NEW APPROACHES FOR BIOLEACHING OF NICKEL LATERITE ORE

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ABSTRACT

There are two principal types of nickel deposits: sulfide and laterite ores. Interest in low-grade Lateritic nickel ores has increased in recent years as high-grade Ni-sulfide deposits are being quickly depleted. However, processing of lateritic nickel ore ores have proven technically difficult and costly, and the development of alternative low-cost biotechnologies for Ni solubilization has been encouraged. In this context, a sample of Brazilian lateritic nickel ore was analyzed mineralogically and subjected to bioleaching tests using a Bacillus subtilis strain. SEM-analysis indicated that the primary Ni carrier mineral is goethite. Chemical analysis by size indicated a homogeneous distribution of Ni. XRF-analysis showed that the ore contains 1% NiO (0.85 % Ni). Bioleaching batch experiments demonstrated that about 8% Ni (0.7 mg Ni/ g ore) were solubilized by the B. subtilis after 7 days. Application of microwave heating as a lateritic nickel ore pre-treatment was also tested. This pre-treatment increased the bioextraction to 26% Ni (2.3 mg Ni/ g ore).

Keywords: Nickel laterite; Bioleaching; Microwave heating; Bacillus subtilis

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1. INTRODUCTION

Nickel is a metal that has much industrial and metallurgical application, being an important metal in modern infrastructure with major uses in stainless steel, metal alloys, and plating. Nickel is commonly found in two types of ore: a) deposits of primary sulfides, or b) weathered laterite deposits, the latter corresponding to about 70% of the known reserves of this metal in the world (Mudd, 2009).

The most abundant deposits of nickel in Brazil are those of the lateritic type, nickel laterite ore, accounting for about 350 x 10^6 tons of ore with an average of 1.5% Ni. These deposits are located in the states of Goiás, Pará, and Piauí, associated with mafic-ultramafic massifs of large dimensions and ultramafic alkaline complexes (Barros de Oliveira et al., 1992).

The development of new hydrometallurgical strategies for the recovery nickel from the low-grade lateritic ores is gaining attention in the last years. Some studies have been carried out using techniques such as solvent extraction (Kursunoglu et al., 2017) and ion exchange resins (Zainol and Nicol, 2009) instead of conventional processes for high-grade ores such as ferronickel (pyrometallurgical) and high pressure (hydrometallurgical) leaching (Xavier and Ciminelli, 2008). However, processing lateritic nickel ores by these conventional technologies involves the considerable use of energy and chemicals; consequently, it is less cost-effective than extracting nickel from sulfide ores.

The use of microorganisms capable of solubilizing metals from low-grade ores is an exciting alternative to be exploited for large-scale operations of metal recovery from ores and has already been used to recovery metals from sulfide deposits (Watling, 2006). Heap bioleaching contributes significantly for world copper production and, every year; new
technologies are developed to improve the bio-dissolution kinetics for commercialization of chalcopyrite (Panda et al., 2015; Zhao et al., 2017).

On the same line, different bacterial and fungal species have been used to exploit the biochemical leaching of nickel laterite ores; however, unsuccessful regarding extraction dynamics or yields. The most studied microbial strain is an autotrophic bacteria belonging to the genus *Acidithiobacillus*, which especially solubilize sulfides through the metabolic production of ferric ions and sulfuric acid, obtained from the oxidation of iron and sulfur compounds (Cameron et al., 2013; Vardanyan et al., 2015).

Microbiological studies have been carried out to investigate the effects of heterotrophic microorganisms such as yeast and fungi on the genus *Aspergillus* and *Penicillium*, and yeasts of the genus *Candida* on lateritic nickel ore solubilization (Valix et al., 2001a; Chaerun et al., 2017). It is a consensus that the chemoorganotrophic bioleaching of oxide ores have high potential for processing low-grade laterite ores, e.g., limonite, and saprolite, since they are capable of producing organic acids that tend to solubilize the nickel metal (Le et al., 2006; Chaerun et al., 2017).

The focus of mineral processing industries is the use of low cost, less energy intensive and eco-friendly technologies for the utilization of low-grade ores. In this way, the objective of this present study was to carry out preliminary solubilization tests of lateritic nickel ore by the action of heterotrophic bacteria *Bacillus subtilis*, since studies on the use of heterotrophic bacteria for the dissolution of lateritic minerals have not been described in the literature. Additional studies applying of microwave heating as a nickel laterite ore pre-treatment were also described.
2. EXPERIMENTAL

2.1. Mineral Sample

The sample used was a lateritic nickel ore from a Brazilian deposit. Approximately 8 kg of sample were crushed by using a jaw crusher and then ground by using a rod mill, as illustrated in Figure 1.

