Bioflotation of apatite and quartz: Particle size effect on the rate constant

Abstract

This work deals with the fundamental aspects of apatite and quartz bioflotation using R. opacus bacteria as a bioreagent. It was observed that the flotability of both minerals depends on the pH value and the mineral particle size. The maximum flatability of both minerals was presented at a pH value of 5, achieving values of 90% and 14% for apatite and quartz, respectively, after seven minutes of flotation. The kinetics analysis showed that the smaller the apatite particle size, the lower its bioflotation rate value. On the other hand, the smaller the quartz particle size, the higher its bioflotation rate value. The first-order kinetic model better fitted the experimental data of both minerals, and a logarithmic relationship between particle size and kinetic rate constant was observed.

keywords: bioflotation; bioreagents; particle size; rate constant; apatite; quartz.

1. Introduction

Currently, it is believed that mineral biobeneficiation is an emerging technology due to its environmental and technological applications (Merma et al., 2013). The most significant application is related to the depletion of the environmental impact, generated by the use of conventional flotation reagents (Sharma and Forssberg, 2001). Since its early years of research, the core of the study and development of mineral bioprocessing (bioflotation and biocoagulation) has been set on the proper understanding of its fundamental aspects. A standard fundamental bioflotation study is normally conducted with pure mineral samples and deals with microorganism growth, equilibrium adsorption fundamentals, flotation and/or flocculation studies; some of them are more specific and may embrace bacterial adsorption thermodynamics (Sharma and Forssberg, 2001; Botero et al., 2008; Farahat et al., 2008, 2009, 2010), kinetics of bioadsorption of the bioreagent onto the mineral surface (Tan and Chen, 2012). Moreover, some works (Sharma and Forssberg, 2001; Sarvamangala et al., 2011, 2012, 2013; Pakudone and Natarajan, 2011) deal with the use of microorganism by-products, extracellular polymeric substances (EPS), or the so-called biosurfactants produced by the microorganisms (Natarajan, 2006). Additionally, literature depicts some relevant works on the bioflotation of ores (Mehrabani et al., 2010; Khoshdast et al., 2012; Elmadhy et al., 2013) and of coal (Abdel-khalek and El-midy, 2013; El-midy and Abdel-Khalek, 2014). The aim of these works was to evaluate the performance of these eco-friendly reagents as biocollectors, biodepressors or biofrothers.

Although Bioflotation and flotation processes are governed by the same fundamental physicochemical principles, very little is known about the influence of the physical properties of minerals on bioflotation. As example, it is known that there is an optimum particle size range for a given flotation system (Santana et al., 2008), but will this range also optimize bioflotation? Moreover, before the bioprocessing of a determined ore could be considered suitable, it is necessary to know the response of each mineral species, present in the ore, to bioflotation. Brazilian igneous phosphate ores are associated with several gangue minerals, such as quartz, magnetite, carbonates and silicates (Oliveira, 2005). Thus, in order to establish the application of a microorganism in the bioflotation of phosphate ores, a detailed bioflotation study of each component is necessary, principally for apatite, quartz, silicate, calcite, and probably dolomite.

Considering the before mentioned situation, the aim of this study was to investigate the effect of particle size on mineral bioflotation. Apatite and quartz samples are the minerals under study and Rhodococcus opacus the strain to act as biocollector and biofrother. Moreover, a kinetic analysis of the flotability is used to help the understanding of the process.

2. Materials and methods

2.1 Sample preparation

The fluorapatite sample, Ca$_5$[PO$_4$]$_3$(Cl, F, OH) (42.33% P$_2$O$_5$ and 54.39% CaO), and the pure quartz sample were provided by a local supplier (Estrada Mining, Belo Horizonte, Minas Gerais). The samples...
were crushed and then dry-screened to -3 mm, followed by dry-grinding in a porcelain mortar and then wet-screened to the desired size fractions. Then, the quartz sample was rested in a KOH (0.1 M) solution during 24 hours to remove the impurities present onto the quartz surface. Afterwards, the samples were washed several times with double-distilled water until the pH suspension achieved the initial pH. Finally, the samples were dried at room temperature and stored in a desiccator, until their use in the various tests.

