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Reductive dissolution by waste newspaper for enhanced meso-acidophilic bioleaching of copper from low grade chalcopyrite: A new concept of biohydrometallurgy

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ABSTRACT

Dumping of low-grade chalcopyrite encompasses several environmental problems. Despite slow dissolution rate, meso-acidophilic bioleaching is preferred for the extraction of copper from such ores. In the present study, meso-acidophilic bioleaching of a low-grade chalcopyrite in the presence of an acid-processed waste newspaper (PWp) is discussed for the first time. The study illustrated a strong catalytic response of PWp with enhanced bio-recovery of copper from acid-conditioned chalcopyrite. A maximum of 99.13% copper recovery (0.36% Cu dissolution/day) was obtained in 6 days of bioleaching in the presence of 2 gL^{-1} PWp in contrast to only 5.7% copper in its absence. FTIR analysis of bioleached residues revealed similar spectral patterns to the original acid-conditioned ore in the presence of PWp, thus indicating less development of passivation layer which was also confirmed through a complementary Raman characterization of the bioleached residues. Further, a reaction mechanism (chemistry) was proposed suggesting the possible role of PWp as the electron donor under oxygen limiting conditions which facilitated microbial reduction of Fe (III). The resulting biochemical changes provided an energy source for the bacteria, thus allowing free flow of electrons through the ore surface, thus contributing towards enhanced bioleaching of copper.

1. Introduction

Chalcopyrite ($CuFeS_2$) is the primary, economically important and most abundant mineral of copper that accounts for about 70% of the global copper reserves today. While depletion of the high-grade copper resources is of serious concern for the mineral processing industries, its judicious utilization to meet the ever growing demand of copper assumes great significance. Furthermore, concurrent increase in the volumes of low-grade copper ores leads to several environmental problems and occupation of extra space/land because of higher dumping activities. Over the past few years, bacterial assisted leaching (bioleaching) has emerged as a strong eco-friendly alternative to the conventional pyro and/or hydrometallurgical processing routes of metal recovery from low grade ores, coal and other industrial wastes (Mishra et al., 2014; Panda et al., 2013a, 2015). As of today, about 20–25% of the world's total copper production is obtained through bio-hydrometallugical processing (Bioleaching–Solvent Extraction–Electrowinning) (Panda et al., 2012a,c, 2014).

The process of bioleaching is carried out by a group of chemolithoautotrophic acidophilic bacteria that efficiently act as potential agents for dissolution of the respective metals from ores through a biochemical mechanism which is now well understood (Sand et al., 2001). Experimental studies on bioleaching of mostly concentrates have shown favorable results of metal recovery using thermo-acidophiles (Gomez et al., 1999; Zhou et al., 2009). However, few disadvantages such as higher sensitivity of microbial cell wall to high pulp densities, low metal tolerance ability, and high energy input for maintenance of bacterial populations have limited its scale up application (Gomez et al., 1999) for which much attention has been paid for the use of meso-acidophiles in large scale bioleaching processes (Panda et al., 2012a, 2013a). Recently, a mixed meso-acidophilic bacterial consortium involving *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*), *Leptospirillum ferrooxidans* (*L. ferrooxidans*) and *Acidithiobacillus thiooxidans* (*A. thiooxidans*) has shown promising results for dissolution of copper from low grade copper ore and is a preferred consortium in large scale heap bioleaching operations (Panda et al., 2012a).

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Considering the importance of chalcopyrite and its recalcitrant behavior to chemical leaching, much effort has been made to improve dissolution rates by the use of certain additives or catalysts to the bioleaching medium. Many researchers have reported the use of silver ions (Ag^{+}) as catalysts to enhance dissolution rates from low grade chalcopyrite in the presence of meso-acidophiles (Feng et al., 2013; Muñoz et al., 2007; Yuehua et al., 2002). Apart from silver ion, the use of NaCl to enhance copper dissolution rates has been recently proposed (Bevilaqua et al., 2013; Feng et al., 2013; Liang et al., 2012). Although these catalysts or additives have responded to enhance the copper dissolution rates from the otherwise difficult-to-treat chalcopyrite, the alternatives are sometimes uneconomical and are often associated with deleterious effects on the microbial populations and the environment. For example, the use of silver is expensive and chloride ions supplemented in the bioleaching media offer stress as well as inhibit growth of the meso-acidophiles for which they try to combat these issues through several adaptation mechanisms (Zammit et al., 2012). If a suitable catalyst is prepared which can: (i) control the oxido-reduction reactions involved in bioleaching; (ii) enhance the dissolution rates and (iii) hold the capability of scale up experimentation, then it would substantially contribute to solve the problems of recovery of copper from low grade chalcopyrite.

In view of the above, we present in this study an acid processed waste newspaper that acts as a catalyst, a reductant for Fe (III) and a low cost reagent in the bioleaching media. The novelty of the present study lies in the attempt that has been made to improve the dissolution rates of copper from a low grade chalcopyrite (considered as an industrial waste) using a waste newspaper. In addition, some fundamental aspects related to the use, variation and optimization of the dosage of waste newspaper, its effect on copper recovery with varying pulp densities and initial iron concentrations have been studied. Furthermore, the original and bioleached residues in the presence or absence of waste newspaper were analyzed and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. Additionally, some probable chemical or biochemical basis of the mechanistic actions of the bacterial consortium and/or the waste newspaper for enhanced leaching of copper from the low grade chalcopyrite ore is proposed.

