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Enhanced recovery of nickel from chromite overburden (COB) using dissimilatory Fe (III) reducers: A novel Bio-Reduction Acid Leaching (BRAL) approach

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ABSTRACT

The nickeliferous chromite overburden (COB) awaits a suitable technology to extract the obstinate nickel ingrained in its goethite matrix. In the present study, a novel Bio-Reduction Acid Leaching (BRAL) approach has been proposed using dissimilatory iron reducing bacteria (DIRB) which is inherently capable of transforming iron mineral phases via bio-reduction (BR). Mineralogical characterization of the bio-reduced COB using XRD and FTIR confirmed the phase transformation of goethite to hematite and magnetite with exposure of the nickel oxide peaks. Further, morphological characterization using FESEM vividly highlighted the changes of acicular goethite to granular magnetite deposits on the extra polymeric substance (a scaffold for electron transfer) secreted by DIRB consortium over the surface of COB. Further, enhanced nickel extraction was achieved with a reductive acid leaching (AL) approach with 6N sulfuric acid and 2% glucose (reducing agent) at 65 °C for 6 h. A cumulative of 83.6% nickel was achieved through this BRAL approach. The pregnant leach solution (PLS) generated as a result of the AL approach was subjected to a hydrometallurgical route to recover metallic nickel. Solvent extraction (SX) of the PLS was performed using 0.5 M NaD2EHPA as extractant. The pregnant nickel-loaded electrolyte was subjected to electrowinning (EW) to recover metallic nickel of 99.6% purity. The process flow-sheet is believed to provide a suitable eco-friendly, potential method to efficiently extract nickel from low grade nickel laterites to meet the ever growing demands caused by depletion of high grade nickel sulfidic ores.

1. Introduction

Rapid depletion of nickel-sulfidic ores has been drawing the global attention of industrialists and researchers to process the nickeliferous, low-grade lateritic ores in order to fulfill the growing demand of nickel metal (McDonald and Whittington, 2008). Since, the nickel value of the nickeliferous laterite is ingrained firmly within the predominant goethite [Fe (III)] phase; its complete recovery by conventional methods is challenging (Valix et al., 2001). In the recent past, reductive pretreatment of low-grade nickel laterite has gained importance in addition to traditional beneficiation process for reduction of the nickel oxide to metallic nickel. The reduction of nickel oxide has been studied using hydrogen (Utigard et al., 2005; James et al., 2003); coke (Li et al., 2009); activated carbon (Xu et al., 2010); solid-state deoxidization method using gaseous and solid reductants (Li et al., 2011); selective reduction using CaO and reductant coal (Zhu et al., 2012). Although the aforementioned studies report enhanced metal extraction rates, the practical application is challenging as it's difficult to achieve control over the CO/CO_2 ratio and there exists an uncertainty over the use of exact temperature for selective reduction of nickel oxide over iron oxide (Zhu et al., 2012). Therefore, a suitable method of extraction from low-grade nickel laterites using an eco-friendly approach is desirable.

In view of this, the use of some selected microorganisms has been gaining importance in the mineral processing sector. Microbial processes for metal recovery from low grade ores and overburdens are believed to offer advantages in terms of low energy consumption, low capital cost, simple technological outlay, etc. (Simate et al., 2010). Numerous heterotrophic and chemolithotrophic microorganisms has been reported for extraction of nickel under aerobic conditions (Simate et al., 2010). However, the oxidic nature of nickeliferous laterites resulted in the futility of the bio-oxidation process by these microorganisms with poor nickel recoveries.

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With such a scenario, the use of a reductive mode of bioleaching/pre-treatment has slowly gained importance over the past few years to process nickel laterites. The reductive dissolution of nickeliferous laterite by the chemolithotrophic bacterium i.e. *Acidithiobacillus ferrooxidans* under anaerobic conditions was studied (Hallberg et al., 2011; Behera et al., 2012). This process requires maintenance of low pH (1.8 ± 0.2) to avoid jarosite formation and use of elemental sulfur as electron donor for bacterial growth which may cause formation of passivation layers in Fe/S rich environments (Panda et al., 2013) along with discharge of the perilous acidic liquor. On the other hand, the use of micro-aerophilic bio-reduction process using dissimilatory iron reducing bacteria (DIRB) has been reported as a suitable pretreatment method to overcome such hurdles (Pradhan et al., 2012; Esther et al., 2013). This process has provided efficient reduction of solid-phase Fe (III) to Fe (II) directly coupled to oxidation of organic carbon source by bacteria resulting in phase transformations of ore matrix. This in turn leads to loosening of goethite matrix thereby exposing the nickel for an enhanced recovery on using acid leaching approach (Esther et al., 2013 and references therein). In spite of slower kinetics, it is believed that the facultative anaerobic conditions required for bio-reduction are a feasible means of metal reduction using indigenous metal reducing bacteria (Chabalala and Chirwa, 2009; Esther et al., 2013). A direct application of such microbes over the dumps of chromite overburdens (COB) might be an appropriate method to naturally treat such wastes that lie unutilized over years. With the aid of engineering tools and designs, the growth and activity of such indigenous microbes can be enhanced, since in the absence of external aeration the core of the dumps below few centimeters from the surface may provide conducive conditions for micro-aerophilic and/or anaerobic growth of microorganisms. In view of the above, proposal of an efficient bio-hydrometallurgical process methodology using DIRB for bio-reduction of COB along with leaching of the bio-reduced ore for nickel recovery is an interesting aspect. Optimization of such bio-hydrometallurgical process (i.e. bio-reduction leaching followed by solvent extraction and electrowinning) is quite essential for flow sheet development for exploration of possibilities for large scale engineered field trials to efficiently utilize and recover metal values from such wastes.

