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Factors affecting crystallization of copper sulfide in fed-batch fluidized bed reactor

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ABSTRACT

This work has assessed factors affecting crystallization of copper sulfide (CuS) under batch conditions and in fed-batch fluidized bed reactor (FBR) using calcium-coated sands as a seed material. Compared with using sodium sulfide nonahydrate as a sulfidation reagent, larger CuS crystals were produced from sodium sulfide pentahydrate, most likely because of the lower surface charge. Due to the partial oxidation of sulfide in the pentahydrate form, the optimum molar ratio of Cu^{2+} to S^{2-} was found to be 1:2, higher than the theoretical ratio. Crystal growth and aggregation were further increased by using calcium ion as a cross-linker among the CuS fines (<100 nm), resulting in an additional 30% decrease in Cu^{2+} concentrations from the effluent of fed-batch FBR. The efficacy of CuS crystallization was also remarkably dependent on the operating factors, i.e., the resting height of the seed material and recirculation rate. Under optimal conditions, >95% of the initial Cu^{2+} (100 mg Cu^{2+}/L) was successfully transformed to CuS crystals within 120 min. The size and crystallinity of the star-shaped CuS crystals were confirmed by FEG–SEM and XRD analyses, respectively. Principal component analysis indicated that the resting height and the seed type were the primary parameters affecting CuS crystallization in the fed-batch FBR.

1. Introduction

Among the common heavy metals, free ionic copper is highly toxic to human and ecosystem health. A direct relation between the concentration of free copper ion and the biological effects has been demonstrated for microalgae and phytoplankton (Sunda and Guillard, 1976; Winner and Gauss, 1986). In 1993, the World Health Organization set a provisional guideline of 2 mg/L for maximum copper content in drinking water. Thus, copper pollution and its removal from water and wastewater have received a great deal of attention during the last several decades. In wastewater, copper is present over a wide concentration range varying from sub-ppb to ppm. For example, copper concentrations in chemical–mechanical polishing wastewater from semiconductor fabrication processing were found to be in the range 45–120 mg/L (Lai and Lin, 2003).

Among separation and refinement technologies of metals, crystallization has been technologically advanced from simple ion removal to value adding process, e.g., industrial manufacturing of salt and sugar, semiconductors, and pharmaceuticals (Demopoulos, 2009). Sulfidation, one of the crystallization reactions, is a well-known process for metal fixation associated with the biogeochemical sulfur cycle (Widdel et al., 1992). Lewis (2010) noted the differences in reaction characteristics of various metals, suggesting the importance of metal sulfidation in hydrometallurgical treatment of ores and effluents. Recently, sulfidation of heavy metals such as copper, zinc, and lead was conducted in fluidized bed reactors (FBRs) (Lee et al., 2004; Lee and Yang, 2005; van Hille et al., 2005; Mokone et al., 2012). Most of these metals were successfully recovered in FBRs under supersaturated conditions. However, Mokone et al. (2012) reported that copper is more difficult to crystallize via sulfidation than other metals (i.e., zinc and lead) because of the small size of CuS particles (ca. 100 nm) and highly charged surfaces (ca. −50 mV). Luther et al. (1996) also pointed out that recovery of CuS is challenging, because copper tends to be reduced under sulfidic conditions, resulting in the formation of bisulfide, sulfide, and polysulfide complexes.

In this study, the methods for improving CuS crystallization yields by employing calcium (Ca)-coated sand as a seed material and operating the FBR in a fed-batch mode were employed. Several batch experiments were performed to investigate the effects of the extent of hydration on copper sulfidation using $Na_2S\cdot5H_2O$ and $Na_2S\cdot9H_2O$ at various pH values. Other operating parameters of the fed-batch FBR such as Cu^{2+} to S^{2-} molar ratios, types of seed, seed height, and recirculation rate

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with respect to residual copper concentration in the supernatant were then optimized. Finally, the contribution of each factor to the overall crystallization process using a statistical method was also evaluated.

