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# LEACHING OF LATERITE NICKEL ORE USING ORGANIC ACIDS

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**Abstract:** Organic acids are easier to handle, biodegradable, do not emit harmful gases into the atmosphere and are less corrosive than inorganic acids. For these reasons, they are called green leachants. Citric acid proved to be the most appropriate organic acid for leaching nickel and cobalt from saprolite ores, having the advantage of being more selective for iron and magnesium compared to sulfuric acid, frequently used in industry. This study aims to identify strains of filamentous fungi that produce citric acid for subsequent production in submerged environments and verify the recovery of Ni and Co contained in laterite ores. Preliminary experiments to select filamentous fungi with greater citric acid production potential were carried out using Foster's medium, with three Aspergillus strains being selected. Simultaneously, atmospheric leaching tests were performed using an incubator shaker, citric and lactic acids. The best nickel and cobalt recovery results, of 81.59% and 84.54%, respectively, were obtained using saprolite ore and citric acid. Due to the fact that nickel is associated with goethite in limonite ore, its recovery was only 27.03%, since, under the conditions used, it was not possible to break the goethite crystal lattice.
**Keywords:** Laterite ore; Leaching; Citric acid; Filamentous fungi.

## INTRODUCTION

The search for alternative leaching routes for depleted ores has led to the use of unconventional routes for metal extraction. Biohydrometallurgy or bacterial leaching is a well-known biotechnological process. The use of bacteria capable of solubilizing metals, through the oxidation of metallic sulfides, is a subject that has been used by several countries for the extraction of copper, uranium and gold, on an industrial scale (OLIVEIRA et al., 2010). However, it is necessary to look for routes that are more selective in certain circumstances, as is the case with laterite ores that contain high iron content. It is known that organic acids such as citric, oxalic and gluconic produced by Aspergillusniger are also capable of removing metals found in the form of silicates and oxides (HOSSEINI, et al., 2020). However, the literature involving extraction with organic acids is scarce compared to that on bacterial bioleaching. And more studies on this subject deserve more attention from the scientific community.

Citric acid, produced mainly by fermentation, and especially by A. niger, is the second largest product obtained by this route, behind only ethanol (FRANCIELO et al., 2008; ALVES et al., 2020). Obtaining citric acid via fermentation enabled its use on an industrial scale by reducing production costs. Currently, this acid has been used mainly in the food industry as a preservative, acidifier, flavoring and antioxidant; and in the pharmaceutical industry as a buffer, chelator and sequestrant (DHILLON et al., 2011). On the other hand, its use is not restricted to the aforementioned industries, mining is also interested in organic acids for removing heavy metals such as uranium, vanadium, zinc, nickel and cobalt, among others (ELOMAA et al, 2019; QIU et al, 2021).

Industrial waste can be used to produce citric acid, including whey and sugarcane molasses. Cheese whey, one of the biggest pollutants in the dairy industry, rich in lactose, is destined for pig nutrition, with little use in human food, and much of it is destined for water bodies, where it generates a high biochemical demand for oxygen (BOD) which causes serious environmental problems (SERPA, PRIAMO, REGINATTO, 2009). Otherwise, molasses, which is a waste from the sugar industry and is used in alcohol plants to produce ethanol, can also be used to produce baker's yeast, feed production and antibiotics (SILVA, 2008), instead of having as a destination some body of water. This way, possible contamination of water bodies, which would lead to imbalance in the aquatic ecosystem, is avoided. Therefore, the objective of the present study was to investigate fungal strains that produce citric acid and quantify the efficiency of this acid in the recovery of Ni and Co from laterite ores.

## METHODOLOGY

In carrying out this research, 6 strains of filamentous fungi were used, which were provided by Fundação Oswaldo Cruz/ FIOCRUZ, and are as follows: Aspergillusniger (IOC 4003, IOC 4616 and IOC 4470), Peliciniumpurpurogenum (IOC 3918) and Penicilliumcorylophilum (IOC 4288 and IOC 4297). Firstly, these strains were grown in test tubes containing Sabouraud culture medium.

