Electroflotation of cassiterite fines using a hydrophobic bacterium strain

Eletroflotação de finos de cassiterita utilizando uma linhagem bacteriana hidrofóbica

Lorgio Gilberto Valdiviezo Gonzales
Departamento de Engenharia de Materiais
PUC-Rio.
lorgiovaldiviezo@gmail.com

Gabriela Alejandra Huamán Pino
Departamento de Engenharia de Materiais
PUC-Rio.
gabriela@esp.puc-rio.br

Maurício Leonardo Torem
Departamento de Engenharia de Materiais
PUC-Rio.
torem@puc-rio.br

Resumo

Nesse trabalho, é apresentada a eletroflotação de finos de cassiterita, utilizando-se o *Rhodococcus opacus* (*R. opacus*) como biorreagente. A avaliação da interação desse micro-organismo com a superfície do mineral foi realizada através de experimentos envolvendo medidas de potencial zeta, ângulo de contato e ensaios de adsorção. Adicionalmente, os efeitos da densidade de corrente e concentração de micro-organismo no tamanho médio de bolhas (*Sauter*) foram também avaliados. Após a interação, foi observado um caráter hidrofóbico nas partículas, como verificado pela medida de ângulo de contato. Além disso, foram observadas mudanças na mobilidade eletroforética das partículas de cassiterita, para valores próximos de zero. O tamanho médio de bolhas, obtido através da técnica de difração laser, foi de 26 µm. A densidade de corrente e a concentração de bactérias mostraram-se como os parâmetros de maior influência no tamanho de bolhas. Os ensaios de eletroflotação constataram uma recuperação máxima em torno de 64,5%, para uma concentração de bactéria de $2{,}87 \times 10^{12}$ células/mL (50 mg cells/L); densidade de corrente de 51,4 mA/cm^2 e pH 5,0.

Palavras-chave: Eletroflotação, finos de cassiterita, *Rhodococcus opacus*.

Abstract

In this work, the electroflotation of cassiterite fine ranges using Rhodococcus opacus (R. opacus) as bioreagent has been carried out. The interaction between R. opacus and mineral surface was valued through the zeta potential, contact angles measurements and adsorption studies. Furthermore, studies were attempted to check the effect of current density and microorganism concentration on mean bubble size (Sauter). After the interaction, the resulting particles exhibited hydrophobic characters, as verified by the increase of the contact angle. Also, the electrophoretic mobilities of cassiterite particles showed a mean value close to zero after interaction with R. opacus. The measurement of bubble size by laser diffraction showed a mean bubble size of 26µm. Current density and bacterial concentration seem to be the main parameters affecting the mean diameter of the bubbles. An electroflotation test reported recovery of around 64.5% at pH 5, concentration of 2.87×10^{12} cells/ml (50 mg/L) and current density of 51.4 mA/cm^2.

Keywords: *Electroflotation, cassiterite fines, Rhodococcus opacus.*

1. Introduction

The use of microorganisms in mineral beneficiation has been elucidated with the recent development in biotechnology; microorganisms and associated extracellular metabolic products are used to selectively separated gangue ores and have been reported as friendly modifiers, collectors and depressants (Govender & Gericke, 2011; Didyk & Sadowski, 2012).

Many studies have been focused on the mineral-bacteria interaction in order to understand the mechanisms behind the flotability and mineral selectivity achieved in the beneficiation process. These microorganisms, both living and dead, and products derived from the organisms are able to affect the surface characteristics and flotation behavior of the minerals. So, they can function as flotation collectors and as flotation depressants and activators (Sharma, 2001; Natarajan, 2006; Rao & Subramanian, 2007; Pecina et al., 2009).

Fine particles typically show slow recovery rates, owing to decreased particle-bubble collision efficiency. Moreover, very small particles tend to have large specific areas and low mass (Pease, 2006; Shahbazi et al., 2010; Miettinen et al., 2010). So, the treatment of mineral fines treatment continues to be one of the major technical challenges for the mineral processing area.

Studies have reported that the recovery of particles in the diameter range of 1-10 µm is increased by decreasing bubble size, which is largely the result of the increased collision efficiency between the particles and the bubbles (Shahjahan Kaisar Alam Sakar et al., 2010; Chipfunhu et al., 2011).

Electroflotation has been suggested as the process for obtaining the smallest bubble diameters (< 60µm), that involve oxidation-reduction reactions. Many applications have been developed with this technique, such as wastewater treatment and mineral processing, especially fine particles.

