

Evaluation of hematite and quartz flotation kinetics using surfactant produced by *Rhodococcus erythropolis* as bioreagent

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Abstract

The use of biosurfactants as reagents represents a promising alternative to the conventional surfactants used in the mineral industry because they may present low toxicity and high biodegradability. Therefore, this research studied the hematite and quartz flotation kinetics using surfactant produced by *Rhodococcus erythropolis* as bioreagent. The flotation kinetics of both minerals were evaluated under established conditions: biosurfactant concentration of 10 mg/L and solution pH of 3. The maximum floatability values were of 99.98% and 17.53% for hematite and quartz, respectively, after 2 minutes of flotation. Finally, the kinetics study indicated that the experimental data of hematite floatability was better fitted to both the first and non-integral order kinetics, while the experimental data of quartz floatability was better fitted to the non-integral order kinetic.

keywords: biosurfactant, kinetic, flotation, hematite, quartz.

1. Introduction

The literature review has shown that some microorganisms can produce surface-active compounds that can vary in their chemical structure and size. These surfactants, often called microbial surfactants or biosurfactants, are considered nowadays as potential substitutes of conventional (chemically produced) surfactants due to their lower toxicity, environmentally friendliness, high biodegradability, and effectiveness over a wide range of temperatures and pH (Khoshdast *et al.*, 2011).

Biosurfactants are amphipathic molecules with both hydrophilic and hydrophobic moieties. They have the same

characteristics of chemical surfactants, so they can be applied in metal treatment and processing industries (Olivera, 2018). It has been described that the genus *Rhodococcus* comprises important producers of biosurfactants, which form surface-active compounds derived from trehalose, especially during the use of water-insoluble carbon sources (Retamal-Morales *et al.*, 2018). The *Rhodococcus erythropolis* bacteria is a non-pathogenic Gram-positive microorganism found in a wide variety of sources such as soils, rocks, groundwater and marine sediments (Olivera *et al.*, 2017).

Currently, biosurfactants are

mainly used in applications related to improved oil recovery and hydrocarbon bioremediation (Zouboulis *et al.*, 2003), but there are not many studies of mineral flotation using biosurfactant as reagent, mainly for hematite and quartz. On the other hand, most developments in mineral flotation of hematite and quartz focused on mineralogical characteristics, application of reagents and their interactions in the process, but did not report data on their kinetic aspects. Therefore, this study evaluates the hematite and quartz flotation kinetics using surfactant produced by *Rhodococcus erythropolis* as bioreagent.

2. Materials and methods

2.1 Materials

All the reagents and chemicals used in the study were of analytical Grade. The samples of hematite (Fe₂O₃) and quartz (SiO₂) used in this study

were provided by a local supplier from Araçuaí in Minas Gerais. The purity of hematite and quartz was confirmed by X-ray fluorescence (XRF) and x-ray

diffraction (XRD). The particle size fraction of -106+75 μm was used in the flotation experiments.

2.2 Microorganism, biosurfactant production media and culture conditions

The *Rhodococcus erythropolis* bacteria was selected for the biosurfactant production. The microorganism was developed in

a TSB (Tryptic soy broth) culture medium. The incubation was carried out on a rotary shaker at a temperature of 28 °C for 6 days.

After that time, the microbial biomass was separated from the fermented media by centrifugation (5000 rpm for 10 min).

2.3 Extraction and recovery of biosurfactant

The extraction and recovery of biosurfactant followed the procedure of Olivera (2018). Ethanol was employed to extract biosurfactant from cell biomass.

The precipitated biosurfactant (crude biosurfactant) was dissolved in deionized water to separate the insoluble part by centrifugation at 5000 rpm and filtration.

The final solution (soluble biosurfactant) was used in the flotation tests and its concentration was determined by the dry weight method.

2.4 Flotation tests

The flotation tests were carried out in a modified *Hallimond* tube with a capacity of 0.16 L total volume of solution. 1.0 g of mineral sample was used for each test. The respective experimental conditions of froth flotation were the

following: biosurfactant concentration of 10 mg/L, solution pH 3, room temperature at 23 °C, conditioning time (with biosurfactant) was 3 min and flotation time was from 30 to 180 s. Air flowrate was kept constant at 23 mL/min through

a compressor/vacuum pump. The settled and floated mineral was carefully separated, washed, dried and weighed. The flotation recovery (floatability) was calculated as the proportion of floated and unfloated mineral particles.

2.5 Flotation kinetics

The kinetics of the minerals were evaluated using the most common kinetic

models: first order model, second order model and non-integral order model. The

integrated equations for the three options above are shown in Table 1.

Model	Equation	
First order	$\ln\left(\frac{m_0}{m}\right) = k_1 t$	$\ln\left[\frac{1}{(1-R)}\right] = k_1 t$
Second order	$\frac{1}{m} = \frac{1}{m_0} + k_2 t$	$\frac{R}{(1-R)} = m_0 k_2 t$
Non-integral order	$\ln\left[\frac{R_\infty}{(R_\infty - R)}\right] = kt$	

m_0 : initial mass of mineral in the flotation cell; m : recovery mass of mineral by flotation; k : kinetic rate constant; t : flotation time; R : mineral recovery at the time “t” and R_∞ : maximum flotation recovery.

