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A procedure for processing of pregnant leach solution (PLS) produced from a chalcopyrite-ore bio-heap: CuO Nano-powder fabrication

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ABSTRACT

The present research work describes a facile and industrial-friendly procedure for producing high quality CuO nano-powder from a PLS of a low-grade chalcopyrite-ore bioleaching. The PLS containing lower than about 1 g Cu/L (obtained from the ore bioleaching) was used as the feed for the procedure in which firstly the iron and other impurities was removed from the PLS, and next the pure copper–ammonia complex was selectively formed from the PLS. Then, the complex was transformed to the precursor (Copper Hydroxide Sulfate Hydrate ($Cu_{2.5}(OH)_3(SO_4)\cdot(H_2O)_2$)) at the room temperature. Finally, the precursor was dried at 60 °C overnight to obtain pure CuO nano-powder (average crystalline size of about 19 nm). The results were confirmed by the characterization analyses: XRD, SEM/EDS, elemental mapping, TEM, FTIR, chemical analyses, and XRF.

1. Introduction

According to the 3D block model of Sarcheshmeh copper complex, about 2700 million tons of ore with the average copper grade of lower than 0.49% have been recently explored at the complex, approximately 700 million tons of which are related to the low-grade chalcopyrite ore. The copper content of this low-grade part of the ore is in the range of 0.15–0.3%. (Bio) processing of such a huge amount of low-grade ore has caused some serious problems for the complex, some of which are: tremendous economical and technical problems in the processing of such low-grades, and also more importantly lower copper-cathode-production efficiency from such a low-concentrated PLS in the solvent extraction and electro-winning (SX-EW) factories.

The main energy-consuming part of the (bio) leaching processes is related to SX-EW (Marsden, 2008; Peacey et al., 2004). The process SX-EW also suffers from environmental pollutions because of the massive organic material utilization (Ochromowicz and Chmielewski, 2011) and organic entrainment problems (Allen et al., 1998). Consequently, alternative processes instead of the conventional SX-EW are of very importance in that the efficiencies of the SX-EW for such low-concentrated PLSs are very low, and in many cases make it uneconomical to process. More particularly, innovative processes to exploit all the potential capacities of PLS such as producing value added CuO nano-powder, and producing iron-rich by-products (the mixtures of iron oxides, oxyhydroxide and oxyhydroxysulphate (schwertmannite, goethite, and jarosite)) may be main solutions to the increasing problems associated with the hydrometallurgical processing of the mentioned low-grade ores.

CuO nano-powder has been synthesized by many reported techniques, some of which are as follows: To obtain mono-dispersed nano-crystals of copper oxide in 7–30 nm, aqueous ammonium carbonate solution (0.3 M) has been rapidly added to 300 ml of aqueous copper acetate ($Cu(OAc)_2$) solution (0.05 M) to synthesize the precursor $CuCO_3\cdot Cu(OH)_2$, the annealing processing of which at different temperatures has produced the desired distributions of CuO nano-particles (Fan et al., 2004). The oriented CuO nanowire films have been synthesized by using a simple method in which the direct heating of the pure copper plates in air has produced the films. By using this method, a black layer of the nano-wires has been formed on the substrate at temperature range of 390–430 °C in reaction times of one day to three days (Zhu et al., 2005). Using different synthesizing conditions and various chemicals, CuO nano-crystals with different shapes, i.e. irregular nanoparticles, nano-belts and nano-platelets have been synthesized. The catalytic properties of as-synthesized nano-architectures strongly depend on their shapes (Zhou et al., 2006). Jia et al. (2009) have described a promising method to synthesize CuO nano-spheres by using urea (0.025 M) and copper acetate (0.025 M), the heating of which at 121 °C for 40 min has produced the nano-spheres. Usual methods have been recently reported for production of CuO nano/

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micro-structures, some of which are: high temperature decomposition (Bakhtiari and Darezereshki, 2011), electro-deposition (Modaresi et al., 2015), gas–solid reaction (Dianzeng et al., 1998), and sonochemical synthesis (Anandan et al., 2012). The disadvantages of the mentioned methods are reactions in high temperatures, long reaction times, expensive apparatus, or complex process. Therefore, the hydrothermal process, the advantages of which are low temperature, simple equipment, environmentally safe process, and the ease of scale-up production, have received more attention as a wet chemical process in which the reactions occur in solutions (Jia et al., 2009; Suea et al., 2011).

A wide range of applications related to CuO nanoparticles has been reported in the associated literature, several of which are as follows: manufacturing sensors for gases such as methanol (Tiong et al., 2014; Zhang et al., 2006), removing arsine impurities from gases containing arsine and hydrogen sulfide (Johnson and Nowack, 1986), applying as antibacterial material (Gedanken et al., 2011; Hans et al., 2013; Aruoja et al., 2009; Rena et al., 2009), utilizing CuO nano-structures in high-tech materials such as dye-sensitized solar cells (Anandan et al., 2005), self-Cleaning materials (Guo et al., 2011), and Li-ion batteries (Waser et al., 2013), sensing violet light using optoelectronic properties (Ko et al., 2014), catalyzing the reactions such as H_2O_2 industry (Bandara et al., 2005), reducing aldehydes to alcohols (Mills and Denton, 1977; Okamoto et al., 1983), converting hydrocarbons (Gladrow and Parker, 1961) such as methanol to gasoline range hydrocarbons (Zaidi and Pant, 2004), oxidizing olefin (Solomon, 1982), phenol (Fortuny et al., 1999). From the advantages of the CuO nanostructures are availability in abundance and non-toxicity in the devices they have been applied (Fan et al., 2004).