The use of the bromocresol green indicator, a component of the Foster medium (1949 apud ALVES et al., 2020 p. 2), used for the comparative evaluation of fungi with greater acid production potential, showed the change in color of the area that surrounded the colonies grown in Petri dishes, due to their physicochemical properties. This allowed the qualitative identification of acid production by the studied fungi, changing the color of the medium from green to yellow. The Foster medium (1949 apud ALVES et al., 2020 p. 2) was initially adjusted to a pH value of 4.5. The Petri dishes were monitored over the course of a week, by measuring the diameter of both the colonies and the yellow diameter around them. The experiment was done in triplicate.

The fungi were inoculated in the center of the Petri dishes using a sterile plastic inoculation loop. The plates containing the fungi were incubated in an oven at 30 °C, where growth was observed over 7 days. The size of the acid and colony diameters were measured from the center of the plate to the edge with the aid of a protractor.

While significant amounts of organic acids were not obtained from the filamentous fungus strains studied, preliminary leaching tests were carried out using commercial organic acids.

These tests were carried out in an Ika model 4000 i incubator shaker, equipped with electronic temperature and speed control. The ore samples and acid solutions were added to 250 mL Erlenmeyer flasks and after the leaching time was complete, the suspensions were vacuum filtered, and the cakes were subsequently washed with distilled water, aiming to remove as much liquor as possible. The concentrations of Ni, Co, Fe and Mg in the bleach and washing water were determined by atomic absorption spectrophotometry.

The compositions of nickel laterite ores, used in the present study, were determined by X-ray fluorescence. While the quantification of mineral phases was carried out using the Rietveld method, which is based on the simulation of a digital XRD spectrum, based on the data crystallochemistry of all crystalline phases contained in the sample.

## RESULT AND DISCUSSION

The body of the article must be typed in Arial font size 12 points, spacing 1.5 cm and without any spacing between paragraphs. Regarding the biological study, using filamentous fungi, it can be said that after 7 days of incubation, the plates were analyzed based on the radial growth of the colonies, as well as the yellow diameter formed around them, due to the presence of the acid- base, bromocresol green. In this evaluation, strains of the Aspergillus genus (IOC 4616, IOC 4003 and IOC 4470) (Figure 1) showed excellent radial growth, in which there was only the formation of a central colony. The diameter of the acid increased significantly, indicating the efficiency of these strains in producing organic acid, whose presence was indicated by the color change of the Foster medium, from green to yellow. Comparatively, strains of the genus Penicillium (Figure 2) were less expressive than Aspergillus with regard to acid production. And in the future, it is intended to use industrial waste to produce citric acid. In the research by Alves et al., (2020) four fungi of the genus Aspergillus, three of the niger species and one of the foetidus species stood out in terms of acid production. Among Penicillium, the citrinum species showed the greatest potential. We can observe that in both researches the results were similar, with Aspergillus having a prominent position.

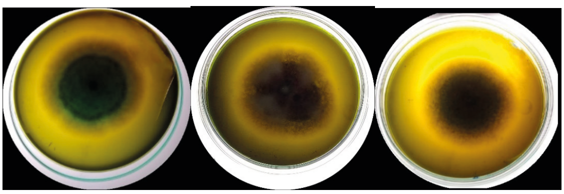


Figure 1: Aspergillusniger IOC 4616, IOC 4003 and IOC 4470, respectively, grown in Foster medium.

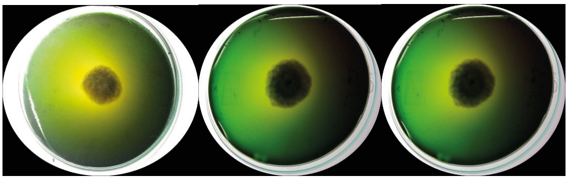


Figure 2. Penicilliumcorylophilum IOC 4297, P. Corylophilum IOC 4288 and Pelicilliumpurpurogenum IOC 3918, respectively, grown in Foster medium.

For environmental reasons, a significant number of studies can be found in the literature using organic acids, including citric, lactic, acetic and oxalic acids in the leaching of nickel and cobalt from saprolite ores. Among these organic acids, citric acid showed the best yield (ASTUTI et al., 2015).