2. Materials and methods

2.1. Ore sample

Low grade chalcopyrite containing 0.3% Cu (0.29% as copper sulfides and 0.01% as copper oxides), 2.6% Fe, 0.82% S and 90.27% acid insoluble matter (Panda et al., 2012a) used in the present study was obtained from the dump disposal site of the Malanjkhand Copper Mine, Madhya Pradesh, India. Mineralogical analysis of the sample quantitatively showed chalcopyrite — 80%, bornite — 5%, pyrite — 10%, chalcocite — 5% and malachite in traces. A detailed mineralogical characterization through XRD and TEM of the low grade copper ore of Malanjkhand has been discussed in our previous studies (Panda et al., 2012a; Sukla et al., 2009). As no other suitable physico-chemical process is available to recover metal value from this low grade ore, bioleaching process was employed for the recovery of copper.

2.2. Preparation of bio-reductant: pretreatment of waste newspaper

Prior to the start of bioleaching experiments, waste newspaper (10 g dry weight) was manually cut into very small fragments of area measuring less than 1 cm^2. 10 mL of concentrated H_2SO_4 was mixed thoroughly with the paper fragments in a 250 mL borosil beaker to ensure uniform mixing. The digestion was performed on an orbital shaker at room temperature operating at a shaking speed of 150 rpm. A completely hydrolyzed clumply mixture (mass) of the paper fragments obtained after digestion (herein referred to as PWp throughout the text) was used during the bioleaching experiments and further analytical studies.

2.3. Microbial leaching studies

2.3.1. Microorganisms and culture conditions

A mixed consortium of acidophilic bacteria is generally considered to be more effective for bioleaching than a pure culture (Akcil et al., 2007; Ciftci and Akcil, 2010; Deveci et al., 2004; Fu et al., 2008). Therefore, a laboratory stock culture of mixed meso-acidophilic chemolithotrophic microbial consortium comprising predominantly *A. ferrooxidans*, *L. ferrooxidans* and *A. thiooxidans* strains was used as the inoculum in the present bioleaching studies. Earlier studies have shown promising results of this mixed consortium for recovering copper from low grade ores (Panda et al., 2012a,b, 2013b). For the growth of the bacterial consortium, the standard medium for growth of meso-acidophilic bacteria, i.e. $9K^{+}$ media containing $(NH_4)_2SO_4$ — 3 gL^{-1}, KH_2PO_4 — 0.5 gL^{-1}, $MgSO_4 \cdot 7H_2O$ — 0.5 gL^{-1}, KCl — 0.1 gL^{-1} and $FeSO_4$ — 44.2 gL^{-1} was used (Silverman and Lundgren, 1959). To ensure activation of the microbial strains, repeated sub-culturing was carried out in the $9K^{+}$ media at 30 °C. Meso-acidophiles possess a unique biotechnological feature of heavy metal tolerance (Hoque and Philip, 2011); therefore the strains were adapted to Cu (1 gL^{-1}) with an incremental increase prior to the microbial leaching experiments. The adapted strains (Iron Oxidation Rate: IOR — 600 kg m^{-3} h^{-1}) were used during the entire leaching period.

2.3.2. Meso-acidophilic bioleaching studies

Bioleaching studies were carried out in 250 mL Erlenmeyer flat bottomed flasks under micro-aerophilic conditions (no shaking; intermittent shaking manually for 2 min at 2 day interval for drawing samples for Cu and Fe analysis), at normal atmospheric temperature using the mixed bacterial consortium. In order to study the effect PWp on copper recovery, two sets of experiments in duplicates were designed. In one set of bioleaching experiments, the original ore (un-acid-conditioned) was grounded to 37 micron size; at 10% pulp density (w/v) using 10% (v/v) of bacterial inoculum was tested for copper recovery with varying PWp concentrations. The dosage of PWp was varied from 1 gL^{-1} to 4 gL^{-1} in different flasks. In another set, the original ore was acid (H_2SO_4) — conditioned prior to bioleaching with all other operating conditions remaining the same. Acid conditioning is quite an essential feature required to neutralize the gangue minerals present in ore and improve bioleaching performance (Panda et al., 2014). In order to notice the recovery of copper in the absence of PWp, a control set of experiment (under similar conditions as the test experiment) using the ore sample and bacterial consortium in the leaching medium was designed. Furthermore, another control set under similar conditions without PWp addition and microorganisms in the leaching medium was carried out to notice the recovery of copper from the low grade chalcopyrite sample.

2.4. Analysis

The concentration of copper in the leaching media at the end of each day was analyzed by Atomic Absorption Spectroscopy (Perkin Elmer AA-400 model). Ferrous iron as well as the total iron were analyzed by the titration method using BDAS as the indicator. Change in the pH of the bioleaching medium was monitored by a digital pH meter (Digital Systronics μ pH Meter Model 361 provided with a combined glass electrode) and adjusted with diluted H_2SO_4. Bacterial counts of the inoculum were carried out using a phase contrast microscope (Nikon H550L Eclipse 80i Model).