Journal of Hazardous Materials 189 (2011) 836–842

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Different strategies for recovering metals from CARON process residue

G. Cabrera[a,*], J.M. Gómez[a], I. Hernández[b], O. Coto[b], D. Cantero[a]

[a] Biological and Enzymatic Reactors Group, Department of Chemical Engineering and Food Technology, Faculty of Sciences, University of Cadiz, Spain
[b] Laboratory of Metals, Department of Microbiology, Faculty of Biology, University of Havana, Cuba

ARTICLE INFO

Article history:
Received 19 January 2011
Received in revised form 3 March 2011
Accepted 13 March 2011
Available online 21 March 2011

Keywords:
Acidithiobacillus thiooxidans
Heavy metals
CARON process residue
Leaching

ABSTRACT

The capacity of *Acidithiobacillus thiooxidans* DMS 11478 to recover the heavy metals contained in the residue obtained from the CARON process has been evaluated. Different bioreactor configurations were studied: a two-stage batch system and two semi-continuous systems (stirred-tank reactor leaching and column leaching). In the two-stage system, 46.8% Co, 36.0% Mg, 26.3% Mn and 22.3% Ni were solubilised after 6 h of contact between the residue and the bacteria-free bioacid. The results obtained with the stirred-tank reactor and the column were similar: 50% of the Mg and Co and 40% of the Mn and Ni were solubilised after thirty one days. The operation in the column reactor allowed the solid–liquid ratio to be increased and the pH to be kept at low values (<1.0). Recirculation of the leachate in the column had a positive effect on metal removal; at sixty five days (optimum time) the solubilisation levels were as follows: 86% Co, 83% Mg, 72% Mn and Ni, 62% Fe and 23% Cr. The results corroborate the feasibility of the systems studied for the leaching of metals from CARON process residue and these methodologies can be considered viable for the recovery of valuable metals.

1. Introduction

Laterites are iron–nickel oxides associated with other metals and they are especially common in warm climates with abundant rainfall. Cuba has the second-largest nickel and cobalt reserves in the world [1]. These reserves include laterite deposits in the country's north-eastern region (Moa, Holguín) and these materials are processed by ammonium carbonate technology (CARON) to extract the nickel. This process generates a solid residue with a complex structure that is physically characterised by its black colour, semi-metallic lustre, fine particle size and predominantly magnetic nature [2], with notable amounts of metals like Ni (0.25%) and Co (0.09%) that are partially oxidised.

The content of heavy metals in this residue has a negative impact on the environment. In recent years, several technologies have been developed with the aim of reducing or removing heavy metals from contaminated media. The physical and chemical processes used to recover metallic species of interest tend to be very costly and generate wastes; hence, microbiological processes have been proposed as an alternative to treat this kind of residue. Prominent among these processes is bioleaching, an inexpensive, clean technology with low energy requirements. This technology uses the capacity of certain microorganisms to produce acids that are employed as leaching agents to solubilise metal species [3–5].

The recovery of metal species from laterite nickel ores by microorganisms is mainly based on the use of organic acids as leaching agents and these are produced by filamentous fungi [3,6–12]. However, the use of fungi suffers from certain limitations and these include: (i) the need to add organic compounds as a source of carbon and energy to culture the fungi, which increases the cost of future commercial processes [13], (ii) the formation of chelates, which hinders the recovery of dissolved metals [14] and decreases the amount of leached metals, (iii) the phenomenon of biosorption by the fungal biomass [12,15–17] and (iv) electrosorption effects [18], i.e. the attraction of metal cations in solution through electrostatic interactions between the gangue and the cation.

The use of bacteria may avoid some of the drawbacks outlined above. *Acidithiobacillus thiooxidans* is an acidophilic, chemolithoautotrophic bacterium that oxidises reduced sulphur compounds and produces sulphuric acid [19,20]. For this reason, *A. thiooxidans* has been widely used in the bioleaching of low-grade and concentrates of sulphide minerals on both laboratory and industrial scales [21–23]. This bacterium has also been used to solubilise nickel and cobalt from wastes from the mining-metallurgy industry, including lateritic overburden [24] and tailings [25–27]. The aim of the work described here was to evaluate the capacity of *A. thiooxidans* DMS 11478 to recover the heavy metals contained in the residues

---

* Corresponding author. Tel.: +34 956016554; fax: +34 956016411.
E-mail addresses: gema.cabrera@uca.es (G. Cabrera), josemanuel.montesdeoca@uca.es (J.M. Gómez), ianeyahd@fbio.uh.cu (I. Hernández), ocoto@fbio.uh.cu (O. Coto), domingo.cantero@uca.es (D. Cantero).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.03.048

from the CARON process in different configurations – the two-stage batch system and two semi-continuous systems (stirred-tank reactor leaching and column leaching).

2. Materials and methods

2.1. Lateritic residue

Lateritic residue from the ammonium carbonate technological (CARON) process carried out at the Comandante Ernesto Che Guevara plant (Moa, Holguín, Cuba) was used. The chemical composition of the residue was determined through the total acid digestion of 0.1 g of residue, previously dried for 12 h at 105 °C; the mineralogical composition was determined by X-ray diffraction.

The speciation of the metals (Ni, Co, Fe, Cr, Mg and Mn) was determined by the sequential extraction process described by Silveira et al. [28] and the metal content in the residual fraction (RF) was calculated by the difference between the total metal content in the residue and its sum in the fractions analysed.