Table 1 shows the compositions of the two laterite ores used in the atmospheric leaching tests. The ores found in the saprolite zone have more significant concentrations of nickel with levels of up to 3.0%, magnesium around 24% and silica close to 35%, while in the limonitic zone, cobalt and nickel are associated with rock masses of oxides of manganese and iron with levels of around 0.10% Co and 1.2% Ni.

| **Type of ore** | **Contents (%)** | | | | | | |
|---|---|---|---|---|---|---|---|
| | NiO | CoO | $Fe_2O_3$ | $SiO_2$ | MgO | $Al_2O_3$ | MnO |
| Saprolytic | 3,10 | 0,06 | 27,80 | 41,90 | 0,38 | 4,74 | 0,30 |
| Limonitic | 1,06 | 0,34 | 75,30 | 6,80 | 16,2 | 7,20 | 1,94 |

Table 1: Compositions of the ores used in the tests determined by X-ray fluorescence

Table 2 presents the quantifications of the mineral phases of the two laterite ores studied using the Rietveld method. Most of the nickel in saprolite ore is closely associated with minerals containing magnesium and silica, such as chlorite and serpentine, both phyllosilicates. While in limonite ore, nickel is associated with goethite, indicating that the effective release of nickel requires the dissolution of the goethite phase by solubilization of iron, before the dissolution of nickel (SITI et al., 2017).

| Phases | Limonitic Min. (%) | Min. Saprolite (%) |
|---|---|---|
| Spinels | 10,30 | 11,63 |
| Goethite | 35,36 | 11,14 |
| Hematite | 42,55 | 7,65 |
| Serpentine | 2,16 | 11,93 |
| Quartz | 3,60 | 18,06 |
| Baby Powder | 3,61 | 0,00 |
| Lithiophorite | 2,42 | 0,00 |
| Chlorite | 0,00 | 34,12 |
| Smectite | 0,00 | 5,47 |

Table 2: Quantifications of the mineral phases of laterite ores

The reaction of Ni with citric acid occurs in three steps. Initially, the carboxylic acid undergoes ionization, generating $H_3O+$, which attacks the mineral's crystalline network, releasing the $Ni^{2}+$ ion into solution, which is subsequently complexed with citrate, as described in the equations below (PETRUS et al., 2018).

$$C_6H_8O_7 + 3H_2O \leftrightharpoons C_6H_5O_7^{3-} + 3H_3O^+ \quad \text{(Eq.1)}$$

$$NiO + 2H_3O^+ \leftrightharpoons Ni^{2+} + 3H_2O \quad \text{(Eq.2)}$$

$$C_6H_5O_7^{3-} + Ni^{2+} \leftrightharpoons [NiC_6H_5O_7]^- \quad \text{(Eq.3)}$$

Figure 3 shows the recoveries of Ni, Co, Fe and Mg obtained in leaching tests of saprolite ore in different concentrations of citric acid. The highest recovery of Ni and Co, 81.59% and 84.54%, respectively, was when the concentration of citric acid used was 2.47 M. The recoveries of Ni and Co did not increase proportionally with the increase in the concentration of Citric acid. This can be attributed to the fact that the increase in citrate concentration does not increase proportionally to that of H3O+, as can be seen in Table 3. That is, if on the one hand the destruction of the crystalline network was favored, the concentration of citrate available for complexation of Ni2+ ions do not undergo significant changes.

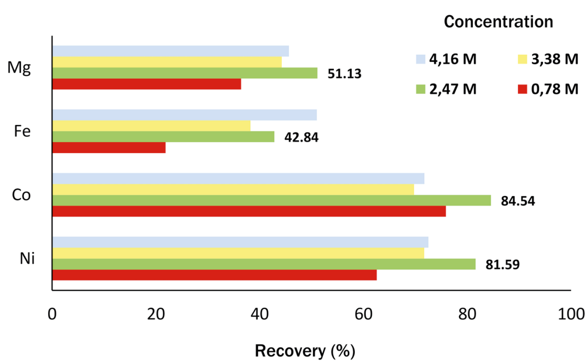



Figure 3. Recoveries of Ni, Co, Fe and Mg in atmospheric leaches at different concentrations of citric acid using saprolite ore. Leaching time 96 hours, temperature 80°C, solids content 20%, rotation 350 rpm.

| $C_6H_8O_7$ (M) | $H_3O^+$ ($10^{-2}$M) | $C_6H_5O_7^{-3}$ ($10^{-5}$M) | pH |
|---|---|---|---|
| 0,78 | 2,42 | 1,59 | 1,62 |
| 2,47 | 4,27 | 1,83 | 1,37 |
| 3,38 | 4,99 | 1,91 | 1,30 |
| 4,16 | 5,53 | 1,96 | 1,26 |

Table 3. Estimated concentrations of H3O+, C6H5O7- and pH, based on the amounts of citric acid used in the leaching tests

Figure 4 presents results from leaching tests on saprolite ore using citric and lactic acids. As expected, the recoveries of both Ni and Co were higher when citric acid was used at all leaching times studied. However, lactic acid showed higher selectivities for iron and magnesium when compared to citric acid, using the same operating conditions.