Table 1
Most common flotation kinetic models used in the flotation process.

3. Results

3.1 Characterization of mineral samples

The results of the X-ray fluorescence chemical analysis showed that the hematite sample had a Fe_2O_3 content of

about 95.63% and the quartz sample had a SiO_2 content of about 99.05%. The X-ray diffraction analysis confirmed that

Fe_2O_3 appears as the mineralogical phase of hematite, while SiO_2 appears as the mineralogical phase of quartz.

3.2 Biosurfactant extraction

Figure 1 shows the biosurfactant extracted from the *Rhodococcus erythropolis* bacteria. The surfactants produced by *rhodococci* are predominantly cell-associated trehalose mycolates (Kuyukina *et al.*, 2001). Trehalolipid surfactants associated

with *Rhodococcus* cells can be effectively isolated by extraction with an organic solvent (Lang and Philp, 1998). Among the great variety of organic solvents that have been used (alone or in combination) in the biosurfactant extraction, include:

methanol, ethanol, diethyl ether, pentane, acetone, chloroform and dichloromethane (Desai and Banat, 1997), as well as methyl tertiary butyl-ether (MTBE) because it is a less toxic and cheaper solvent (Kuyukina *et al.*, 2001).



Figure 1
Biosurfactant extracted from *Rhodococcus erythropolis*.

3.3 Flotation tests

The flotation results of hematite and quartz as a function of time are shown in Figure 2. From these, it was observed that hematite had better floatability than quartz in the time range studied. This indicated that there was a predominance

of functional groups of biosurfactant that interacted on the hematite surface, rendering the particles hydrophobic and, consequently, the mineral recovery was greater (Olivera, 2018). The maximum floatability values were 99.98% and

17.53% for hematite and quartz, respectively. On the other hand, the mineral recovery remained almost constant with the increase of flotation time from 120 to 210 s (for hematite) and 180 to 210 s (for quartz).

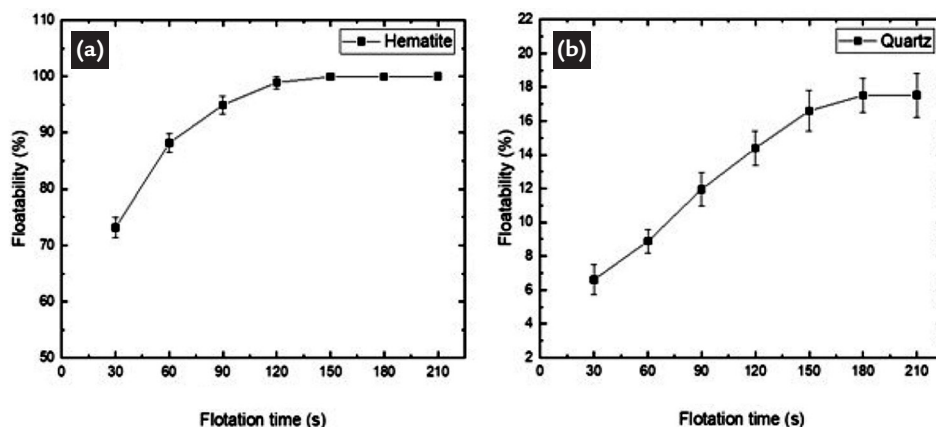


Figure 2
Floatability as a function of flotation time (pH 3 and biosurfactant concentration of 10 mg/L). a) Hematite flotation. b) Quartz flotation.

3.4 Flotation kinetics

Chemical kinetics is the study of the transformation rates of chemical compounds from reactant species in products (Donaldson and Wren, 2015). Therefore, if we relate froth flotation with chemical reaction kinetics, we would be considering the bubble and the particle as reactants and

consequently the product would be the aggregate of bubble and particle. Considering this point of view, the flotation rate would depend on several factors, such as the particles and bubbles concentration, the collision frequency, the efficiency of particles adherence in the collision and the adherence

stability (Wills and Finch, 2015). There are different mathematical models that describe froth flotation as a rate process (Hernández and Calero, 2001; Hernández et al., 2005). Among these are the kinetic models based on chemical analogy, represented by the following differential equation:

$$\frac{dC}{dt} = -kC^n \tag{1}$$

where: C - particles concentration, t - time, n - order of flotation kinetics, and k - flotation rate constant.

The flotation rate constant can be determined by considering three different orders (first, second and non-integral). Each of these was described in detail by Hernández and Calero (1996) and their integrated equations were shown in Table 1.