2.2 Microorganisms, Culture and growth

According to Mesquita et al. (2003) the non-pathogenic Rhodococcus opacus strain presents a hydrophobic behavior (Contact angle around 70°), and it was the main reason for its use in this study. The strain, supplied by the Brazilian Collection of Environmental and Industrial Microorganisms (CBMAI-UNICAMP), was developed in a YMG solid media, containing: glucose 10.0 g L\(^{-1}\), peptone 5.0 g L\(^{-1}\), malt extract 3.0 g L\(^{-1}\), yeast extract 3.0 g L\(^{-1}\), and agar-agar 12 g L\(^{-1}\).

2.3 Flotation experiments

The microflotation study was conducted in a modified Hallimond tube. The mineral sample (1.0 g) was placed in the tube (volume: 0.16 L) containing a cellular suspension of known concentration. The suspension was mixed by constant stirring for about 5 minutes (conditioning time), and then the pH was adjusted to the desired value with diluted HCl and NaOH solutions. Finally, the mineral flotation tests were carried out using an air flow of 15 ml min\(^{-1}\) during a known time of minutes. The floated and non-floated fractions were carefully separated, washed, dried and weighed in order to calculate the flotability. For the kinetics analyzes, the flotation was conducted during 7 min. and samples were collected after 0.50, 0.75, 1.00, 2.00, 3.00, 5.00 and 7 minutes of flotation.

2.4 Kinetics of bioflotation

The flotation rate can be defined as a measure of the flotation recovery expressed per unit of time (Bulatovic, 2007), it means, the amount of floated particles with regard to flotation time (Hernániz and Calero, 2001). Different models have been proposed to evaluate the flotation kinetic behavior (Hernániz and Calero, 2001; Hernániz et al., 2005, Yalcin and Kelebek, 2011; Polat and Chander, 2000; Su et al., 1998; Zhang et al., 2013).

Although there are many approaches to describe mineral flotation kinetics, the most widely used models are based on analogy with a chemical reactor, which means that a flotation cell can be approximated by perfectly mixed CSTR (Hernániz et al., 2005, Yalcin and Kelebek, 2011; Polat and Chander, 2000; Su et al., 1998; Zhang et al., 2013). Considering, that bioflotation and flotation are governed for the same physicochemical principles, it is correct to assume that previous kinetic models can be used to describe the kinetics of bioflotation. This was also assumed in some bioflotation works (Amini et al., 2009; Pecina et al., 2009; Mehrabani et al., 2010; Khoshdast et al., 2012). Therefore, this paper also presents a kinetic analysis of the mineral bioflotation using kinetic models based on chemical reactor analogy. This equation may be expressed by:

\[
\frac{dC}{dt} = -k \cdot C^n
\]

\[
R(\%) = \left(1 - \frac{C}{C_0}\right) \times 100
\]

where “C” is the concentration of solids, “C\(_0\)” is the initial concentration, “t” flotation time, “n” order of the process, and “k” is the flotation rate constant. Considering that the mineral recovery (R) is a function of C (equation 2), we can obtain the models in function of such recovery.

It is commonly accepted that the order “n” and the rate constant “k” are dependent on the flotation conditions, some related to ore characteristics such as mineralogy, particle size and surface chemistry, and others, related to operations conditions such as air flow rate, reagents, etc. (Pecina et al., 2009; Deo et al., 2001; Yalcin and Kelebek, 2011). According to Brozek and Mlynarczykowska (2007), the flotation kinetics order changes during the process summarized as follows: at the beginning, the particles with the uppermost flotation properties may present a zero order value, but with time, the particles present a decreasing ability to float and, simultaneously, the order of the flotation kinetics increases. In this work, however, three approaches to determine the rate constant were considered, explicitly: first-order (n=1), second-order (n=2) and non-integral-
order models. The integrated equations for the three models mentioned are shown in Table 1.

