Replacing Synthetic with Microbial Surfactants as Collectors in the Treatment of Aqueous Effluent Produced by Acid Mine Drainage, Using the Dissolved Air Flotation Technique

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Abstract Dissolved air flotation (DAF) is a well-established separation process employing micro bubbles as a carrier phase. The application of this technique in the treatment of acid mine drainage, using three yeast biosurfactants as alternative collectors, is hereby analyzed. Batch studies were carried out in a 50-cm high acrylic column with an external diameter of 2.5 cm. High percentages (above 94%) of heavy metals Fe(III) and Mn(II) were removed by the biosurfactants isolated from *Candida lipolytica* and *Candida sphaerica* and the values were found to be similar to those obtained with the use of the synthetic sodium oleate surfactant. The DAF operation with both surfactant and biosurfactants, achieved acceptable turbidity values, in accordance with Brazilian standard limits. The best ones were obtained by the biosurfactant from *C. lipolytica*, which reached 4.8 NTU. The results obtained with a laboratory synthetic effluent were also satisfactory. The biosurfactants removed almost the same percentages of iron, while the removal percentages of manganese were slightly higher compared with those obtained in the acid mine drainage effluent. They showed that the use of low-cost biosurfactants as collectors in the DAF process is a promising technology for the mining industries.

Keywords Biosurfactants · Flotation · Effluent treatment · Heavy metals · *Candida* · Low-cost substrate

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Introduction

Mining, in general, has been a source of severe environmental impact, especially the acid mine drainage (AMD), resulting from the natural oxidation of sulfide minerals exposed to the interplay of water and oxygen [1], in the presence of bacteria [2, 3]. AMD of effluents is generated before plowing in the open or underground deposits of tailings and waste rock containing pyrite [3–5] and/or marcasite, settling basins and storage yards of ore where the oxidized compounds appear as white and yellowish crusts on the surface of exposed rocks and sediments [6].

In Brazil, the AMD has seriously affected the quality of soil and water resources in regions near coal mining areas in Santa Catarina state and, to a lesser degree, in Rio Grande do Sul state. As a result, there is an urgent need to adapt current technologies to prevent or eliminate the environmental liabilities within the framework of sustainable development [7].

Flotation was first used in mineral processing and as such has been used for a long time in solid/solid separation applications using stable froths to recover the mineral particles [8–10]. Dissolved air flotation (DAF) processes involve the removal of a solute, such as toxic metal ions, by adsorption, co-precipitation or occlusion into the in situ formed carrier floc, which is then floated by the addition of a suitable surfactant [11–14].

The use of flotation as a separation process, either as part of pollution control or during water treatment, has been sometimes criticized due to the likely toxicity of the collectors. The development and use of fully biodegradable surfactants may ease this concern and enhance the further acceptance of this separation technology [15].

Surfactants are amphiphilic compounds that reduce the free energy of the system by replacing the bulk molecules of higher energy at a given interface. Surfactants have been used industrially as adhesive, flocculating, wetting and foaming agents, de-emulsifiers, and penetrants [16]. They are used for these purposes due to their ability to lower surface tensions, increase solubility, detergency power, wetting ability, and foamimg capacity [17]. Good surfactants can lower the surface tension of water from 72 to 35 mN/m [15]. The surface tension correlates with the concentration of the surface-active compound until the critical micelle concentration (CMC) is reached. The CMC is defined as the minimum concentration necessary to initiate micelle formation. Efficient surfactants have a low CMC [18].

Considerable attention has been given to the production of surface-active molecules of biological origin to replace synthetic surfactants due to the advantages such as higher biodegradability, higher foaming [19], less toxicity, better environmental compatibility [20], more tolerant to pH, salt, and temperature variation [21], higher selectivity for metals and organic compounds and the ability to be synthesized from renewable feedstocks [22].

The solubilization and emulsification of toxic chemicals by biosurfactants have been described [23, 24]. Most biosurfactants used in soil bioremediation are produced by bacteria, especially species of *Pseudomonas* [20] and *Bacillus* [25–27] and few have been used in the removal of heavy metals [20, 22, 23, 28].

Recently, novel biosurfactants with attractive properties have been produced and isolated from *Candida* species. Sobrinho et al. [29] described a low-cost medium for the production of an anionic surfactant from the yeast *Candida sphaerica*. The medium was based on distilled water supplemented with ground-nut oil refinery residue plus corn steep liquor as substrates. The biosurfactant produced showed high surface tension reducing activity (26 mN/m) and a small CMC value (0.08%), while Rufino et al. [30] produced an anionic biosurfactant from *C. lipolytica* grown in vegetable oil refinery residue and glutamic acid which reduced the surface tension to 26 mN/m at 0.03% concentration. More recently, Luna et al. [31] described the use of statistical experimental designs and response surface

methodology to optimize the concentrations of soybean oil refinery residue and corn steep liquor for biosurfactant production by *C. sphaerica*. The biosurfactant showed a surface tension of 25 mN/m and a CMC of 0.03%.