In India, about 97% of the 189 MTs of low-grade nickeliferous lateritic reserves are found in the chromite overburdens (COB) of Sukinda Valley region of the state of Odisha. Pursuit towards development of an efficient process is still in progress to effectively extract metallic nickel from this nickeliferous COB. Hence, in the present study, a fundamental bio-hydrometallurgical process flow sheet using a novel BRAL (BR: bio-reduction, AL: acid leaching) approach has been proposed to treat COB of Sukinda Valley in Odisha, India using an adapted DIRB consortium. In view of scale up of the bioprocess, a bench scale study at higher pulp density has been carried out with development of an entire process flow sheet. In addition, analytical characterization studies using X-ray diffraction (XRD), Fourier Transformation Infrared Spectroscopy (FTIR), and Field Emission Scanning Electron Microscope (FESEM) were carried out to highlight some of the major mineralogical alteration in the original COB following bio-reduction and acid leaching of the bio-reduced COB. Reductive acid leaching of laterites using elemental sulfur, sulfur dioxide, cuprous and ferrous ions and few metal salts have shown enhanced dissolution (McDonald and Whittington, 2008; Senanayake et al., 2011). However, they carry their own disadvantages (Senanayake et al., 2011) which can be easily overcome by the use of organic carbon source as reductant for enhanced nickel extraction from the COB as described in this study. Remarkably, few to no literature are available regarding reductive acid leaching of nickeliferous lateritic ore using an organic source as reductant. Furthermore, it is very interesting to note that, the process flow-sheet development with enhanced recovery of nickel from chromite overburden using a bio-reduction acid leaching (BRAL) approach has not been reported in the literature.

2. Materials and methods

2.1. Ore sample

Chromite overburden (COB) consisting of low-grade oxidic nickel laterites obtained from Odisha Mining Corporation (OMC), India was used in the present study. The ore sample was ground to a particle size of ~75 μm prior to bio-reduction experiments. Chemical analysis of the sample indicated the presence of 0.78% Ni, 0.09% Co, 42.7% Fe, 0.62% Mn and 1.2% Cr. COB was found to majorly contain goethite as its mineral phase along with traces of hematite and magnetite as analyzed by X-ray diffraction (Esther et al., 2013).

2.2. Dissimilatory Iron Reducing Bacteria (DIRB) and bio-reduction of COB

Soil samples for enrichment of DIRB consortium was collected from the paddy fields (3–5 cm deep) of Sundarpada area, Bhubaneswar, Odisha and suspended in vials containing sterile distilled water. The mineral salt medium used for enrichment and growth of DIRB was adapted from Kanso et al. (2002) with modifications (Esther et al., 2013) along with 2% (w/v) pulp density of COB as Fe (III) source (electron acceptor) and 10 mM glucose as carbon source (electron donor). The autoclaved media was inoculated with 10% (v/v) of the soil suspension with a layer of paraffin oil to maintain anaerobic conditions and was kept in the dark at room temperature. The 7 day old seed-culture was enriched through five successive transfers under the same growing conditions. The enriched culture with potential Fe (III) reducing capacity was thereafter used as the inoculum for the experimental work.

In this study, mineral salt media (MSM) constituting (g/L): KH_2PO_4 — 0.8; K_2HPO_4 — 3.0; KCl — 0.2; NH_4Cl — 1.0; $MgCl_2$ — 0.2; $CaCl_2$ — 0.1 and yeast extract — 0.05 with 10 mM glucose (as electron donor) and 10% (w/v) pulp density COB (as electron acceptor) for growth of DIRB was autoclaved in a 1 L anaerobic glass vessel system. Following activation of the strains, a 10% (v/v) inoculum from the enriched DIRB culture was added to the sterile system for bio-reduction of the COB. In order to maintain an anaerobic condition, the contents of the system were layered with paraffin oil and kept unstirred in the dark at room temperature. The carbon source for DIRB i.e. glucose was added every week to the culture medium in the vessel and shaken thoroughly for homogenous distribution. At a particular time interval of 7 days, sampling was performed to study the rate of Fe (III) reduction. The experiments were continued until maximum Fe (III) reduction was achieved. Following termination of the experiment, the bio-reduced COB was harvested and oven-dried in closed glass petri plates for characterization using XRD and FTIR.

2.3. Acid leaching of bio-reduced COB

Following treatment of the COB sample with the DIRB consortium, the bio-reduced COB (100 g) was subjected to acid leaching to further test the maximum achievable recovery of nickel. In order to achieve faster extraction rates, the bio-reduced ore was tested for the maximum efficiency in the presence of a reducing agent such as glucose (Coupland and Johnson, 2008; Furlani et al., 2006). Consequently, the bio-reduced COB was subjected to treatment with 6 N H_2SO_4 in the presence of 2% (v/w) glucose as reducing agent at 2% pulp density for 6 h at 65 °C. Sampling was performed every hour to analyze the rate of metal leaching. AAS analysis (PerkinElmer AA-400 model) of the liquor samples gave estimate of the metal content being leached.

2.4. Downstream processing of leach liquor for metal recovery

As of today, hydrometallurgical routes have been the most preferred routes of metal enrichment and extraction from acidified leach liquors (Panda et al., 2012a). Subsequent to acid leaching of the bio-reduced COB, the leach liquor generated from the leaching unit was subjected