Selective Bioflocculation of Ultrafine Hematite Particles using the Yeast Candida stellata

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Abstract. The loss of ultrafine particles has been one of the biggest problems in mineral recovering during concentration process. One alternative to solve this problem is the use of biological raw material in processes like flotation, coagulation and flocculation, however, there are few studies related to ore treatment involving the bioflocculation process. This research aims at a study of the processing of ultrafine hematite particles using the biosurfactant extracted from the yeast Candida stellata. The bioflocculation experiments will be evaluated by jar-test assay, evaluating the influence of parameters like pH, solid concentration and biosurfactant concentration. The interaction of the bioreagent onto the mineral surface will be evaluated by FTIR (Fourier Transform Infra-red) analyzing the functional groups absorbed and surface tension measurement. This research aims as a sustainable route for the recovery of ultrafine hematite particles using a biodegradable material with high efficiency meeting with the requirements demanded for this purpose.

Keywords: Hematite, Quartz, Bioflocculation, Biosurfactant, Iron Ore.

1. Introduction

In mineral processing, the size of the particle is one of the biggest problems about mineral recovering. Depending on the nature of the mineral, the concentration process will not work effectively. For iron ores, froth flotation is not worthy in size particles less than 10 μm [1-4]. In these cases, an operation like coagulation, flocculation, magnetic separation or leaching are more useful for hematite recovery [5-6].

The flocculation can be realized by chemicals or by microorganisms and their byproducts, which absorb onto the mineral surface and changes their characteristics (electrostatic charge and hydrophobic feature), act like surface modifiers [7-10]. The bioflocculation has some advantages for being a eco-friendly, low cost and flexible operation and has a high efficiency to separate the valuable mineral from the gangue [5]. Yeasts are eukaryotic microorganisms and they are delimited by a plasma membrane containing phospholipids, which have proteins in their composition. [11] The biosurfactant extracted from the yeasts are commonly used in the food and pharmaceutical industry, but in mineral processing, there are few studies about it. The Candida stellata can produce a biosurfactant called sophorolipids, a glycolipid formed by a hydrophilic part (sepharose) and a hydrophobic part (a long chain of fatty acid) [12-15].

In this work, the biosurfactant extracted from the yeast Candida stellate is used for the selective flocculation of hematite particles. In the flocculation assays, we evaluated the best conditions of pH,
solids concentration and biosurfactant concentration for the hematite recovery. The interaction of the biosurfactant onto the mineral surface is evaluated by FTIR and surface tension.

2. Materials and Methods

Mineral samples
The quartz samples were obtained from a local supplier in Belo Horizonte, Minas Gerais State - Brazil, and the mineral was comminuted in a jaw crush and dry-ground in a porcelain mortar to achieve the required particle size. The hematite sample was provided by Sigma-Aldrich in a powder form (>96%, 5 μm).

Biosurfactant Extraction and yeast culture
The Candida stellata strain was provided by the collection of Reference Bacteria on Health Surveillance (CBVRS) – Oswaldo Cruz Foundation. The solid medium and the broth composition was by YMG type, that consists of 20.0 g/L glucose, 5.0 g/L peptone, 3.0 g/L malt extract, 3.0 g/L yeast extract and 20.0 g/L agar (only for solid medium). A six days incubation in a rotatory shaker at 151 rpm, 28° C is imposed on the broth. After that time, a centrifugation operation (3200g, 8 min) is needed to separate the culture medium from the cells, requiring a re-suspending with deionized water. According to Moreau et al. [16], the extraction of the biosurfactant begins with a centrifugation and a re-suspending of the culture medium in ethanol for one day and then passed to an autoclave (20min, 1 bar, 121 °C) for sterilization. After that, another centrifugation was realized to separate the soluble part from the cells and dried for 24 hours at 45 °C and then the material was dissolved in deionized water and a filtration (8 μm) was done to separate de insoluble part, finally getting the final solution. The biosurfactanct concentration was obtained by dry-weight measurement.

Flocculation Tests
The flocculation tests were conducted by jar-test and the minerals were studied individually and analyzed the influence of pH, solids concentration and biosurfactant concentration. The experiments were made from 5 to 120 minutes time, in a 500 mL graduated cylinder, a 5 minutes time for the interaction of the biosurfactant and the mineral and 20 minutes of vigorous mixing. After that, the flocculation was started so the time and clarified height were recorded.

For the pH experiments, the solids and the biosurfactant concentrations were fixed. The range of pH was from 3 to 11. The solids concentration influence, the best condition of pH and the biosurfactant concentration were constant. The values of solids concentration vary from 0,1% (0.50 g) to 2.0% (10.0 g). The last tests were made in order to evaluate the influence of biosurfactant concentration, fixing the best conditions of the last tests. The values vary from 50.0 mg/L to 200.0 mg/L. A solution of NaOH and HCl was used for the adjustment of pH.

Surface Tension Measurement
DCA-200S tensiometer (Surface Electro optics) was used for the surface tension measurement. For the first experiment, the concentration of the biosurfactant was analyzed in a range from 0 to 250 mg/L at pH 3. The critical micelle concentration (CMC) was obtained. Aliquots of NaOH and HCl were used to adjust the pH values.

Fourier Transform Infrared – FTIR
Nicolet FTIR 2000 spectrophotometer (Attenuated total reflection) was used for the FTIR analysis. The pre-treatment of the samples was a drying at temperature of 50 °C. The analyses were made before and after the interaction of the biosurfactant with the minerals.

3. Results and Discussions
Bioflocculation of hematite and quartz
The agglomeration of particles depends on the balance of forces between the particles (attractive and repulsive), the electrostatic repulsion keeps the minerals in suspension before the interaction, because they had a surface charge. According to the literature, the higher flocculation of hematite is expected near of its isoelectric point (IEP), around 7, and the quartz flocculation will be higher near its isoelectric point, around 2, but the experiments were conducted in higher pH values [17-18].