| Model                  | Formula                                      | Description                                      |
|------------------------|----------------------------------------------|--------------------------------------------------|
| Classical first order model \((n=1)\) | \(\ln(1 - R) = K - t\)                      | \(R = \) recovery percentage of the mineral.     |
| Second order \((n=2)\)   | \(\frac{R}{(1 - R)} = k_2 \cdot m_0 \cdot t\) | \(m_0 = \) initial mass of the mineral in the flotation cell. |
| Non-integral order      | \(\ln\left(\frac{1}{R} - \frac{1}{R^*}\right) = k_n \cdot t\) | \(R^* = \) recovery percentage of the mineral at infinite time. |

Table 1 Description of the three flotation kinetic models used in this paper

3. Results and discussion

3.1 Flotation studies

The microflotation studies were carried out in order to evaluate the effect of the mineral particle size and pH on the bioflotation of apatite and quartz, using the \(R\). opacus bacteria as biocollector. It was shown that the \(R\). opacus strain has a strong capability of acting either as a biocollector or a biofrother (Merma et al., 2013). This previous work pointed out that the highest flotability value of both minerals was achieved using 0.15 g L\(^{-1}\) of the bacteria.

3.1.1 Effect of the pH and particle size on the biofloation of quartz and apatite

The pH of the solution is one of the most important factors affecting the biofloation. This affects the speciation onto the mineral surface as well as the activation of the functional groups present on the wall cell. Thus, the pH value affects the surface properties of the mineral, as the hydrophobicity and, therefore, the biofloation response of the minerals. The flotability of apatite and quartz as a function of pH value is presented in Figs. 1 and 2, respectively. It can be observed that for both minerals, the highest flotability was presented in an acidic medium, around pH 5, after two minutes of flotation. Moreover, in a very acidic medium, the flotability presented lower values, whereas declines were observed in an alkaline medium. This is in accordance with several bioprocessing studies (Farahat et al., 2008, 2010, 2012; Mesquita et al., 2003; El-midany and Abdel-Khalek, 2014), where the highest flotability of the minerals was achieved around the isoelectric point value of the bacteria, which generally has an acidic pH value. At this point, it is believed that the electrostatic repulsion between mineral particles and bacterial cells is suppressed, and specific interactions would let the adsorption of the bacterial cells onto the mineral surface, which would increase the hydrophobicity of the mineral and hence a higher flotability would be observed. It was also observed that particle size affected in a different form the flotability of quartz and apatite. The smaller the particle size, the higher the quartz flotability value, achieving flotability values around 18% and 10% for the finest and the coarsest particle size, respectively (Fig. 2); while for apatite the smaller the particle size the lower the flotability value, achieving flotability values around 69% and 43% for the coarsest and the finest particle size, respectively (Fig. 1). The behavior of the quartz sample can be explained due to the fact that microorganism cells essentially did not adsorb onto the surface of the quartz particles, which consequently maintain hydrophilic. Hence the recovery of the quartz particles depends on the air flow (entrainment). Therefore, small quartz particles, with lower mass, could be more easily carried into the concentrate by mechanical entrainment (Konopacka and Drzymala, 2010). On the other hand, the hydrophobized apatite particles presented an opposite behavior. It is possible to mention two factors which would explain the lower flotability value of apatite attained when the smallest particle size was used: (1) there was higher collector consumption due to the larger surface area of the smaller particles (Smith, 1997) and (2) the small particles present a lower efficiency in the bubble-particle collision (Chen jin et al., 1998). According to the previous, a lower flotability of the apatite would be expected when the finest size range was used, only if the initial bacterial concentration was maintained.

