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Fungal assisted bioleaching process optimization and kinetics: Scenario for Ni and Co recovery from a lateritic chromite overburden

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ABSTRACT

A comprehensive study on the bioleaching of nickel and cobalt from the lateritic chromite overburden of Sukinda mines of Orissa was conducted using oxalic acid producing *Aspergillus niger* NCIM 548. Culture filtrate bioleaching was found to be the best possible leaching method among the three methods described. Three most important bioleaching parameters were optimized using RSM coupled with Box Behnken design keeping the best method and pulp density (2%) fixed. Optimal values of the three different parameters for the maximum recovery of 70.49% Ni and 66.93% Co were; temperature of leaching 80 °C, days of fermentation 21 days and sucrose concentration 10%. The leaching data of nickel fitted the "Ginstling Brounstheim" equation while for cobalt a mixed kinetic model consisting of "spherical geometry" and the "Ginstling Brounstheim" equation was followed. The activation energies of the leaching processes were found to be 55.84 kJ/mol for nickel and 24.9 and 46.91 kJ/mol for cobalt.

1. Introduction

Indiscriminate exploration of high grade ores to bridge the ever increasing gap between the demand and supply for the daily human life, has led to the exhaustion of valuable resources all over the world. Overburdens that are generated during the mining, occasionally contains low concentration of valuable metals. The recovery of metal values from these low grade waste products was found to be advantageous at the industrial scale as secondary resources [1,2]. In this respect different chemical and/or biochemical leaching processes have been addressed in the literature [3–7]. However, in comparison to chemical leaching, bioleaching technology is much more environment friendly and cost effective [8,9] and thus it is a promising alternative to currently used physical and chemical methods for the recovery of valuable metals. Chromite mines of the Sukinda valley, Orissa (India) is one of the major chromite reservoirs globally and it also stands out to be the sole known source of nickel in India. The chromite mines of Sukinda valley generate almost 6–7 tons of lateritic chromite overburden containing nearly (0.4–0.9%) nickel and (0.02–0.05%) cobalt, where the former is entrapped within the goethite (FeOOH) matrix [10,11] while the latter is associated with the manganese phase [5,12].

Nickeliferous minerals can be classified into two distinctive categories (i) the sulphidic and (ii) lateritic (oxidic). The sulphidic ores have been exploited globally over decades until presently when the deposits have started getting depleted [13]. Against this backdrop, the lateritic deposits are being considered with much thrust so that these can be exploited for the production of nickel albeit the fact that these are not easily amenable to metallurgical processing due to their complex mineralogy. The difficulties in processing ores via conventional hydrometallurgical and pyrometallurgical routes still remain and these processes are way behind when it comes to environmental friendly issues [14].

The situation is now conducive enough for considering biohydrometallurgy as an alternative route for processing of such lateritic minerals and wastes. Microbial leaching of minerals opens up an entire new arena of science and technology. Although the phenomenon was known to human kind since ages, but it was developed technologically a few decades back with proper scientific knowledge of the natural process which is essentially due to microbial activities. Transformation of insoluble metal complexes in their soluble form is the main concept behind development of novel process of bioleaching and bio-beneficiation of ore and minerals [15]. In bioleaching process, the metals are leached out by means of catalysis with an acid or a base. There are considerable amount of populations of prokaryotic and eukaryotic microbes in nature with the ability of mobilizing metals employing either of the following mechanisms: (i) through production of organic or inorganic acids (protons); (ii) oxidation and reduction reactions and (iii) the excretion of complexing agents [14,16]. So far, bioleaching processes are accomplished mainly by employing three categories of microorganisms: autotrophic bacteria, heterotrophic bacteria and fungi [14]. Bacterial species which are used

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extensively in bioleaching of sulphidic ores belong to the genus *Acidithiobacillus* (*Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* both are chemolithoautotrophs). On the other hand heterotrophic fungi of the genera *Aspergillus* and *Penicillium* are the most widely utilized bioleaching organisms [4]. Generally the process of bioleaching relies on acidophilic microorganism assisted oxidative process because the metals of interest are in a reduced oxidation state housed in a sulphidic framework. The mineral used in the present study is an oxide and does not contain any redox sources of energy therefore simple dissolution may be all that is required to liberate metal values. Heterotrophic leaching which includes fungal assisted bioleaching is the most suitable and effective process for recovery of metals from minerals designated as oxides, carbonates and silicates. The present study along with the previous articles by our group [10,12] vouch for the above mentioned concepts which indicates that the methods described hereunder are feasible and most effective, making it very different from the existing literatures on the same subject [5,11]. *Aspergillus niger*, a member of the genus *Aspergillus* and phylum ascomycetes, is one of the most extensively studied fungi with proven advantages over bacterial leaching, such as its ability to grow under a wide range of pH (higher as well as lower), ability to produce high concentrations of organic acids (oxalic, citric and gluconic), they can survive high metal exposures and a faster leaching rate [17]. The organic acids produced by the fungi are well known metal chelating agents thus being useful in metal leaching [18] process. In our previous study [19] we found that oxalic acid exerted the maximum leaching efficiency among the other two organic acid types, e.g. citric acid and gluconic acid. Thus in the present study we investigate the bioleaching process of chromite overburden of Sukinda mines, India, for the extraction of nickel and cobalt using *A. niger* NCIM 548 strain. This strain is capable of producing oxalic acid as the major secondary metabolite. The roasted ore was used in the present study which brought about the maximum metal recovery in comparison to the raw ore. Three influencing parameters that are involved in the leaching process were optimized, which were later considered for the investigation of the leaching kinetics.

