Recovery of copper as clean nanoparticles of CuS from acid rock drainage and mine process water

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Abstract

Metal-sulfide micro and nanoparticles have been recently researched due to their important technological properties as advanced nanomaterials in many industrial fields. Copper sulfides (CuS) have been demonstrated as promising candidates for novel applications, including the development of or use in photocatalysis, solar cells, antibacterial activity, and novel applications in the biomedical area, e.g, as photothermal agents for cancer treatment.

In this study, we evaluated the synthesis of copper sulfide (CuS) nanoparticles through a simple method based on the formation of biogenic H_2S from a low-pH sulfidogenic bioreactor. A synthetic solution (SL) containing copper sulfate, acid rock drainage (ARD), and a bioleach liquor (PLS) were used as a source of soluble copper to form nanoparticles of CuS.

For the SL and ARD, nanoparticles of CuS with a diameter between 30–45 nm were obtained in a simple one-step method contacting the biogenic H2S with copper-containing water. The PLS was filtered and transferred into a second vessel to increase the pH to 3.5 with NaOH to promote the precipitation and removal of ferric iron. The iron-free PLS was contacted with biogenic H2S produced by the sulfidogenic bioreactor. Images obtained by the scanning electron microscopy (SEM) of the particles showed spherical-like shapes with a diameter of ≈ 60 nm, and energy-dispersive x-ray spectroscopy (EDS) analysis demonstrated that the composition was mainly Cu and S. X-ray photoelectron spectroscopy (XPS) analysis of the nanoparticles obtained for each mine water showed that the main contribution was associated to Cu-S bonds, confirming the recovery of clean and valuable CuS nanoparticles using biological H_2S generated from a low pH- sulfidogenic bioreactor with minimal engineering complexity.

This study demonstrated the feasibility of producing high-value nanomaterials which can be easily scalable to produce "clean" nanoparticles free from bacterial cells.

Introduction

Mining influenced water (MIW) can contain elevated concentrations of acidity, transition metals and sulfate that can cause severe environmental issues. More specifically, the generation, migration, and pollution caused by acid rock drainage (ARD) is considered of global concern. The conventional technology to treat ARD is via chemical neutralization, a process whereby basic materials such as lime are mixed with ARD to raise its pH and remove the bulk of (semi-)metals via precipitation of metal hydroxides. Although effective, this approach requires not only the continuous supplies of chemical reagents, energy and manpower but also the effective disposal of sludge generated by the process (Hernandez et al. 2022). Moreover, this treatment does not allow the recovery of valuable metal contents. In one study, biogenic hydrogen sulfide gas (H_2S) produced by a sulfidogenic metal remediation process was used to produce zinc sulfide quantum dots possessing optical properties analogous to those prepared commercially (Murray et al. 2017). The synthesis of copper sulfide (CuS) nanoparticles has attracted increasing attention due to their important technological properties for advanced nanomaterials including novel applications

in the biomedical area, e.g., as photothermal agents for cancer treatment (Colipai et al. 2019; Segura et al. 2023). Here we describe the biosynthesis of CuS nanoparticles through a simple method based on biogenic H_2S ($Cu^{2+} + H_2S \rightarrow CuS_{(s)} + 2H^+$) produced from a low pH sulfidogenic bioreactor. We demonstrate the generation of CuS nanoparticles from different sources and to compare the type of particle obtained. The synthetic solution (SL) containing copper sulfate, acid rock drainage (ARD) and a complex bioleach liquor (PLS) were used as a source of soluble copper to form nanoparticles of CuS.

Materials and Methods

Synthesis of CuS Nanoparticles

CuS nanoparticles were synthesized by combining biogenic H2S with a synthetic aqueous solution of 5 mM (318 mg/L) Cu (SL) and a "real" ARD (12 mM of Cu; 762 mg/L). In addition, a complex bioleach liquor (PLS) with 1 mM (64 mg/L) Cu was filtered through a 0.22 μm membrane and transferred into a second vessel to increase the pH to 3.5 with NaOH to promote the precipitation of ferric iron. The iron-free PLS was then contacted with biogenic H2S. For the generation of H2S, a 2.3-L working volume bioreactor (Fermac 200; Electrolab Biotech, Tewkesbury, United Kingdom) was operated as an upflow biofilm continuous sulfidogenic bioreactor. The moderately low pH bioreactor fed with sulfate (≈ 30 mM) was used to produce H2S based on a similar system (Gonzalez et al. 2019). The sulfidogenic bioreactor was dominated by the sulfate-reducing genera Desulfomicrobium, Desulfobacterium and Desulfovibrio, which were obtained from blackened sediment in different ponds in the Salar de Huasco, Chile., The bioreactor was initially maintained in batch mode for 20 days before starting the operation under continuous flow mode and adding autotrophic basic salts and trace elements (Gonzalez et al. 2019) supplemented with 45 mM of lactate as the electron donor and carbon source, with a hydraulic retention time (HRT) of 25 h. The system was maintained at 30 °C and stirred at 50 rpm. The H2S produced by the bioreactor was removed using an oxygen-free nitrogen stream (OFN), keeping the flow rate at 100 mL/min. The H2S was delivered to an off-line vessel containing Cu (present in the SL, ARD, and PLS).