Figure 1
Biofloation of apatite as a function of pH at different particle sizes; bacterial concentration \(0.15\) g L\(^{-1}\), time of flotation: 2min.
3.1.2 Effect of the flotation time on the bioflotation of quartz and apatite

The flotability of apatite and quartz as a function of time for different particle sizes can be seen in Fig. 3 and Fig. 4, respectively. It shows that the flotability of apatite increased regularly as a function of time, but decreased as the particle size was increased. Achieving flotability values around 92% and 80% for the coarsest and the finest particle sizes, after seven minutes of flotation. On the other hand, quartz presented low values of flotability (around 14%) for the coarsest size range, increasing monotonically as a function of time. Furthermore, for finer particles: the higher the flotation time, the higher its flotability values, achieving around 52% after seven minutes of flotation.

3.2 Kinetics studies

The kinetic study was developed in order to have a better understanding of the effect of particle size on the bioflotation rate of apatite and quartz. As mentioned before, the existing literature shows few works dealing with bioflotation kinetics, hence, this subject is not very well known. However, as in flotation, bioflotation should be controlled by surface characteristics and knowing that the flotation recovery depends on the particle size fraction, (Santana et al., 2008; King, 1982) as well as the rate constant (Jameson, 2012), it should be right to affirm the same about bioflotation.

3.2.1 Apatite

The flotability of apatite (plotted in Fig. 3) has been examined from a kinetics point of view, using the three approaches mentioned before, in order to determine the rate constant. The kinetics parameters obtained from this analysis are given in Table 2, with their corresponding correlation coefficients ($r^2$) obtained from a linear regression. From these coefficients, it was able to assume that the first-order model best fitted the experimental data. This supposedly is correct, since, the mineral suspension inside the Hallimond tube was perfectly mixed by magnetic stir-
where, the exponent “m” could be calculated from the logarithmic representation of “kq” against the average particle size “d”.

Thus, the logarithmic representation of “kq” against the average particle size can be seen in Fig. 5. The linear regression showed that the first-order and second-order models attained high correlation coefficient values, and therefore, verifies the previously mentioned relationship. On the other hand, the low correlation value attributed to the non-integral model did not support a relationship between particle size and rate constant.

Therefore, considering the previous analysis, it was confirmed that the apatite bioflotation experimental data were properly fitted by using the first-order kinetic model. And the rate constant for apatite bioflotation decreased as the particle size decreased. These results are in good accordance to those observed by Su et al. (1998) and by Abkhoshk et al. (2010) for apatite and coal flotation, respectively.

### Table 2

| Particle Size (µm) | 1° order | 2° order | Non-integral order |
|-------------------|----------|----------|--------------------|
|                   | k (min⁻¹) | r²      | k (g min⁻¹) | r² | k (min⁻¹) | r² |
| +106 -150         | 0.449    | 0.95    | 2.094     | 0.88 | 0.841    | 0.858 |
| +75 -106          | 0.392    | 0.924   | 1.375     | 0.932 | 0.8721   | 0.904 |
| +38 -75           | 0.271    | 0.967   | 0.624     | 0.983 | 0.503    | 0.984 |

According to the authors, the relationship between rate constant and particle size is of the kind:

$$k_q \alpha d^m$$
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The bioflotation of apatite and quartz particles using R. opacus as bio-reagent was found to be dependent on the pH and the mineral particle size. The highest flotability value of both minerals was achieved at pH 5. For the coarsest fractions, the apatite presented its higher flotability value (around 70%) after 2 min. of flotation, while the quartz presented its higher flotability value (around 18%) for the finest particle size. The results showed that the bioflotation rate of apatite is higher, achieving flotability values of around 92% and 52% for apatite and quartz, respectively, after 7 minutes of flotation. Also, it was observed that the bioflotation rate of the apatite decreased as the particles sizes decreased, in contrast to the bioflotation rate of quartz, which increased. Finally, the first-order kinetic model showed a better fit to the experimental data of both minerals and a direct relationship between the rate constant and the mineral particle size was observed. Nevertheless, the non-integral models also fitted the experimental data. However, it was not possible to observe a clear relationship between the rate constant and particle size when this model was used.

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