In this work, the electroflotation of fine cassiterite using *R. opacus* as bioreagent was investigated. The effects of solutions *p*H, microorganism concentration and current density on flotation recovery and bubble size were studied in batch experiments. Furthermore, the mean bubble sizes were determined.

2. Materials and methods

Bacteria strain

R. opacus obtained from the culture collection of the Tropical Foundation of Searches and Technology André Tosello - São Paulo, was used in this study. The bacterium was grown at 28°C in agitated liquid media containing, yeast extract, 3 g/L; peptone, 5 g/L; glucose, 10 g/L and malt extract 3.0g/L. The medium was sterilized by autoclaving at a pressure 1 atm for 20 minutes. The *p*H was adjusted to 7.2 with diluted NaOH solutions. Growth was allowed to proceed for 48 h on a horizontal shaker operating at 250 rpm. After microorganism growth, the culture was separated by centrifugation, and the obtained solid material was washed with deionized water and suspended in NaCl 0.1 mM, later being sterilized at 1 atm of pressure during 20 min. The cellular quantification was determined by dry weight.

Mineral sample

Mineral sample de cassiterite was obtained from Zé Estrada Mineração, MG, Brazil. The sample was properly ground and sieved for the experimental test. The mean particle size (d_{50}) of the fine fraction (-37µm) was found to be 8 µm, using Malver mastersizer model 2000 particle size analyser. FRX analysis confirmed the purity of mineral sample (84.7%).

Electrokinetics experiments

Zeta potential of the cassiterite was determined in the presence and absence of bacteria using a Malvern Zeta-sizer. The zeta potential of bacterial cells was measured at a concentration of 600 mg/L ($3{,}4x10^{14}$ cells/ml). All measurements were conducted at the same ionic strength (10^{-3} M NaCl). To measure the zeta potential of cassiterite after interaction with bacteria, the sample was first conditioned with *R. opacus* under required conditions (pH, adsorption time and cell concentration) and then unattached cells were removed by centrifugation at 2000 rpm for 3 min. The cassiterite particles were resuspended in 10^{-3} M NaCl and the pH was readjusted to the initial value.

Adsorption studies

In the adsorption experiments, 0.5 g of mineral sample was added to 50 ml of cellular suspension with a known initial concentration of bacteria. The mixture was agitated in a mechanical shaker for 15 minutes at 150 rpm and 28°C and subsequently centrifuged at 200 rpm for 3 min to settle the minerals. The bacterial concentration in the supernatant was determined using the optical density method. The concentration of bacteria adsorbed at the mineral surface was taken as the difference between the inoculated concentration of bacteria and the concentration of bacteria remaining in the supernatant after 15 min contact time. Adsorption studies were performed as a function of the pH values of the suspension with a 10^{-3}M NaCl as a supporting electrolyte.

Contact angle measurements

Contact angle on mineral powders was obtained by sorption measurement using Kruss Tensiometer K 100. The Washburn equation is used to measure the contact angle on powder samples. When a column of powder bed is in contact with liquid, the pores between the particles act like small capillaries and the rise of liquid is measurable. The capillary constant in the Washburn equation was determined using toluene and water respectively. Mineral samples of -210 µm +106 µm size fraction were used. A 2 g of mineral was placed into a glass sample tube and was carefully and equally packed each time. Each measurement was repeated at least 3 times.

Bubble size measurement

An electroflotation cell was constructed of acrylic material with 1 L of capacity operated in batch mode. A polished stainless steel with 8.5 cm of diameter and total surface area of 56.7 cm^2 was used as cathode. It was placed in the bottom of the cell and a Ti/RuO_2 mesh supplied by De Nora, Brazil, was used as anode (3 mm above the cathode.) This configuration has been chosen to measure both the hydrogen and oxygen bubbles produced at the same time. The electrical current was applied using a TECTROL mod.–TCA-30-10XR1A DC power supply with a maximum current rating of 10 A at an open circuit potential of 30 V. All experiments were performed at an ionic strength of 0.1 M NaCl.

The micro-bubbles produced in the electrochemical cell were determined with Mastersizer 2000SM - equipment from Malvern Instruments, UK, through light scattering. This instrument is capable of analysis in the range from 0.1 to 2000 µm. Pumping speed was kept low (1000 rpm), to avoid undesired bubble formation through atmospheric air entrance. Analysis was started immediately, to avoid bubble coalescence or collapse imposed by shear.