![Flowchart of the beneficiation route for the nickel laterite ore sample.](image-url)

Figure 1. Flowchart of the beneficiation route for the nickel laterite ore sample.
The products of the preparation consisted on a coarse sample -2.00+0.150 mm and a fine sample, -0.150 mm. The size distribution of the fine sample was measured producing additional 5 sub-samples, namely-0.150+0.106, -0.106+0.075, -0.075+0.053, -0.053+0.038 and -0.038 mm. The results of elemental analysis for each fraction are given in Table 1. The bioleaching tests were performed with the -0.150 mm fraction in shaken flasks.

The products of the sample preparation stages were characterized by chemical analysis (X-ray fluorescence) and mineralogical characterization (X-ray diffraction and scanning electron microscopy coupled to EDS).

The analysis for mineral identification of the fractions was performed with a Bruker D8 Endeavor X-ray diffractometer with Cu Kα radiation and with generator operating at 40 kV and 40 mA. The goniometer velocity was 0.02º (2θ) per 0.5 seconds in the interval between 3 and 80º (2θ).

The chemical analysis was carried out with a PANalytical Axios mAX spectrometer, and the fractions were prepared in a VANGE automatic press in molding conditions of 20 mm, with pressure of 20 tons and time of 30 seconds, using boric acid as caking (H₃BO₃) in proportions of 1:0.1.

Scanning electron microscopy analyses were performed on a TM3030 plus model from HITACHI. The samples were metalized with gold on a BAL-TEC SCD 005 Sputter Coater metallizer.

2.2. **Bioleaching experiments in shaken flasks**

To prepare the inoculum, *Bacillus subtilis* was transferred to Petri dishes containing TSA-YE medium (yeast extract, 5 g/L; tryptone soya broth (TSB), 30 g/L; and agar, 20 g/L); which were incubated for 24 hours in a bacteriological stove. After this period, a loopful from Petri dishes was used to inoculate 500 mL erlenmeyer flasks containing 200 mL of liquid
TSB-YE medium (yeast extract, 5 g/L; TSB, 30 g/L) (Takahashi et al., 2005) during 48 h, 150 rpm at 30 °C.

The bioleaching experiments were conducted in 500 mL Erlenmeyer flasks containing 2 mL of the inoculum described above, 10 mL of 10% (w/v) glucose, and 90 mL of the liquid medium; and adjust the pH to 7.0 with 1M NaOH. Two types of N sources were examined: inorganic salts medium (KH₂PO₄, 0.5 g/L; MgCl₂·6H₂O, 0.5 g/L; MgSO₄·7H₂O, 0.2 g/L; KCl 0.2 g/L, and (NH₄)₂SO₄, 0.1 g/L), and organic TSB-YE medium. The laterite nickel ore was added at different pulp densities according to the experimental tests, ranging from 0.25 to 1.0 g, corresponding to the solid-liquid ratio of 0.25-1.0% (w/v). The cultures were kept under constant stirring at 100 rpm, 30 °C for 1 or 2 weeks. All experiments were performed in replicates of 3, and the results represent the mean value ± SD. All analyses were compared with a control test without the addition of inoculum (abiotic control).

The nickel bioleaching efficiency was taken as an index and calculated using the following Equation 1:

\[ \eta = \frac{C \cdot V}{\alpha \cdot m} \times 100\% \]  

(1)

where \( \eta \) is the nickel bioleaching efficiency (%), \( V \) is the leachate volume (mL), \( C \) is the nickel concentration in leachate (g/mL), \( m \) is the mass of lateritic nickel ore (g), and \( \alpha \) is the nickel content in lateritic nickel ore (wt %).

2.3. Microwave pre-heating process

To evaluate the microwave heating as a pre-heating process, the lateritic nickel ore was submitted to 1 min of pre-processing time in a kitchen-type microwave oven (at 2.45 GHz frequency) on 800 W of microwave power. The bioleaching experiments were
conducted in 500 mL Erlenmeyer flasks containing 2 mL of the inoculum, 10 mL of 10% (w/v) glucose, 90 mL of inorganic salts medium, and lateritic nickel ore. The cultures were kept under constant stirring at 150 rpm, 30 °C for 1 or 2 weeks. All experiments were performed in replicates of 3, and the results represent the mean value ± SD. All analyses were compared with a control test without the addition of inoculum (abiotic control).

