9—Reactor; 10—pH meter)