Electroflotation experiments

The electroflotation cell used in this work (Figure 1) is a modification of the Hallimond tube such as to incorporate the electrolytic cell directly below the flotation column. The arrangement and electrode material were similar to those used for bubble sizes measurements. A magnetic stirrer bar was placed in the middle of electrodes to provide enough energy to maintain the ore suspension homogeneous. The pulp density was kept constant at 1%, and NaCl 0.1 M was used as electrolyte. The pulp was conditioned for two minutes. All flotation experiments were repeated twice.

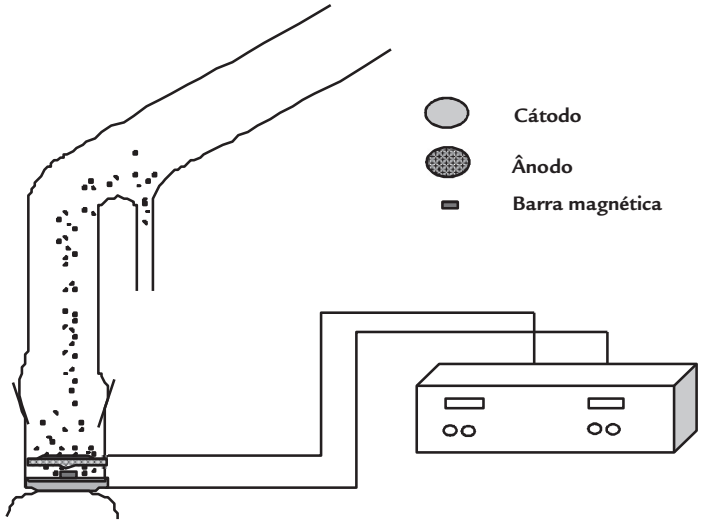

Figure 1
Schematic diagram for electroflotation cell.

3. Results and discussions

Electrokinetic experiments

Figure 2 shows zeta potential curves for *R. opacus* and cassiterite (before and after interaction). The surface charge of R. opacus decreased with decreasing pH and reached an IEP at pH 2.42. The IEP for cassiterite untreated is 5.9. According to this data, in the range between pH 2.42 to 5.8 an electrostatic interaction between *R. opacus* and cassiterite is expected to be favorable because of their different surface charges. It is interesting to note that the surface charge of cassiterite after conditioning with *R. opacus*, was close to zero. This may indicate that the adsorption of R. opacus cells onto cassiterite surface formed biocoagulates and the non-electrostatic forces, such as hydrogen bounding and chemical forces, may govern the *R. opacus* and cassiterite interaction.

Bacteria and yeast and products derived from them can be excellent biocoagulating agents and in some cases can function as selective coagulating agents. Kuyumcu et al. (2008) have demonstrated that Sacchharomyces cerevisiae and Yarrowia lipolytica are excellent coagulants for sphalerite and galena (below 10 µm).

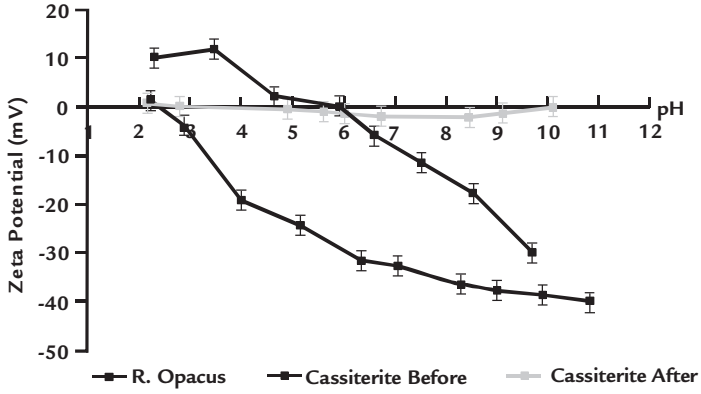

Figure 2
Zeta potential of *R. Opacus* and cassiterite particles (before interaction and after interaction with *R. Opacus)*.

Adsorption studies

The amount of adhesion of *R. opacus* cells to cassiterite particles as a function of pH values is presented in Figure 3. It is evident that the adhered quantity of microorganisms increased in the acid region, where cassiterite and *R. Opacus* have different surface charges and consequently are highly subject to electrostatic interaction. However above the IEP of cassiterite, the non-electrostatic forces such as hydrogen bounding and chemical forces, may govern the adsorption process.