The Kinetic constants of hematite and quartz flotation were calculated. The results achieved are shown in Table 2. It was observed that the experimental data of hematite floatability was better fitted to both the first and non-integral order

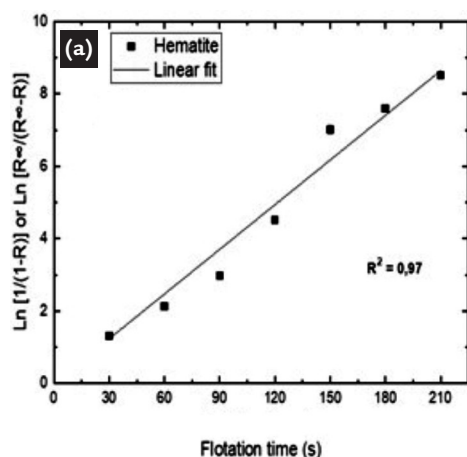
kinetics with a correlation coefficient (R^2) of 0.97, while the experimental data of quartz floatability was better fitted to the non-integral order kinetic with a similar correlation coefficient ($R^2 = 0.97$). The linear fit of the flotation results of hematite ($n = 1$ or $n =$ non-integral) and quartz ($n =$ non-integral) flotation are shown in Figure 3-a and Figure 3-b, respectively. These results are basically consistent with the findings of previous investigations. For instance, Hernández and Calero (2001) and Hernández et al. (2005) in the celestite and calcite flotation and phosphate ore flotation, respectively, obtained better

results of flotation kinetics following the non-integral order model. Already, Yalcin and Kelebek (2011) and Olivera et al. (2017) in the pyritic gold ore flotation and hematite flotation, respectively, obtained better fits using the second order kinetic model. Other authors such as Merma and Torem (2015), studied the quartz flotation kinetics using *Rhodococcus opacus* as a bioreagent. The experimental results were best fit using the first-order kinetic model. Similarly, this was observed in the article of Larsen and Kleiv (2015), where the quartz flotation followed the first order kinetic model.

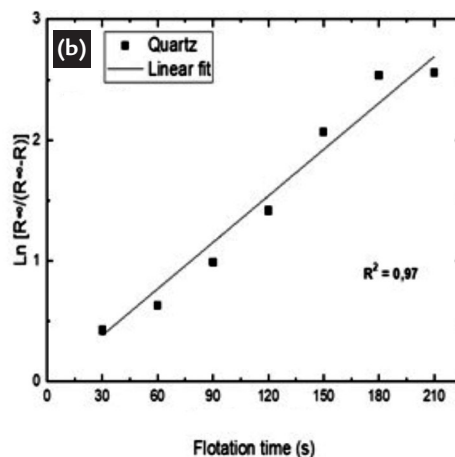
Order \ Mineral	n = 1		n = 2		n = non-integral		
	K_1 (min ⁻¹)	R^2	K_2 (g ⁻¹ .min ⁻¹)	R^2	R_∞	K_3 (min ⁻¹)	R^2
Hematite	0.0412	0.97	12.6130	0.50	1.00	0.0412	0.97
Quartz	0.0011	0.66	0.0012	0.74	0.19	0.0128	0.97

Table 2
Rate constants of the hematite and quartz flotation kinetics.

From Table 2, it was observed that the values of kinetic constants of hematite flotation are the same, both in the first order



model and in the non-integral order model because the value of “ R_{∞} ” was 1. On the other hand, the second order model (for hematite),



as well as the first order and second order models (for quartz) were rejected due to their low adjustment to the experimental results.

Figure 3

a) Linear fit of hematite flotation using both the first order model and the non-integral order model. b) Linear fit of quartz flotation using the non-integral order model.

4. Discussion

This investigation showed coherent and relevant results for the mineral industry. The biosurfactant extraction process with ethanol (ethyl alcohol) was efficient and adequate because the product obtained (biosurfactant) had recovery values close to 100% of hematite in the flotation tests performed on modified *Hallimond* tube.

5. Conclusions

The flotation results showed that the biosurfactant produced by *Rhodococcus erythropolis* had more selectivity for hematite than quartz and can act as a collector reagent for hematite. The maximum floatability values of hematite and quartz were

Therefore, considering the flotation results achieved (Figure 2), it was concluded that the biosurfactant produced by *Rhodococcus erythropolis* has more selectivity for hematite than quartz. It means that biosurfactant molecules prefer to adsorb in greater proportion on the hematite surface than on the quartz surface. On the other hand,

the results of hematite and quartz flotation kinetics presented in Table 2 showed that the flotation rate was much more rapid for hematite than for quartz, with a mineral recovery of 88% in the first 60 s. It means that biosurfactant molecules prefer to adsorb in greater proportion on the hematite surface than the quartz surface (Olivera, 2018).

99.98% and 17.53%, respectively. The kinetics study indicated that the experimental data of hematite floatability was better fitted to both the first and non-integral order kinetics with a correlation coefficient of 0.97, while the experimental data of quartz floatability

was better fitted to the non-integral order kinetic with a similar correlation coefficient ($R^2 = 0.97$). The flotation rate was much more rapid for hematite than for quartz, due to the strong affinity of the biosurfactant molecules on the hematite particles.

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Erratum

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