Optimization of a process is always of central importance in industrial scale, especially for the biochemical processes, where a small improvement in the response value can cause huge commercial success. Generally, there are two types of optimization; the first is termed as topological optimization which deals with the topology or arrangement of the process equipment, and the second type termed as parametric optimization, which is concerned with the operating variables for a given process [20]. In this study, parametric optimization was considered using a statistical based optimization strategy called response surface methodology (RSM) to determine the optimum conditions such as pulp density, days of fermentation, temperature of leaching and sucrose concentration for the fungal leaching process. RSM is one of the most popular techniques for experimental design, evaluating the effects of different parameters and their interactions and also for searching the optimum conditions of the parameters that can produces a maximum or minimum response [21,22] value. The Box–Behnken design (BBD) methodology was used in the present case to collect the data for fitting the second order response. It requires much less number of experiments than the full factorial designs (FFD) and was proved to be sufficient to describe the majority of steady-state responses [23].

2. Materials and methods

2.1. Source and description of chromite overburden

The lateritic chromite overburden sample was collected from the major mining site of Kaliapani open cast mines of Orissa Mining Corporation at Sukinda Valley, Orissa, India. It is highly weathered and is rich in oxides of iron; it contains minor amounts of nickel, and cobalt. The size range of $-75 + 53$ μm (selected by sieve analysis) was used in this work. The overburden sample was taken in an alumina boat followed by roasting at 600 °C in a horizontal electric tube furnace for 5 h. The method was standardized previously based on the basis of DT-TGA analysis in this laboratory [10]. The chemical analysis of the chromite overburden was done by the conventional chemical digestion method as described in Ref. [12].

2.2. Microorganism and chemical

A. niger NCIM 548 was procured from National Chemical Laboratory, Pune, India. All chemicals were analytical grade reagent (AR). All aqueous solutions were prepared using deionized (d.i) water.

2.3. Fungal growth condition and spore suspension

A. niger NCIM 548, an oxalic acid producer, was maintained on potato dextrose agar medium. The medium used for bioleaching experiments contained sucrose as the C-source and had the following composition in g/L: $NaNO_3$ – 1.5; KH_2PO_4 – 0.5; $MgSO_4{\cdot}7H_2O$ – 0.025; KCl – 0.025; Sucrose – 100 and yeast extract – 1.6. The pH of the medium was adjusted to 6.8 with 4 M NaOH prior to sterilization at 121 °C for 15 min. Spores from the 7-day stationary culture grown at 30 °C in potato dextrose broth were suspended in 0.1% Tween 20 (v/v) solution and were counted under a light microscope in a Neubauer chamber. One mL of suspension containing (6×10^7 spores) was added to 100 mL liquid medium in a 500-mL conical flask for bioleaching experiments.

2.4. Effect of sucrose concentration

A separate set of experiment was carried out to investigate the influence of sucrose concentration (1%, 5.5% and 10%) in fungal growth medium on the recovery of metals. The bioleaching experiments were performed using varying sucrose concentration with the method which yields the best results among the processes described in Section 2.5.

2.5. Methods of bioleaching

All the bioleaching experiments were performed in 500-mL Erlenmeyer flasks with the roasted chromite overburden at various pulp densities (2%, 5% and 8%, w/v). Sterilization was achieved by autoclaving at 121 °C for 15 min prior to inoculation. Direct bioleaching experiments were carried out in an orbital shaking incubator at 30 ± 1 °C and 150 rpm. Culture filtrate bioleaching was set in a closed chamber shaking water bath where the temperature was maintained between 60–80 ± 1 °C. Direct bioleaching was carried out by two methods: (i) the fungus was incubated together with the medium and the roasted ore (one step bioleaching), (ii) the fungus was first grown in sucrose medium without chromite overburden for 48 h, and after a sudden drop in pH (the beginning of organic acid production), the roasted ore was added (two-step bioleaching). In the indirect bioleaching method, the fungus was first grown in sucrose medium for up to 21 days and a set was harvested after every 7 days. Culture was first filtered through a non-absorbent cotton bed and then though a 0.2 l mm (Millipore) filter to obtain the cell-free culture filtrate, containing only microbe-produced metabolites, which was used for leaching of roasted ore. The control experiments were also conducted using fresh sucrose medium.