The effect of the initial bacteria concentration on the quantity of microorganism adsorbed onto cassiterite is depicted in the same figure. Even though the bacterial cells tended to adhere on mineral surface for all concentration tested, the quantity of microorganisms adsorbed increased with the initial microorganism concentration.

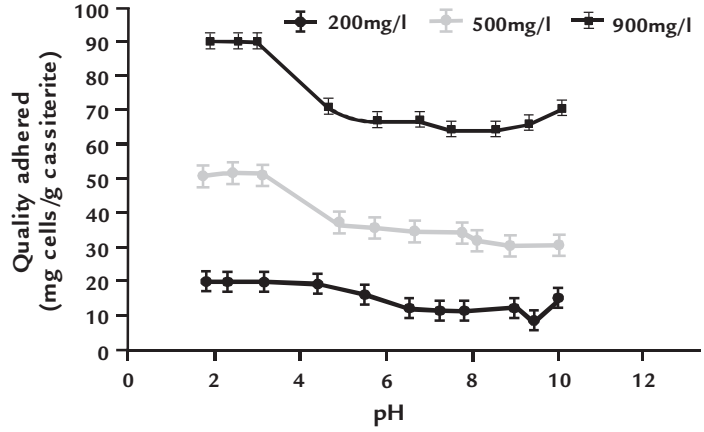

Figure 3
Adsorption of bacterial cells onto cassiterite at different pH values.

Contact angle measurements

The effect of the microbial cell-cassiterite interaction on the surface properties of the mineral was determined by measuring the contact angle of cassiterite sample before and after biomodification. Figure 4 shows the effect of bacterial adhesion in the contact angle of cassiterite as a function of initial bacteria concentration.

The pH value of 3 was chosen because the highest adsorption verified in the adsorption test. Before the interaction with the microorganism, the cassiterite surface was completely hydrophilic, since its affinity for the air bubble was completely nil (values of contact angle such as zero). After the interaction, a hydrophobic character was founded, as verified by the increase of the contact angle. So, prior to the interaction, the contact angle was 0° (hydrophilic) and after conditioning with $34.47x10^{12}$ cells/mL (600 mg/L), the contact angle increased to 80°.

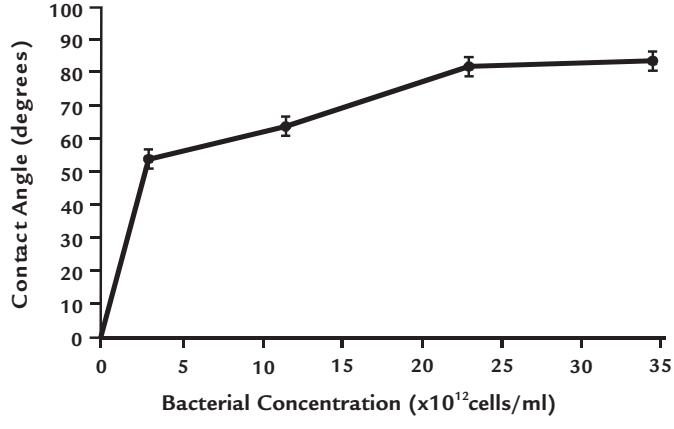

Figure 4
Contact angle for cassiterite as a function of concentration of *R. opacus*, after conditioning with cells of *R. Opacus*, at pH 3.

Bubble size measurement

The bubble size measurement was performed in the absence of mineral but it considered equivalent reagent concentration. Figure 5 shows the effect of *R. opacus* concentration and current density on mean bubble diameter. In the absence of microorganisms, big bubbles were formed, while for concentration greater than $2.87x10^{12}$ cells/mL, the average bubble size decreased substantially (from 45 µm to 15 µm). These results indicated coalescence as the main mechanism determining the size.

Figure 5 also shows bubble size produced at different current densities. Within the range studies (20-95 mA/cm^2) high current density promotes the formation of small bubbles. In accordance with Shahjahan Kaisar Alam Sarkar et al (2010), more nucleation sites are expected to become active at higher current density as the solution adjacent to the electrode surface becomes more supersaturated (less amount of dissolved gas before detachment). As detachment time is less, fine bubbles are expected in the case of higher current densities. Finally, low current densities lead to large bubbles sizes and thus they should be avoided to prevent non-effective electroflotation separations.

