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A novel biphasic leaching approach for the recovery of Cu and Zn from polymetallic bulk concentrate

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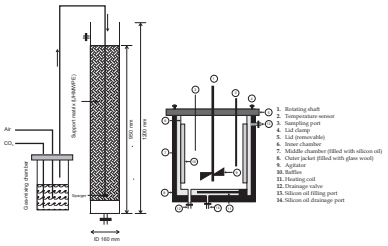
HIGHLIGHTS

- Consortium gave highest IOR of 3909 mg/L/h at no metallic stress in column reactor.
- It showed 51 times higher IOR compared to wild type consortium in metallic stress.
- Bioregenerated ferric iron yielded 52.2 and 2.6 g/L Zn and Cu, respectively.
- CYANEX® 301 used first time for metal recovery from PBC leachate.
- First biphasic process for PBC and recovery of metals.

GRAPHICAL ABSTRACT



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ABSTRACT

In scale-up biphasic leaching process of polymetallic concentrate, the ferric bioregeneration cycles were performed in 15.0 L down flow packed bed reactor; whereas the chemical leaching cycles were done using the biogenerated ferric in an indigenously designed 10.0 L stirred tank reactor. The consortium took 25 cycles for proper biofilm formation. It showed highest iron oxidation rate (IOR) of 3908.21 mg/L/h at 25th cycle under no polymetallic stress. Even under stressed conditions, it was 2650–558 mg/L/h. Cu extractions were 86.63–46.51 and Zn extractions were 67.89–14.74% in 1st–4th cycle, respectively. The developed consortium exhibited 17–51 times higher IOR compared to original wild type consortium. Extraction isotherm for zinc with 30% Cyanex® 301 indicated that a total of two stages are required for its complete extraction using the phase ratio of 2:1 at equilibrium pH 1.5, leaving behind Fe(II) in the raffinate.

1. Introduction

Ferrous iron re-oxidation is essential in the bioleaching process because Fe^{3+} is an important electron shuttle and a chemical oxidant. Ferrous iron can be oxidized chemically in acid solutions, but microbial oxidation occurs 10^5–10^6 times faster as compared to the chemical oxidation (Bosecker, 1997). Recirculation of Fe^{2+} containing leach solutions back to the process has been practiced in two stage leaching techniques like BRISA (Biolixiviación Rápida Indirecta con Separación de Acciones: Fast Indirect Bioleaching with Actions Separation) and IBES (Indirect Bioleaching with Effects Separation) (Carranza et al., 1997). Due to the fast metal extraction rate and the reuse of the spent iron, these biphasic leaching operations are the promising and economic future technologies which make use of autotrophic as well as heterotrophic acidophilic iron oxidizers in controlled bioreactors (Ehrlich, 2001). However, it leads to the accumulation of high concentrations of both dissolved iron

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and heavy metal in the leach liquor (Nurmi et al., 2009). This creates adverse condition for the activity of iron oxidizers.

The biphasic leaching operation (BLP) is a brilliant unconventional option for the treatment of base metal concentrates, which have been extensively evaluated over the years. In the biphasic process, the bacterial oxidation of ferrous iron to ferric iron is performed in a separate vessel/reactor (first phase), which is physically separate from the leach reactor (second phase). (Carranza et al., 1997, 2004). The sulphidic feed material in the leach reactor is contacted with Fe^{3+} iron solution generated by bacteria. From the reactor product, the liquid and solid phases are separated, with the liquid phase proceeding to metal recovery by, for example, solvent extraction and electrowinning (SX–EW) and returning to the first phase, which completes the liquor circulation loop between the leach reactor and the biooxidation vessel. (Fomchenko and Biryukov, 2009; Palencia et al., 2002; Romero et al., 1998, 2003).

The process is based on bioleaching by the indirect contact mechanism (Sand et al., 2001). According to this mechanism, metallic sulphides are chemically oxidized by ferric sulphate leading to elemental sulphur and copper in solution Eqs. (1) and (2). The resulting ferrous iron Eqs. (1) and (2) is again converted to ferric iron by iron oxidising microorganisms Eqs. (3):

$$CuFeS_2(\text{chalcopyrite}) + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^0 \quad (1)$$

$$ZnS(\text{sphalerite}) + 2Fe^{3+} \rightarrow Zn^{2+} + 0.125S_8 + 2Fe^{2+} \quad (2)$$

$$2Fe^{2+} + 0.5O_2 + 2H^+ \xrightarrow{\text{Iron oxidising acidophiles}} 2Fe^{3+} + H_2O \quad (3)$$

Two major reasons given by the authors (Fomchenko and Biryukov, 2009; Palencia et al., 2002) to separate the chemical from the biological stage are: (1) the possibility to perform the chemical leaching at high temperature in order to increase the kinetics as suffered in heap and stirred tank bioleaching reactors; and (2) the inhibition of the bacterial growth by heterogeneous ecosystem (heap leaching) and the harmful physico-chemical effects that exert on the bacteria when using a single stirred tank bioleaching reactor (Ballester et al., 2007).