In the present study, the three yeast biosurfactants described above were examined, for the first time, as alternative collectors for DAF. The removal of Fe(III) and Mn(II) from an aqueous effluent from AMD was studied in a DAF batch unit, and the process effectiveness was monitored by measuring the residual content of metal and the supernatant turbidity.

Materials and Methods

Materials

All chemicals were of reagent grade. The aqueous effluent produced by AMD was supplied by Carbonífera Metropolitana S.A., located in Siderópolis city, Santa Catarina state, Brazil. The initial pH, dissolved oxygen, iron, manganese, cadmium, and mercury content and turbidity of the effluent were determined according to APHA [32] and are shown in Table 1. A synthetic effluent was also prepared in the laboratory with the same metal concentrations of the effluent in order to compare the results and analyze the influence of the limiting factors found in aquatic ecosystems.

Biosurfactants

The biosurfactants produced by *C. lipolytica* UCP0988 and *C. sphaerica* UCP0995 were examined as alternative collectors to the synthetic sodium oleate. They were produced, isolated and characterized regarding surface tension and CMC from sterilized broth according to previous work [29–31]. The biosurfactant described by Rufino et al. [30] was named biosurfactant R, while the ones described by Sobrinho et al. [29] and Luna et al. [31] were identified as Biosurfactant S and L, respectively.

Sample Preparation

The effluent pH was adjusted to 8.5 with a 5% solution of CaO prior to use. Aqueous solutions of the biosurfactants isolated from *C. lipolytica* and *C. sphaerica* at 0.02% concentrations were prepared, while sodium oleate was used at 0.75% concentration.

Table 1 Acid mine drainage effluent physical-chemical properties

Properties	Value	Maximum permitted[a]	Analytical method
pH	3.0	6.0–9.0	Potentiometry
Dissolved O_2 (mg/l)	9.5	≥5.0	Potentiometry
BOD (mg/l)	5	5	BOD test
Fe (mg/l)	61.98	0.30 (dissolved)	Atomic absorption
Mn (mg/l)	4.0	0.1	Atomic absorption
Hg (mg/l)	0.0002	0.0002	Atomic absorption
Turbidity (NTU)	142	100	Nephelometer

[a] Maximum values permitted according to the Brazilian legislation [33]

Pressurizing System

In this work a pressurizing tank built of steel was used, as illustrated in Fig. 1. The procedure consists of saturate the liquid effluent, which has been previously placed in the tank (1 l), with compressed air during at least 20 min, at a measured pressure (DOVER manometer, USA) controlled by a pressure regulating valve (DOVER, model number 014RPE00, USA). The saturated water was discharged through a needle valve into the flotation equipment, undergoing sudden decompression and producing micro air bubbles.

Batch Operation Unit

The initial work on the effluent was carried out batchwise, using a flotation column built of acrylic (external diameter of 2.5 and 50 cm in height), as illustrated in Fig. 1. The column was previously loaded from the top with the effluent. Next, the liquid was saturated with air from the tank was discharged into the column producing the flotation process. In all experiments, 50 mL of one of the two biosurfactants or the sodium oleate were used as collectors. A recycle rate of 50% and a saturation pressure of 405.3 kPa was used. After 1 min of operation, samples of the treated effluent were collected for analysis of Fe and Mn content, by atomic absorption analysis using flame spectrophotometry and turbidity by a nephelometer (HACH model 8431), and pH.

Results and Discussion

Methods of flotation—in which hydrophobic particles are efficiently separated by air bubbles from hydrophilic base minerals with addition of surfactants or froths (concentrate foams)—have been used in mineral processing. The addition of surfactants in the pressurized water in dissolved air flotation is used to lower the air/water surface tension in the saturator, improving the separation process [15]. The unit used in this work employed a process of neutralization of the effluent with calcium oxide (CaO), conditioning with four different surfactants followed by DAF as a step in solid–liquid separation.
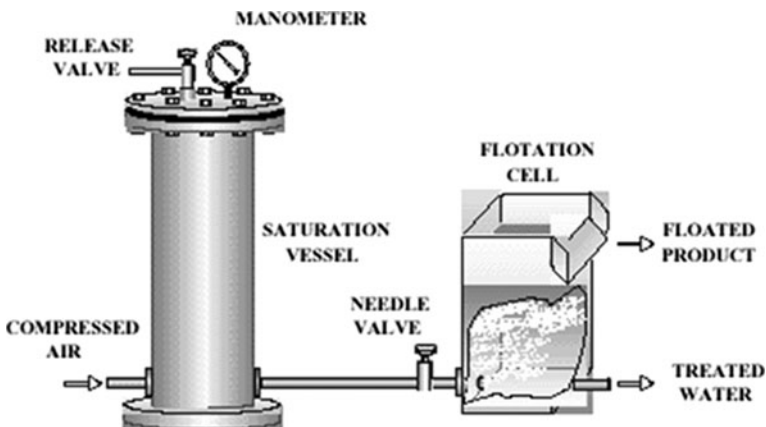

Fig. 1 Batch dissolved air flotation (DAF) unit [7]

The results obtained for the removal of the heavy metals Fe and Mn and for the effluent final pH and turbidity are shown in Table 2. As the concentration of mercury detected in the effluent before treatment is within the maximum allowed, the tests were not carried out for this metal.