2.4. Analytical Methods

Cell growth was determined by counting the colony forming units (CFU) by the spread-plate technique. For this purpose, successive dilutions of the sample were performed, and each dilution was spread on two Petri dishes containing TSA medium and 0.1 mL of culture medium after bacterial growth. After plating and incubation for 48 h at 30 °C, the CFUs were counted at the appropriate dilution.

Determination of the final concentration of Ni, Al, Si, Cr, and Fe in solution was performed using atomic absorption spectrometry (AAS). The glucose determination was conducted by the reducing sugars method described by Somogyi (1945) and Nelson (1944).

3. RESULTS AND DISCUSSION

3.1. Mineralogical characterization of the nickel laterite ore

The resulting size distribution of the lateritic nickel ore sample is shown in Figure 1.
The results of the granulochernical analysis of the studied sample are presented in Table 1. It can be seen that Si (46.4%), Mg (32.6%), Fe (7.9%), Al (1.7%) and Ni (1.0%) are the significant elements. There were no significant differences (p < 0.05) in the MgO, Al₂O₃, SiO₂, Cr₂O₃, Fe₂O₃ and NiO contents found in the different granulometric fractions. In this way, it can be concluded that the elements present in this sample, and especially Ni, do not present a tendency to concentrate in a certain granulometric fraction.
Table 1. Chemical analysis of the lateritic nickel ore.

<table>
<thead>
<tr>
<th>Particle size fraction (mm)</th>
<th>Sample weight (g)</th>
<th>Oxides (W%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MgO</td>
</tr>
<tr>
<td>&lt; 2.000</td>
<td>859.80</td>
<td>32.6</td>
</tr>
<tr>
<td>&lt; 0.150</td>
<td>245.20</td>
<td>31.8</td>
</tr>
<tr>
<td>0.106</td>
<td>59.90</td>
<td>32.8</td>
</tr>
<tr>
<td>0.075</td>
<td>33.20</td>
<td>32.9</td>
</tr>
<tr>
<td>0.053</td>
<td>18.90</td>
<td>32.2</td>
</tr>
<tr>
<td>0.038</td>
<td>42.80</td>
<td>32.3</td>
</tr>
<tr>
<td>&lt; 0.038</td>
<td>90.40</td>
<td>31.1</td>
</tr>
</tbody>
</table>

The mineralogy of nickel laterite is considered as being complex and is classified as oxide deposit, clay silicate deposit, and hydrous silicate deposit. Nickel is found incorporated within or adsorbed by, some secondary oxides and silicate minerals (Gleeson et al., 2003).

According to the X-ray diffractograms shown in Figure 3, the most significant peaks found were quartz (SiO₂) and halloysite (Al₃Si₄OH₈O₁₀₈H₂O). These results were expected since the silicon is present in large quantities in the sample according to the chemical analysis. Peaks of kaolinite (Al₂Si₂O₅(OH)₄), vermiculite ((MgFe,Al)₃ (Al,Si)₄O₁₀(OH)₂.4H₂O) and goethite (FeO(OH)) were also observed.
**Figure 3.** X-ray diffraction of the lateritic nickel ore sample.

Scanning electron microscopy (SEM) analyzes (Figure 4) indicated that nickel is mainly concentrated in the finer fractions and associated with iron oxides and hydroxides.

**Figure 4.** Image of the sample of lateritic nickel ore and EDS analysis of the region marked with the yellow circle.

### 3.2. **Bioleaching of the nickel laterite ore**

Current bioleaching operations use mainly acidophilic prokaryotes (bacteria and archaea) to dissolves sulfide minerals by oxidative dissolution. The biological solubilization of sulfide ores is favored by the presence of iron and sulfur compounds which act as an
energy source for the growth of autochthonous bacteria (naturally found in mineral samples) and also of the autotrophic strains inoculated in bioleaching piles (Brierley and Brierley, 2013; Vera et al. al., 2013).

Since in lateritic ores, nickel is associated with oxidized ferric iron minerals such as goethite, bioleaching cannot be accomplished through classical oxidative mechanisms. Lateritic ores do not contain any source of energy that contributes to microbial growth, requiring the addition of nutrients that favors microbial growth and metabolism.

For chemolithotrophic bacteria, this energy source corresponds to the addition of ferrous sulfate or pyrite (FeS₂) (Simate et al., 2010). However, both heterotrophic bacteria and fungi use a carbon source for their growth and production of metabolites as iron chelating organic acids which interact with mineral surfaces and contribute to the dissolution of them. These organic acids play a crucial role in the biosolubilization process, providing complexing protons and anions that contribute to mineral dissolution (Bosecker, 1986; Gadd, 1999).