From known diverse iron oxidising microorganisms, *Acidithiobacillus ferrooxidans, Leptospirillum ferrooxidans* and *Leptospirillum ferriphilum* plays a pivotal role in the oxidation of Fe^{2+} iron (Rawlings, 2005). For many years *A. ferrooxidans* was considered the dominant iron-oxidizing microorganism. However, based on kinetics reasoning (Boon et al., 1999a,b) and molecular ecology studies (Rawlings et al., 1999), it was reasoned that *L. ferrooxidans* might be the most important microorganism for ferrous iron oxidation. The optimal pH for the growth of *A. ferrooxidans* is reported to be within the range of 1.8–2.5 (Rawlings et al., 1999). *L. ferrooxidans* is more acid-resistant than *A. ferrooxidans* and can grow at lower pH values (<1.0). With regard to the temperature, *A. ferrooxidans* is considered to be more tolerant to low temperatures and less tolerant to high temperatures as compared to *L. ferrooxidans* (Rawlings et al., 1999).

Moreover, as reported by Galleguillos et al. (2009), the metal resistance ability of the *L. ferriphilum* is far greater than *A. ferrooxidans* and *L. ferrooxidans*, which make it the candidate of choice for bioreoxidation of Fe^{2+} iron from leachate containing high concentration of different metals. However due to the development of above mentioned adverse situation for biooxidation activity process need to be optimised and the concerned microorganisms require adaptation.

In attempt to develop an efficient BLP for a polymetallic bulk concentrate (PBC), the development of a laboratory scale down flow packed bed column reactor (first phase) involving an efficient *L. ferriphilum* dominant iron oxidising consortium has already been attempted with the optimisation of the chemical leaching process parameters on bench scale level (Patel et al., 2012a). The development of the efficient consortium required for BLP and its efficiency under very high multi-metal stress has also been optimally studied (Patel et al., 2012b).

In this paper, an attempt has been put in place to describe the scale-up in biphasic leaching process of polymetallic bulk concentrate (PBC) and the purification of metals by solvent extraction (SX) using Cyanex® 301.

2. Methods

2.1. Polymetallic bulk concentrate

The polymetallic bulk concentrate (PBC) was supplied by the Gujarat Mineral Development Corporation (GMDC), Ambamata Multimetal Mine Project, Gujarat, India. The PBC majorly contained sphelarite along with chalcopyrite, galena, pyrite and sulphur (Patel et al., 2012a,b).

2.2. Iron oxidizing consortium

Recently developed multistress resistant, *L. ferriphilum* dominated iron oxidising consortium (Patel et al., 2012b) was used for the generation of ferric iron at pH 1.8in 90 mL SDB1 medium consisting (g/L): $(NH_4)_2SO_4$ 3.0, $MgSO_4{\cdot}5H_2O$ 0.5, K_2HPO_4 0.5 supplemented with $FeSO_4{\cdot}7H_2O$, 20.0 g/L.

2.3. A cyclic biphasic leaching operation

2.3.1. First phase: ferric regeneration in 15.0 L down flow packed bed column reactor

The larger PVC (polyvinyl chloride) bioreactor (Fig. 1) used in the study was of 1200 mm height and 160 mm inner diameter with the basic construction features as described by Patel et al. (2012a). The column was packed with 3.0 kg prewashed shredded threads of Ultra High Molecular Weight Polyethylene (UHMWPE) as supporting matrix. As shown in schematic diagram (Fig. 1), the air and CO_2 were first mixed in a gas-mixing chamber filled with distilled water and then supplied through a sparger located at the bottom of the column. The air was fed at a rate of 3.0 L/min using a mini oil free air compressor and CO_2 was supplied at a concentration of 0.3% (v/v) of the total aeration. The active biofilm was developed as described by Patel et al. (2012a) with some modifications in the steps. Briefly, the prepared column was filled with 14.5 L of culture medium having pH 1.8 and 420 mV, which contained g/L: $(NH_4)_2SO_4$, 3.0; K_2HPO_4, 0.5; $MgSO_4{\cdot}7H_2O$ 0.5 and $FeSO_4{\cdot}7H_2O$ 20.0. A 500 ml of actively growing SR-BH-L consortium having 4×10^8 cells per mL were inoculated. Throughout the study, whole column reactor was set up in a specially designed incubator chamber with temperature set at 32 ± 2 °C. Once 95% oxidation of Fe^{2+} iron was achieved, 50% volume of the medium from the column was withdrawn and 50% new medium was fed to the column. The cycle was repeated for 10 times to develop required biofilm. The development of the biofilm was checked by running five consecutive cycles of ferrous iron biooxidation with complete removal of the spent medium from the column and 100% new medium was added in the column. Biofilm formation was also confirmed by the microscopic observation. Single cycle was considered when >90% Fe^{2+} iron was oxidised.

With a fully developed biofilm, the ferrous biooxidation was continued till the Fe^{3+} iron concentration reached to 1.5% (w/v) in the solution. The produced biogenic Fe^{3+} iron was used for the chemical leaching of metals in second phase as described in following section. This was considered as one cycle of biphasic leaching operation. The next cycle was started by filling the column reactor