2. Materials and methods

2.1. Chemicals

All the reagents ($CuSO_4 \cdot 5H_2O$, $Na_2S \cdot 5H_2O$, $Na_2S \cdot 9H_2O$, and $CaCl_2$) used in this study were analytical grade and used as received from Sigma-Aldrich Korea, Ltd. (Yongin, Korea). All solutions were freshly prepared with deionized (DI) water (>18 MΩ cm; Millipore, Billerica, MA, USA) before each experiment. Due to the hygroscopic nature of the salts, $Na_2S \cdot 5H_2O$ and $Na_2S \cdot 9H_2O$ were used after oven-drying for 30 min at 60 °C. The solution pH was adjusted to the desired value using 0.1 M HCl or 0.1 M NaOH.

2.2. Selection of crystallizing reagent

2.2.1. Speciation of sulfur in two different hydration states

Changes in total dissolved sulfide ($S^{2-} + HS^- + H_2S$ (aq)) and sulfate (SO_4^{2-}) concentrations in two different sulfidation reagents, $Na_2S \cdot 5H_2O$ and $Na_2S \cdot 9H_2O$ with time over 1 h were measured using a sulfide ion-selective electrode (Orion 94-16; Orion Research, Inc., Cambridge, MA, USA) and an ion chromatography (Dionex, Sunnyvale, CA, USA), respectively. All experiments were conducted in triplicate at room temperature (25 ± 2 °C).

2.2.2. Surface charge and size distribution of CuS crystals

The surface charge of CuS at various pH values was evaluated by conducting a batch equilibrium experiment: 4 mL of 30 mM Na_2S solution was added to 40 mL of 1.5 mM $CuSO_4$ solution and the initial pH (pH_i) of the solution was adjusted from 1.0 to 6.0 with 0.1 M HCl or 0.1 M NaOH. The values of pH higher than 6 were not considered because this would result in the formation of insoluble $Cu(OH)_2$ precipitate. The suspensions were sonicated at 20 °C for 5 min and then the zeta potential of each sample in the equilibrated solution was measured using a zeta potential analyzer (Zetasizer Nano ZS90; Malvern Instruments, Malvern, United Kingdom). To determine the effects of Ca^{2+} and various types of seed on surface charge, samples varying in these respects were prepared using the same procedure.

2.3. Batch kinetics for CuS crystallization

Batch kinetic experiments were carried out to determine the reaction kinetics of CuS crystallization. Forty milliliters of 30 mM $Na_2S \cdot 5H_2O$ solution were added to 400 mL of 1.5 mM $CuSO_4$ solution. The mixture was then agitated at 150 rpm using a horizontal shaker. An aliquot of the sample was taken from the bottle and filtered through a 0.45-μm pore size cellulose acetate membrane filter (Whatman, Germany) prior to conducting ICP-OES (Vista PRO; Varian Inc., Palo Alto, CA, USA) analysis for total copper (i.e., the sum of Cu^{2+} and CuS presented as fines) and calcium. Another set of batch experiments was performed to verify the effect of Ca on the crystal growth of CuS. These samples were prepared following the same procedures described above with the addition of 1 mL of 1000 mg Ca^{2+}/L $CaCl_2$ solution.

The X-ray diffraction (XRD) patterns for the recovered copper sulfide were recorded using a D/max-2500 X-ray diffractometer (Rigaku Corp., Tokyo, Japan) using Cu K_α radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 100 mA with a scan speed of $2° \min^{-1}$ over 10–90°. The morphologies and compositions of the selected samples were also examined using a field emission gun–scanning electron microscopy (FEG–SEM, Inspect F50; FEI, Eindhoven, The Netherlands) operated at 10–20 kV, equipped with an energy dispersive spectroscopy (EDS) analyzer. All samples were dried in a vacuum oven for 6 h at 60 °C before analysis.