Characterization techniques

The morphology and size of the synthesized nanoparticles were observed with a transmission electron microscope (TEM; Hitachi HT7700, 120 kV) and field emission scanning electron microscopy (FE-SEM) in a JEOL JSM-7100F electron microscope, equipped with energy-dispersive X-ray spectrometry (EDS; X-MAXN, OXFORD). X-ray photoelectron spectroscopy (XPS) was carried out in an ultra-high vacuum chamber using a hemispherical analyzer (SPECS Phoibos 100MDC-5, Berlin, Germany).

Results and Discussion

Fig. 1 shows FE-SEM and TEM images of the two kinds of copper sulfide nanoparticles. CuS nanoparticles synthesized from a synthetic aqueous solution (SL, Fig. 1a and 1c) showed a high dispersion, with a main particle size of 37 ± 9 nm and a spherical-like shape. Similarly, CuS nanoparticles recovered from the real ARD (Fig. 1b and 1d) showed a very similar size (41 ± 12 nm) and shape. However, the nanoparticles from the ARD solution showed a higher degree of agglomeration, which makes it somewhat difficult to distinguish individual particles. The images demonstrated that using real ARD as a copper source produced CuS nanoparticles with similar shape and size as those produced from a synthetic copper source.

Chemical analysis of CuS nanoparticles from the SL and ARD solutions by XPS demonstrated the presence of four elements: C, O, Cu and S, suggesting that only Cu is precipitated during the first hours of sparging with H2S, due to the low solubility of this metal at low pH (data not shown). For the PLS, after increasing the pH to 3.5 to promote the precipitation of ferric iron, the supernatant was recovered to obtain an iron-free PLS solution. The biogenic H_2S was quickly delivered to the iron-free PLS solution, promoting the precipitation of CuS nanostructures. Fig. 2a shows an SEM image of the resulting CuS precipitates,

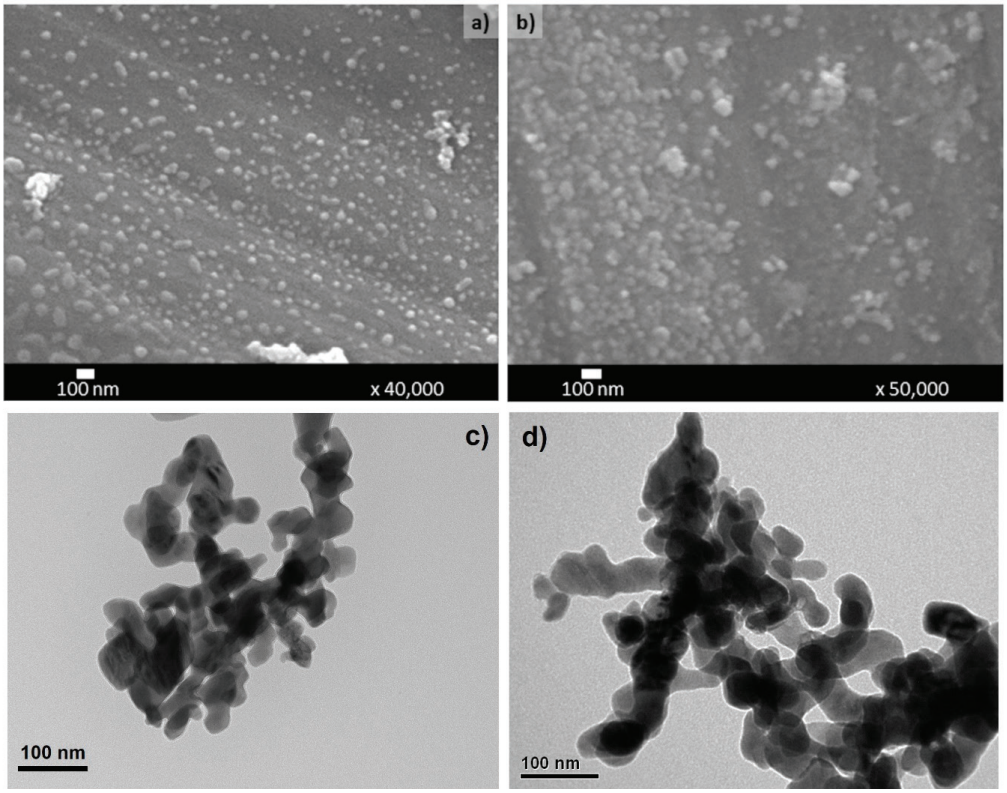

Figure 1 *FE-SEM images of a) CL and b) ARD nanoparticles. TEM images of c) SL and d) ARD.*