In the present study, a heterotrophic Bacillus subtilis bacterium was evaluated for dissolution of lateritic nickel ore. Bacterial metabolic activity is strongly influenced by culture media, which may contain precursors, inducers, and inhibitors of different metabolites secreted by microorganisms (Chaurasia et al., 2014). In this way, a comparison of lateritic nickel extraction rates by B. subtilis strain was made using two culture media: an inorganic medium, composed by KH₂PO₄, MgCl₂·6H₂O, MgSO₄·7H₂O, KCl and (NH₄)₂SO₄; and an organic medium, formed of yeast extract and tryptone soy broth. Table 2 shows the variation of the nickel bioleaching extraction at different culture mediums used in bioleaching process.
Table 2. Nickel laterite bioleaching extraction by *Bacillus subtilis* grew in different micronutrient medium.

<table>
<thead>
<tr>
<th>Culture medium</th>
<th>% Ni extraction</th>
<th>Ni bioleaching efficiency (ƞ)</th>
<th>Cell growth (UFC/g)</th>
<th>Residual glucose (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td>8.10 ±0.33</td>
<td>0.66 ±0.03</td>
<td>2.2 x 10^8</td>
<td>0.098</td>
</tr>
<tr>
<td>Organic</td>
<td>5.09 ±0.00</td>
<td>0.48 ±0.00</td>
<td>3.4 x 10^7</td>
<td>0.166</td>
</tr>
<tr>
<td>Abiotic control</td>
<td>4.63 ±0.66</td>
<td>0.40 ±0.06</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

According to Table 2, it can be observed that, after 1 week, an inorganic medium favored microbial growth in a unit of magnitude (from 10^7 to 10^8 CFU/g). The excellent growth of the bacteria in both culture medium used as leachate was also verified by the high sugar consumption indexes, which reached 99%. Carbon source substrates have a fundamental role in the functioning of the metabolic pathways for the microbial production of organic acids, which act as leaching agents in the mineral solubilization processes (Ghosh and Paul, 2016).

Nickel laterite bioleaching results showed Ni extraction rates by *B. subtilis* of 8.10% in inorganic medium and 5.09% in an organic medium. In comparison to abiotic control (not inoculated), the addition of *B. subtilis* cells resulted in a 2.3-fold increase in Ni solubilization from lateritic ore when the inorganic medium was used as leachate medium. Also, the presence of *B. subtilis* improved in 65% the Ni bioleaching efficiency, from ƞ=0.40 in abiotic experiments to ƞ=0.66.

Abiotic solubilization occurs by the physical (autoclavation, agitation, temperature) and chemical (nutrient medium as leachate) conditions. Once the bacterial cells are inoculated, mineral solubilization is favored by the presence of organic acids, which can act as complexing, chelating and precipitating agents (Chaurasia et al., 2014; Chaerun et al., 2017).
The second step of batch bioleaching experiments was performed using the inorganic medium at different ore pulp densities. Table 3 showed that the increase in the density of lateritic nickel pulp did not significantly interfere ($p < 0.05$) in microbial growth, which in this assay can be measured by the glucose consumption that remained on average by 99%.

Table 3. Effect of different pulp densities on nickel laterite bioleaching efficiency by *Bacillus subtilis*.

<table>
<thead>
<tr>
<th>Lateritic ore (% m/v)</th>
<th>% Ni extraction</th>
<th>Ni bioleaching efficiency ($\eta$)</th>
<th>Residual glucose (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>14.26 ± 3.59</td>
<td>1.12 ± 0.33</td>
<td>0.098</td>
</tr>
<tr>
<td>0.5</td>
<td>4.20 ± 0.54</td>
<td>0.66 ± 0.33</td>
<td>0.058</td>
</tr>
<tr>
<td>1.0</td>
<td>1.91 ± 0.18</td>
<td>0.60 ± 0.33</td>
<td>0.023</td>
</tr>
</tbody>
</table>

Higher initial nickel laterite pulp densities adversely affect Ni extraction percentages, which decreased by 87% when compared to rates of total nickel extraction at 0.25% m/v (14.26% Ni) and 1.0% m/v (1.91% Ni) of ore. However, the Ni bioleaching efficiency decreased in only 1.9-fold, from $\eta = 1.12$ to $\eta = 0.60$.

Increasing pulp density appears to be a problem for biosolubilization studies for both sulfide and lateritic minerals since they contribute to the increase of the intolerance of the microorganisms to the high concentrations of both the mineral samples and the dissolved metals in solution. Pre-acclimation assays of microbial strains in successive mineral sample concentrations have been described in the literature (Le et al., 2006).