2.4. Optimization of operating conditions for fed-batch fluidized bed reactor

2.4.1. Preparation of seeds

Various materials, including fine, coarse, and Ca-coated sands, were introduced as seeds into the fed-batch FBR. Joomoonjin sand, widely used as filtration sand in Korea, was employed as a seed. The sand was separated into two size classes, fine (passing No. 6 sieve) and coarse (retained on No. 6 sieve). The particle size of the fine and coarse sand was less than 1 mm and 1–5 mm, respectively. Prior to use, all sands were washed with 0.1 M HCl to remove impurities from the surface. The Ca-coated sand was prepared by placing the both types of sand in 1 M $CaCl_2$ solution overnight with stirring. After washing thoroughly with DI water, the sands were dried at 60 °C for 12 h and held in a desiccator until use.

2.4.2. Fed-batch fluidized bed reactor operation

A fed-batch FBR with an inner diameter and height of 20 and 200 cm, respectively, was constructed using acrylic plastic (Fig. S1). Four different types of seeds, i.e., fine, coarse, and Ca-coated fine and coarse sands, were placed in the FBR at various depths of 10, 20, 30 and 40 cm. In the FBR, the solutions were recirculated from the top to the bottom at various flow rates of 25, 125, 250, and 470 mL/min. Throughout the experiments, 600 mL of 1.5 mM $CuSO_4$ (ca. 100 mg Cu^{2+}/L) and 60 mL of Na_2S solutions were fed to the reactor bottom at the beginning of each run, using various molar ratios of Cu^{2+} to S^{2-} of 1:0.5, 1:1, 1:2, and 1:5.

The efficacy of CuS crystallization for both the batch and fed-batch FBR experiments was calculated according to the following equations, modified from Mokone et al. (2012);

$$\text{Process efficacy}(\%) = \frac{Cu_{in} - Cu_{out,filtered}}{Cu_{in}} \times 100 \qquad (1)$$

$$\text{Conversion}(\%) = \frac{Cu_{out,total} - Cu_{out,filtered}}{Cu_{out,total}} \times 100 \qquad (2)$$

where Cu_{in} is the initial copper concentration and the concentration in the influent in the batch and fed-batch experiments; $Cu_{out,filtered}$ is the copper concentration in the effluent filtered through 0.45-μm filters; and $Cu_{out,total}$ is the copper concentration in the effluent without filtration.

3. Results and discussion

3.1. Changes in speciation of sulfur in water depending on hydration state

Sulfur, used as a crystallizing reagent in this study, is an element with variable oxidation states. Since the pK_{a2} of H_2S is fairly high (ca. 13), bisulfide (HS^-) and dissolved hydrogen sulfide (H_2S (aq)) are the dominant species in water at neutral pH and room temperature. Depending on the hydration state, several types of sodium sulfide are available; pentahydrate ($Na_2S \cdot 5H_2O$) and nonahydrate ($Na_2S \cdot 9H_2O$) are the most common. Changes in the speciation and fractionation of sulfur complexes in 0.6 mM Na_2S solutions prepared with these two hydration states, $Na_2S \cdot 5H_2O$ and $Na_2S \cdot 9H_2O$, are shown in Fig. 1. In both cases, the loss of gaseous H_2S was negligible (<3%). During exposure to the atmosphere for 120 min, more than 50% of the total dissolved sulfide in the $Na_2S \cdot 5H_2O$ solution was readily oxidized to SO_4^{2-} and reached equilibrium within 5 min while only ca. 1.5% of total sulfide was oxidized to SO_4^{2-} in the $Na_2S \cdot 9H_2O$ solution, indicating that chemical stability might be strongly affected by its hydration state. In some cases, the degree of hydration can affect the steric structure, leading to conformational change. As a result, this could affect the chemical stability (Sagarik and Dokmaisrijan, 2005). Thus, the availability of the total sulfide ion should be considered when calculating the required dose of $Na_2S \cdot 5H_2O$ as a sulfidation reagent.