In the experiments with pH 3 before the interaction, the quartz recovery (~63%) was higher than the hematite recovery (~54%) due to the proximity of the quartz IEP. After interacting with the biosurfactant the flocculation results suffered a modification. The recovery of hematite increased from ~54% to ~91%. At pH 7, the effect of the biosurfactant is very unnoticeable, related to a non-adsorption of the biosurfactant onto the mineral surface.

Figure 1. Recoveries and terminal velocities of hematite and quartz particles before and after interacting with the biosurfactant as a function of pH. Solid concentration: 0.10% and Biosurfactant concentration: 50 mg/L.

The quartz bioflocculation had a similar profile as the hematite experiments, having a higher recovery at pH 3 than pH 7, this could be related to a higher adsorption at pH 3 than at pH 7. But compared to the hematite, the increment of the quartz recovery was lower (around 15%) while the hematite recovery grows around 40%.

The best response for this stage were the experiments at pH 3, but it doesn’t show a selective separation of the hematite from quartz, according to the recovery. However, the terminal velocities could help to explain the separation. In acidic conditions, the terminal velocities in both minerals had grown after interacting with the biosurfactant, being higher for the hematite at pH 3. At pH 3, the terminal velocities of hematite and quartz were around 0.22 cm/min and 0.12 cm/min, respectively (obtained in 20 and 40 minutes, respectively) hence that the separation of hematite from quartz could be achieved during the beginning of the flocculation.

Figure 1 shows the recovery and the terminal velocities of hematite and quartz before and after the interaction with the biosurfactant, respectively.

Figure 2 shows the recovery and terminal velocities of the hematite and quartz mineral as a function of the solids concentration. The higher hematite recoveries were at 0.25% (1.25 g) and 0.50% (2.50 g) >95% and for quartz, the maximum recovery was at 2.00% (10.0 g), ~90%. Previous studies indicated that solids concentration has influence on the collisions in the initial moments of the flocculation due to high sediment concentration and low turbulence. However, high solids concentration promotes an increment of the flocs breakage and influence the settling rate. Therefore, a medium solids concentration is ideal for the operation [19].
Figure 2. Recoveries and terminal velocities of hematite and quartz particles before and after interacting with the biosurfactant as a function of solids concentration. pH: 3 and biosurfactant concentration: 50 mg/L.

Figure 3 shows the flocculation tests of hematite and quartz as a function of biosurfactant concentration, at pH 3 and solids concentration of 0.25% (1.25 g), before and after interacting with the biosurfactant. For the hematite recovery, the best responses were at 75 mg/L biosurfactant concentration (~99%) and 100 mg/L (~95%) and for the quartz, the best conditions were at 150 mg/L and 200 mg/L biosurfactant concentration (~85%). These results suggest that the biosurfactant had an affinity with the hematite and adsorbs into the hematite surface, making it hydrophobic. For a selective flocculation of the hematite particles, a 75 to 100 mg/L biosurfactant concentration is enough to achieve the maximum recovery. Using a higher concentration indicates a lower recovery of hematite, which can be explained by a restricted adsorption into the hematite surface, reducing the hydrophobicity [20].

Surface Tension
For the analysis of the biosurfactant surface tension as a function of concentration, after mathematical regression, the critical micellar concentration around 150 mg/L was founded. The surface tension was decreased to 30 mN/m. These results are accorded to previous works [17-18]. Figure 4 shows the surface tension as a function of the concentration.
Figure 4. Surface tension of the biosurfactant as a function of biosurfactant concentration.

**FTIR Analysis**

The infrared analyses were studied between 3500 and 100 cm\(^{-1}\) because the characteristic bands for both minerals are found below 1000 cm\(^{-1}\) and the biosurfactant extracted from microorganisms have complex compositions with several functional groups, which can be seen in the region of infrared spectrum between 3500 and 1000 cm\(^{-1}\) [21-23].

Figure 5 and 6 show the FTIR spectra of hematite and quartz particles before and after the interaction at pH 3, respectively. The FTIR spectra of the hematite, Figure 5, evidence strong adsorption onto the mineral surface. According to literature, this result suggests a chemisorption driven force, in order to remove weak attached substances. After the interaction, several peaks were included, the 2924 and 2853 peaks correspond to alkyl C-H stretch, the peak between 1780 and 1630 correspond to carbonyl stretching absorption and the peak at 1090 corresponds to phosphate group in teichoic acid [17; 24-25].

Figure 5. FTIR spectra of hematite before and after interacting with the biosurfactant pH 3.

The FTIR spectra of quartz was observed, no changes of the quartz after the interaction, Figure 6, evidencing a weak adsorption of the biosurfactant, concluding a higher selectivity of the biosurfactant onto the hematite surface.
4. Conclusions
The biosurfactant extracted from the yeast Candida stellata behaves as a good flocculant for hematite particles compared to the quartz. The best conditions for the jar test flocculation assays were: pH 3 (~91%), a 0.50% (1.25 g) solids concentration (~96%) and a 75 mg/L biosurfactant concentration (~99%), besides having the best terminal velocities. The interaction of the biosurfactant onto the hematite surface was confirmed in the FTIR analysis, confirming the non-adsorption onto the quartz surface. The surface tension measurement confirms the surfactant properties of the biosurfactant compounds, owning a CMC of 150 mg/L at pH 3. From this research, further studies can be carried out in order to obtain more information about hematite bioflocculation technique using a biosurfactant extracted from a yeast. Other parameters that could be analyzed for its influence are the time of process conditioning, volume of the test tube and the mechanical stirring time provided before the flocculation process.

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