According to the abovementioned comments, the salient features defined as the main purposes of this research work were as follows:

The first purpose of this work was to present a procedure through which in fact a series of chemical precipitations were conducted to produce CuO nano-powder from pregnant leach solution (PLS) without any needs for significant energy consumptions, the huge amounts of which is the main drawback of the conventional solvent extraction and electrowining (SX-EW).

The next purpose was to develop an advantageous process, the facileness of which made it possible to produce CuO nano-powder from the low-concentrated PLS. Thus, it may be possible to define the capacity of the powder-producing unit according to the PLS flow-rate entering to that. This process could be operated at any capacity according to the capital investment limitations.

As a progressive innovation, the third aim was to almost completely eliminate the iron as iron oxides which prevented their accumulation in the bio-heap process. This might be very effective in efficiency of bio-heap leaching process.

The fourth goal pursued during this project was to design an engineered process such that the all recycled chemicals utilized in the process might be used in a bio-heap process without any detrimental effects to the bio-chemical reactions taking place in the bioheap. The chemicals not only had no harmful effect to the bio-chemical reactions in the bio-heap process, but those such as K^+ and NH^{4+} were also exploited by the autotroph microorganisms as their nutrients for growth and activity.

Of the other purposes defined for this project were to present a process with significantly lower energy requirements in comparison with the conventional SX-EW, and to eliminate application of detrimental organics in PLS processing.

2. Materials and methods

2.1. Bioleaching process

Bioleaching process was conducted by using around 600 kg of a low-grade chalcopyrite ore (0.3% Cu; 4.86% Fe) in a smart column (Robertson et al., 2005; http://www.mintek), pregnant leach solutions of which were collected into a PLS container. The PLS was used as the feed material for producing CuO nano-powder.

2.2. CuO nano-powder preparation procedure

The chemical analysis of the PLS is shown in Table 1. To design the process flow-sheet, a 100 ml of the PLS was firstly micro-filtered to remove any microbial and other tiny solid parts. Then, the purified solution was directed into the process (sub-process 1) to precipitate any iron (as main impurity) and other impurities (such as Al, Mg, Mn, Si). At the next step (sub-process 2), the copper-ammonia complex was entered into the process 2 to produce the precursor (Copper Hydroxide Sulfate Hydrate ($Cu_{2.5}(OH)_3(SO_4).(H_2O)_2$)) from the complex. And, finally the precursor was washed three times with distilled water. All of the effluents from the nano-powder producing processes were added in lixiviant and also bacterial nutrients to irrigate the simulated bio-heap process (the smart column). All the chemicals KOH, (NH_4OH, 25–30% of ammonia), and distilled water used in this study were of analytical grade.

2.3. Characterization

The solutions were analyzed for copper and iron concentrations by using an atomic absorption spectrophotometer (AAS, Varian 220). Additionally, the representative solid samples of the operations were characterized by using the scanning electron microscope (SEM)-based image analyses equipped with a multipoint energy- dispersive X-ray spectrometer (EDS) (Cam-Scan MV 2300). XRD diffraction (Philips X'pert-MPD system, CuKα, $\lambda = 0.154$ nm, 40 kV, 40 mA) and X-ray mapping were used to examine the crystalline structure of the CuO nano-powder. The nanoparticle size distribution and the morphology of the CuO nanoparticles were determined by using transmission electron microscopy (TEM;PhilipsCM20) and back-scattered scanning electron microscopy (SEM;TescanVega-II). Fourier transform infrared (FTIR, RT-DLATGS) spectrum were recorded with KBr pellet on a Bruker tensor 27 Fourier transform in the range of 400–4000 cm^{-1} with a spectral resolution of 4 cm^{-1} in transmittance mode.

3. Results and discussion

3.1. Design of the process flow-sheet

Fig. 1 shows the processing flow sheet to produce CuO nanoparticles from the simulated bio-heap PLS. Every unit operation of the whole process has been optimized to reach the possible maximum efficiency. Even, the type and dosage of the chemicals used in every stage were carefully selected to coordinate with the bio-heap leaching process, the bacterial activity of which is so critical for the process success.

Using the appropriate process engineering and washing medium, the synthesis procedure was conducted at room temperature without any additional thermal treatment required. To meet the economical requirements of low-grade chalcopyrite ore bio-processing, all the unit operations indicated in the flow-diagram of the process were optimized to perform well at room temperature.

Table 1
Chemical analysis of PLS before and after forming the copper–ammonia complex.

Aqueous solutions	Chemical analysis	
	Cu (g/L)	Fe (g/L)
PLS (in 100 mL)	0.31	1.10
Cu–ammonia complex (in 130 mL)	0.23	Tr