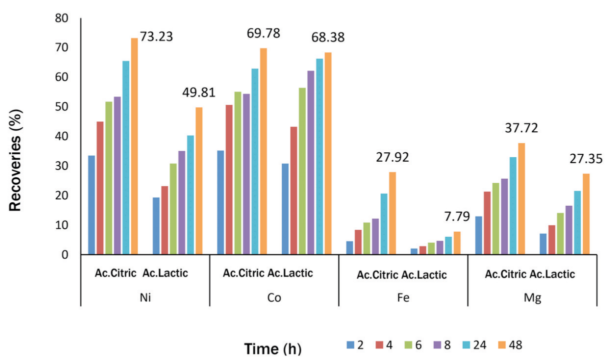


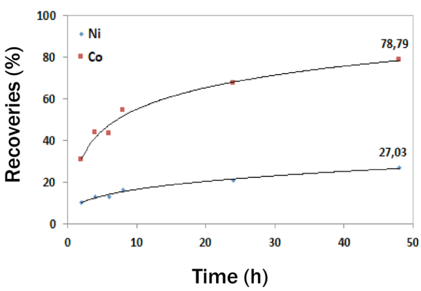

Figure 4. Recoveries of Ni, Co, Fe and Mg in atmospheric leaching at different times, using saprolite ore and citric (1.7 M) and lactic (1.9 M) acids. Temperature 80°C, solids content 20%, rotation 350 rpm.

Comparing the recovery efficiency of nickel and cobalt in the different studies found in the literature is a complex task due to the distinct mineral characteristics of each sample and the operating conditions used.

However, the results obtained in the present study are compatible with those presented by Astuti et al., (2023) who managed to leach around 90% of the Ni from a laterite ore, using a 1.0 M acid solution at 80 °C, density of pulp of 100 g/L, for a period of 5 h.

In the graphs in Figure 5 you can see the recoveries of Ni, Co, Fe and Mg from limonite ore whose composition and quantification of the mineral phases can be seen in Tables 1 and 2.

Because Ni is associated with goethite, the low recovery of this metal can be attributed to the fact that under the conditions used, citric acid was not able to attack the goethite crystal lattice, not releasing $Ni^{2+}$ ions into solution. This analysis is corroborated by the low iron recoveries, when compared to those obtained with saprolite ore. According to Tzeferis and Agatzini-Leonardou (1994), this result can be improved by using a mixture $H_2SO_4/C_6H_8O_7$ so that the $H_2SO_4$ maintains a low pH value, favoring the destruction of the crystalline network of the limonite ore with the release of $Ni^{2+}$, and the subsequent formation of organometallic complexes due to the presence of $C_6H_5O_7^{3}$ ions.



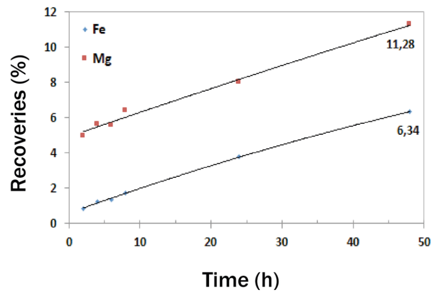




Figure 5. Recoveries of Ni, Co, Fe and Mg in atmospheric leaching at different times, using limonite ore, 2.5 M citric acid solution at 80°C, 20% solids content and 350 rpm rotation.

## CONCLUSIONS

It can be concluded that fungi of the genus Aspergillus showed greater potential for the production of organic acids, given the greater change in color, from green to yellow, in the environment in which they were cultivated, which corroborates the hegemony of this filamentous fungus in the production of citric acid on an industrial scale.

The results obtained in the leaching tests indicated that it was possible to recover 81.59% of the nickel and 84.54% of the cobalt contained in the saprolite ore studied.

The low recovery of nickel, 27.03%, when using laterite ore is due to the fact that under the conditions used, it was not possible to break the goethite crystalline network.

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