The pH of the lateritic residue was determined on samples containing 4 g of solid and 10 mL of water, measured on the basis of a 1:2.5 ratio (soil:water (w/v)).

2.2. Culture medium and microorganism

A. thiooxidans DMS 11478 was cultured in a 0 K medium (pH 3.0, 30 °C) with 1% (w/v) elemental sulphur as an energy source [24]. Free bacterial population was represented by counting cells in a Neubauer chamber using an optical microscope with a phase contrast (Olympus BH-2).

2.3. Bioleaching in a two-stage batch system

During the first stage, *A. thiooxidans* DMS 11478 was cultured for 7 days at 30 °C; the culture was filtered through a nitrocellulose membrane (pore size 0.22 μm). During the second stage, supernatant (bioacid cell-free) from the first stage was added to 10 g of autoclave-sterilised residue and incubated at 60 °C for 31 h at an agitation rate of 150 rpm. Both steps were carried out in 250 mL Erlenmeyer flasks with a 100 mL working volume. Abiotic control was performed with a sterile 0 K medium. The experiment was carried out in triplicate.

2.4. Semi-continuous bioleaching

2.4.1. *A. thiooxidans* culture

A basic preliminary study on batch systems was carried out in order to determine the best conditions to generate leaching agent from *A. thiooxidans* culture. The inoculum volume [10% and 20% (v/v)] and agitation rate (300 rpm and 500 rpm) at an air rate of approximately 1.0 vvm were studied in a stirred-tank reactor (Reactor 1) with a 1 L capacity and a working volume of 800 mL.

When the bacterial culture reached pH 1 under selected conditions [20% inoculum (v/v) and 500 rpm], the reactor was fed with a sterile 0 K medium at a feed rate of 60–70 mL/day.

2.4.2. Stirred-tank reactor leaching

The leaching was performed in a stirred-tank reactor (Reactor 2) with the same configuration as the one used for bacterial growth (Reactor 1) (Fig. 1a). The experiment began with the addition of 80 g of residue (0.30–0.50 mm of particle diameter), 60 mL of bioacid from Reactor 1 and magnetic agitation at 500 rpm. Daily doses of 60–70 mL of bioacid were added to complete an effective volume of 800 mL of medium. During this initial preparatory phase, the pulp density in the reactor fell as the leaching agent was added until 10% (w/v) was reached. Once this level was achieved, 70 mL of leach liquor was extracted each day and replaced by an equal volume of fresh bioacid.

2.4.3. Column leaching

A 60 mL glass column with 50 g of residue (0.75–2.50 mm particle diameter) was used (Fig. 1b). The bioacid from the biological reactor (Reactor 1) was added to the column by a peristaltic pump at rate of 60–70 mL of bioacid/day and, from this time on, the system was maintained in a semi-continuous regime. In order to increase contact and to improve the solubilisation, after 34 days of the experiment, the leachate was re-circulated in the column by a peristaltic pump at rate of 7 mL min^{-1}.

2.5. Analytical methods

The pH of the leachates and cultures was measured with a CRISON (52-02) pH meter with an Ag electrode. Proton concentration was determined by titration with 0.02 N NaOH; sulphate ion concentration was determined by the turbidimetric method (readings at 450 nm) on an HP 8453 spectrophotometer [29]; the samples were centrifuged for 2 min at 10,000 rpm to avoid interference from other suspended components. Metal concentrations in solution were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS Intrepid). The samples were diluted with 0.14 M HNO_3, filtered (0.45 μm) and stored at 4 °C prior to analysis.

3. Results and discussion

3.1. Chemical characterisation of the tailing

The main mineralogical phases detected (Fig. 2) were: 41.5% maghemite (γFe_2O_3), 15% hortonolite ($FeSiO_4$), 10.2% Mg–chromite [(Mg, Fe)Cr_2O_3], 7.5% quartz (SiO_2) and 9% chabazite (Mn-exchange). These results are similar to those obtained by Rojas and Turro [2] who reported that Fe maghemite oxides constitute the main mineral phases of the residues of CARON from the Ernesto Che Guevara plant (Moa, Cuba).

The six metallic species determined by the sequential treatment (Ni, Co, Fe, Cr, Mg and Mn) were mainly associated with crystalline iron oxides (F6) (Table 1). This shows that during the mineral reduction phase in the CARON process, chemical reactions involving oxidation and hydrolysis of the iron ions occurred and resulted in the formation of a solid residue that retained metals such as Ni and Co, among others [2]. The concentrations of cobalt (absence), iron (4.5%) and nickel (17.2%) in the residual or lithogenic fraction (RF) showed that these metallic species had the highest bioavailability in the solid analysis, unlike chromium, which remained in a higher proportion (59.4%) in that fraction.

3.2. Bioleaching in two-stage batch system

The metal solubilisation percentages (Fig. 3) were favoured by the two-stage batch leaching system in which the incubation temperature was increased in the second stage (chemical leaching). As can be seen in Fig. 3, the highest recovery percentages were achieved after the first 6 h of contact between sulphuric bioacid and residue (46.8% Co, 36% Mg, 26.3% Mn and 22.3% Ni). From that time on, a significant variation in the recovery of these metal species was not observed. This indicates that the metal leaching stopped when there were still significant amounts of metal left in the processed raw material. This behaviour may be explained by the rapid consumption of the leaching agent after just 6 h of the experiment [30]. During this 6 h the leachate pH doubled from 0.99 to 2.15 and steadily increased until the end of the experiment (pH 2.83) due to