Mohapatra et al. (2009) evaluated the lateritic nickel bioleaching using *Aspergillus niger* strain. For this organic acid producing fungus, the predicted maximum Ni extraction was around 30% with an ore pulp density of 8.75% after 37.5 days. In similar conditions, 7% Ni was leached after 3 days also using *A. niger* (Coto et al., 2008). One of the problems of carrying out the bioleaching process in larger times is the apparent loss of solubilized Ni
contents through adsorption and accumulation within the biomass (Boseker, 1985; Tzeferis et al., 1994). The mechanism by which metals are lost is often complicated by the difficulty in separating the microorganism from the ore substrate (Valix et al., 2001b).

### 3.3. Effect of microwave pre-heating on the bioleaching of nickel laterite ore

Pre-processing using microwave heating for ore enrichment as a size reduction method have been used in recent years as a pre-thermal treatment for metal recovery in hydrometallurgical processes (Agacayak and Koseler, 2015). Unlike conventional systems used in the ore pretreatment steps, in microwave pre-heating, the heat moves inside the material outwards. The inner parts of the material are warmer than their surface so that evaporation of water from the inside out and diffusion is simpler (Menéndez et al., 2010).

Microwave pre-heating may cause rock strength to decrease, and specific fracture rates are increased which increases the metal extraction and reduces leaching time (Yang et al., 2016). In the present study, the microwave pre-heating was used as a pretreatment for nickel recovery from B. subtilis bioleaching experiments as showed in Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction (%)</td>
<td>26.22</td>
<td>10.25</td>
<td>0.86</td>
<td>0.59</td>
<td>0.72</td>
</tr>
<tr>
<td>±0.27</td>
<td>±0.15</td>
<td>±0.22</td>
<td>±0.17</td>
<td>±0.18</td>
<td></td>
</tr>
<tr>
<td>Bioleaching</td>
<td>2.26</td>
<td>22.23</td>
<td>0.04</td>
<td>0.16</td>
<td>0.01</td>
</tr>
<tr>
<td>efficiency (%)</td>
<td>±0.02</td>
<td>±0.32</td>
<td>±0.01</td>
<td>±0.05</td>
<td>±0.00</td>
</tr>
</tbody>
</table>

Table 4. Effect of microwave pre-heating on nickel laterite bioleaching by Bacillus subtilis.

It can be observed that the microwave pre-heating favored the solubilization of nickel, which increased about 3-fold (from 8.10% to 26.38%) in comparison to experiments without
pretreatment. On the other hand, additional elements previously detected in the nickel laterite ore sample in X-ray fluorescence were also solubilized to the leachate, which did not occur in the bioleaching experiments without thermal pretreatment.

The use of the pretreatment of lateritic nickel for better extraction of nickel in hydrometallurgical processes has been described (Zhai et al., 2010). In microwave-assisted leaching of lateritic nickel ore, Ni extraction (~80%) has been increased with increasing microwave power and preheating time (Agacayak and Koseler, 2015)

4. CONCLUSIONS

Granulochemical analysis showed that the nickel laterite ore sample studied corresponds to a low-grade nickel ore (1% NiO), which showed a uniform Ni distribution along the grain size fractions. Mineralogical characterization indicated that the ore sample consists of quartz, kaolinite, goethite, haloysite, and vermiculite. Through the X-ray diffractograms, no nickel-bearing minerals were identified. Scanning electron microscopic analysis coupled to EDS indicated that nickel is found very dispersed in the lateritic ore and is most commonly found associated with iron oxides and hydroxides.

The experiments carried out showed the bioleaching capacity of lateritic nickel ore by the heterotrophic bacterium Bacillus subtilis. It can be concluded that the inorganic medium appeared to favor the production of secondary metabolites that acted to increase the solubilization of Ni. Microwave pre-heating associated to bioleaching had increased the Ni extraction.

The commercial application of bioleaching in engineered systems has necessitated essential advances in the fundamental research of the microorganisms involved and how these microorganisms interact with the minerals, and the detailed engineering of heaps and stirred tanks to accommodate the microorganisms and their functions. Leaving aside the cost of
microbial substrates (e.g. glucose or sucrose) required and relatively poor yields of nickel extracted; the advantages such as low-carbon footprint, low energy consumption, simple equipment technology and low capital costs needed for atmospheric heap leaching are responsible for considering the biohydrometallurgical processing route as a viable alternative to nickel extraction from nickel laterite ores.

5. ACKNOWLEDGMENTS

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