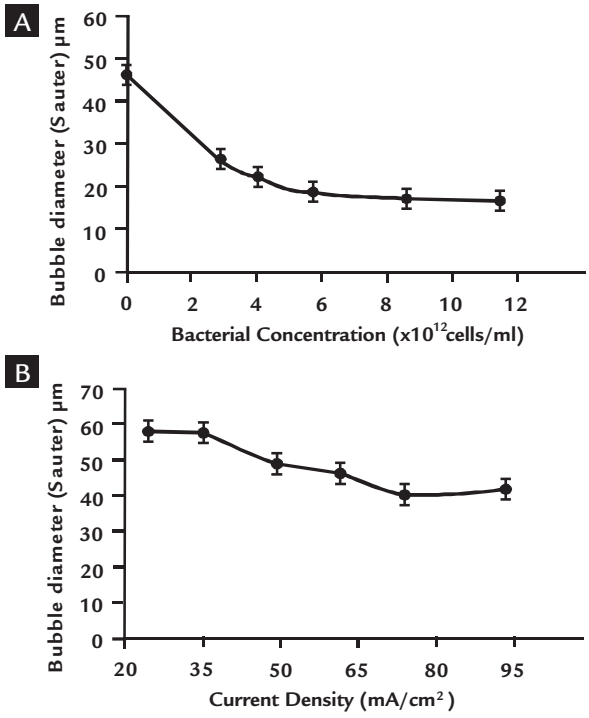

Figure 5
Bubble size as a function of:
A) Concentration of *R. opacus.*
B) Current density, at pH 5.

Electroflotation experiments

Since *R. opacus* cells have hydrophobic properties and can easily adsorb onto cassiterite surface under acid conditions, we investigate the use of *R. opacus* as collector or surface modifier for cassiterite electroflotation. The electroflotation of fine cassiterite as a function of bacterial concentration in the absence of a conventional collector is presented in Figure 6. Experiments were carried out at pH 3 in the presence of 0.1 M NaCl for a conditioning time of 5 min and flotation time of 6 min. The highest flotation recovery of 64.5% was observed with a $2.87x10^{12}$ cells/mL (50 mg cells/L) of initial bacterial concentration, which decreased to 50% when the *R. opacus* concentration increased. This decreased recovery could be the result of very large flocs that formed and could not be levitated by the fine bubbles produced. Such behaviors have been reported in literature (Dubel et al., 1992 and Botero, 2007).

The observed average recovery of cassiterite is similar that of Quin Wen-Quing et al (2012), who reported recoveries of 62% using a mixer of salicylhydroxamic acid and tributyl phosphate collectors in fine cassiterite electroflotation system.

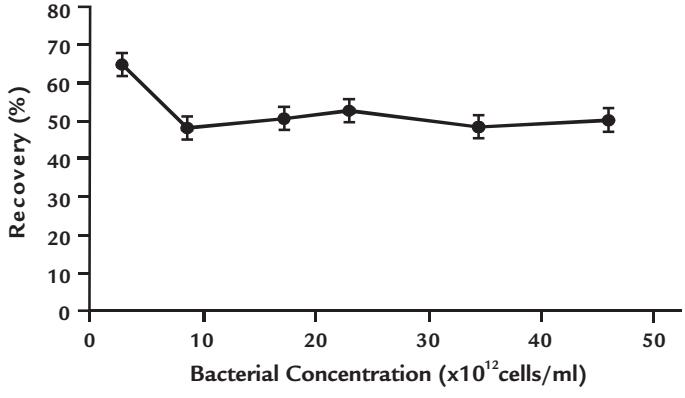

Figure 6
Effect of bacterial concentration on flotation recovery of cassiterite fines at pH 3.

4. Conclusions

Zeta potential results showed that *R. Opacus* cells were positively charged under acidic conditions (pH < 2.42) and negatively charged under neutral and alkaline conditions, with an IEP at pH 2.42. Moreover, cassiterite particles showed and IEP at pH 5.8. The quantity of cells adsorbed onto the cassiterite surface was higher at pH 3 due to electrostatic attraction forces. Interactions of *R. opacus*-cassiterite under acidic conditions changed the surface proprieties and charge to a degree dependent on the initial bacterial concentration: at 600 mg cells/L, the average surface charge was around 0 and contact angle was 80°. Current density and initial bacterial concentration were very important parameters in the electrolytic production of bubbles; high current densities and bacterial concentration promote the formation of small bubbles. The electroflotation test using *R. opacus* at the concentration of $2.87x10^{12}$ cells/mL (50 mg cells/L) at pH 3 gave 64.5% cassiterite recovery.

5. Acknowledgement

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