exhibiting nanoparticles with a spherical-like shape, a mean diameter of 60 nm, and a tendency to agglomerate. EDS analysis of the particles shows mainly the presence of Cu and S (Fig. 2b), with some residual O and K, confirming the formation of copper sulfides. XPS characterization was also performed to identify the kind of copper sulfide obtained. Fig. 2c shows the Cu 2p band in which the main contribution appears at 932.1 eV of binding energy, corresponding to Cu-S bonds. In addition, another minor contribution appears at 933.6 eV of bind energy that can be correlated to non-stoichiometric copper oxides. CuS nanoparticles showed similar physicochemical properties for the different concentrations and water sources used in this study. The nanoparticles obtained from the ARD (the higher concentration used in that work) showed slightly larger particle sizes but similar crystallinity, though additional studies should be carried out to examine the potential application using higher concentrations of dissolved copper (above 1000 mg/L).

Conclusions

This study provides the proof-of-concept for an approach of recovering copper as CuS nanoparticles from synthetic laboratory and mine water sources using biogenic H_2S. The product can be made in a scalable way that produces CuS nanoparticles that are free of bacterial cells and that harnessed a continuous sulfidogenic process to generate H_2S.

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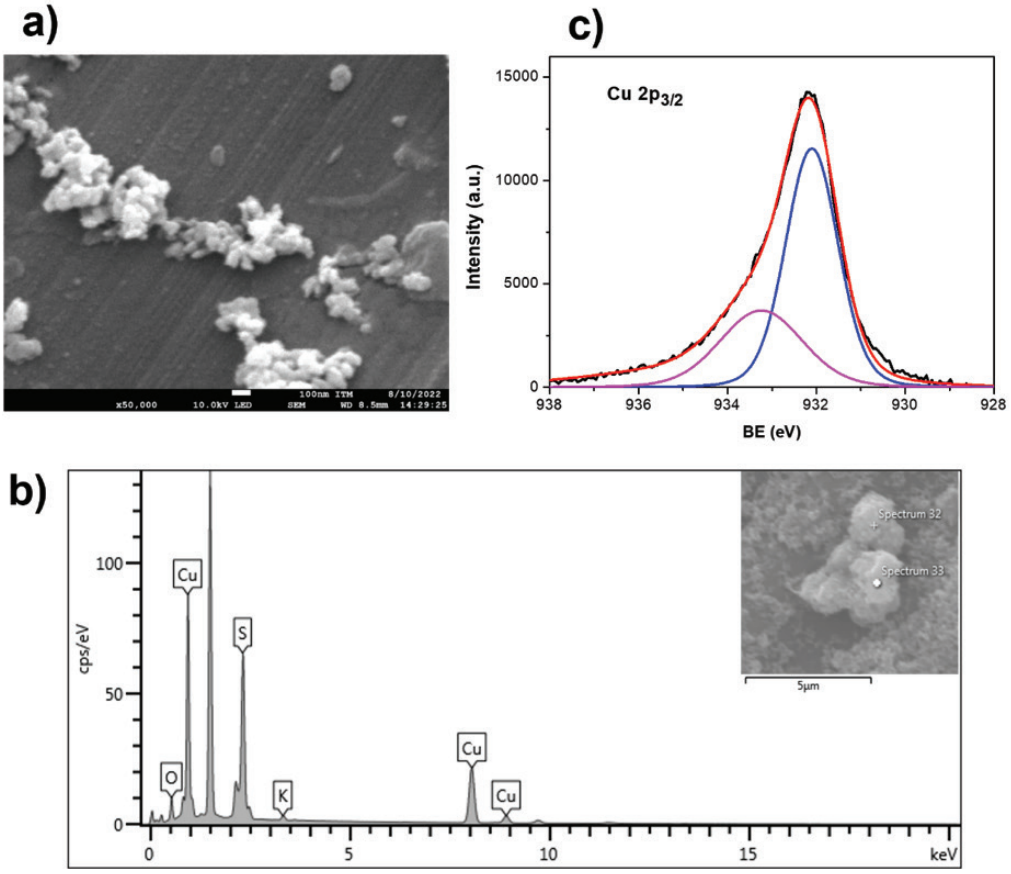

Figure 2 *(a) SEM image of CuS nanoparticles recovered from the PLS; (b) EDS spectrum of CuS nanoparticles with a SEM image of the CuS particles; (c) XPS spectrum showing the Cu 2p band*

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