The possible mechanisms for recovery of toxic metals by biosurfactants are ion exchange, precipitation-dissolution, and counter-ion binding. The anionic biosurfactant carries a negative charge, so when the molecule encounters the cationic metal that carries a positive charge an ionic bound is formed. The polar head groups of micelles can bind metals. This makes the metals more soluble in water. It is likely that surfactant monomers acted to solubilize the adsorbed metal through the formation of dissolved complexes [22].

The DAF operation with both surfactant and biosurfactants, tested in the same conditions, achieved acceptable turbidity values, and the best ones were obtained by the biosurfactant R, which reached 4.8 NTU (lower than 5 NTU, the Brazilian standard limit).

It is important to emphasize that biosurfactants were used in concentrations below the CMC, suggesting that their use in or above the CMC will allow higher rates of removal.

It can be observed that biosurfactants were able to remove high percentages of iron and manganese, with removal efficiency comparable to those obtained with sodium oleate, the latter being in highest concentration. According to Brazilian legislation [33], the maximum allowed for Iron and manganese in wastewater is 0.3 and 0.1 mg/l, respectively. The results showed that the residual concentration of Fe in the effluent was 0.26 and 0.11 mg/l, after treatment with the biosurfactant R and with sodium oleate, respectively. Moreover, the concentration of residual iron after treatment with the biosurfactant S was 0.77 mg/l. For manganese, the concentration observed after treatment with the biosurfactant R and with sodium oleate was the same, 0.22 mg/l, being just above the permitted, while for the treatment with the biosurfactant S, a residual concentration of 0.16 mg/l was observed.

The results obtained with the laboratory synthetic effluent are described in Table 3. It could be observed, as for the original effluent, that the biosurfactants removed almost the same percentages of iron, while the removal percentages of manganese were slightly higher compared to those obtained in the acid mine drainage effluent.

Although the chemical structures of biosurfactants have not been fully explained to date, results showed that when compared to the chemical surfactants, these biomolecules presented, in general, have a greater affinity for the metal ions Fe(III) and Mn(II) during the treatment process. This may have occurred because of structural differences between sodium oleate and biosurfactants and/or due to the influence of other agents interfering in the sample.

Analyzing the precipitation range of metal ions, the pH of the samplers were set at 8.5 during the process. This was favorable to the ion Fe(III), since it precipitates above pH 4.5,

Table 2 Results obtained by DAF using the acid mine drainage effluent

Collector	pH	Removal (%)		
		Turbidity	Fe	Mn
Biosurfactant R	8.3	96.6	99.5	94.5
Biosurfactant S	7.7	92.8	98.7	96.0
Sodium Oleate	8.6	93.8	99.8	94.5

A recycle rate of 50% and a saturation pressure of 405.3 kPa were used

Table 3 Results obtained by DAF using the laboratory synthetic effluent

Collector	Volume (ml)	Removal (%)	
		Fe	Mn
Biosurfactant R	75.0	99.2	99.0
	100.0	99.5	98.0
Biosurfactant S	75.0	99.8	99.5
	100.0	99.5	99.2
Biosurfactant L	75.0	99.7	99.5
	100.0	99.0	98.2
Sodium oleate	75.0	97.6	97.0
	100.0	99.1	99.0

A recycle rate of 50% and a saturation pressure of 405.3 kPa were used

while the Mn(II) precipitates at a pH greater than 8.0. Therefore, the medium conditions favor the precipitation and subsequent reaction of Fe(III) with the collectors, while the fact that a certain amount of ions Mn(II) was not precipitated, may have been hindered by the presence of ionic strength, impairing its reaction with the collectors and therefore their removal in relation to Fe(III), giving to this part of the flotation process characteristics of ionic and not of precipitated, as described by Matis [34].

Recycling rates have played quite a positive role in the clarification and removal of metal ions. On the other hand, when analyzing the variation of the concentration of metal ions before and after treatment—as well as the suspended material—it must be noticed that the increased amount of water in the recycling after the addition of surfactants or biosurfactants caused a decrease in the concentration of those ions not previously precipitated or aggregated by the collector, rather than their total removal by flotation, a factor that led to a low concentration of ions in the treated effluent.

Although the recycle rate has not affected the collectors' ability to remove metals, its role should be considered in analyzing the efficiency of the process according to the law of dilution.

Conclusions

This is the first report on the treatment of aqueous effluent produced by acid mine drainage by dissolved air flotation using yeasts biosurfactants. The results obtained show that the process proposed in this work is a promising technology in the mineral processing industries. The results showed that the yeast biosurfactants are as effective in removing heavy metals as the synthetic collector sodium oleate. The possibility of biosurfactants to be recycled or naturally degraded in ecosystems makes them likely to replace the synthetic surfactants in waste water and industrial effluents treatment by flotation, giving best results from the environmental point of view. However, for future development there are many factors to be researched thoroughly. Biosurfactant type and concentration, operational parameters and the effectiveness of batch and continuous operations must be deeply investigated.

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