Using Tanflos SG to Remove Fine and Ultra-Fine Iron Mineral Particles from Water

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Abstract. One of the biggest challenges in the mineral scenario is concentrating and removing fine particles, as consequence of that, there are a high concentration of mineral inside the Ganga and this reality needs to be changed. Seeking to contribute significantly, this research used the process of DAF (dissolved air flotation), because in this process the bubbles are less than 100 µ, what is fundamental because the fines and ultrafine particles. For the pretreatment was used the biosurfactant Tanfloc SG as much as flocculant and coagulant. Other techniques such as FTIR (Fourier-Transform infrared), Zeta potential and contact angle was used to show the mineral and the biosurfactant characteristics. As a conclusion, the IEP (isoelectric point) was close to pH 8.5 for Tanfloc, but for hematite, with Tanfloc the pH went down to 5.3 - 6.5 and the DAF depends the biosurfactant concentration, the best results were between 140 and 175 mg/L.

Keywords: Fine, ultra-fines, biosurfactant, DAF, Tanfloc SG.

1. Introduction
Dissolved air flotation (DAF) can be an efficient alternative for treatment of fine iron particles, because it is possible to generate bubbles less than 100µ. Reports are confirming, collision efficiency and adhesion tend to increase with decreasing bubble size [5]. Moreover, this process only works in the presence of chemical agents capable of altering the surface characteristics of the particles.

Tanfloc SG biosurfactant was used because it is a cationic organic polymer of vegetable origin. This biosurfactant has low molar mass and positive electric charge, acting on colloids by neutralizing charges and forming bridges between these particles an is efficiency covers pH range between 4.5 and 8.0 [4], without changing it, precisely because it does not consume the alkalinity of the medium [9].

The objective of this work is to separate hematita from quartz of iron ore fines by dissolved air flotation using the biosurfactant Tanfloc SG. Several parameters and variables, that influence hematite selectivity and recovery, such as pH and bioreagent and depressor concentration, were evaluated throughout this work to determine the optimal conditions where the highest selectivity and flotability occurs.

2. Materials and methods
Iron ore, hematite and quartz were purchased from Mineração Zé da Estrada Ltda. Chemical analyses showed 54% of Fe in the iron ore and 99% of purity in the hematite and quartz samples. Biosurfactant Tanfloc SG was obtained from TANAC. Sodium hydroxide was obtained from Merck, hidrocloric acid...
was purchased from Vetec and toluene and potassium chloride was obtained from Próquimios. For flotation, an Aquaflot Dissolved Air Flotator was used on a laboratory scale. It has 3 L of water capacity, using a pressure in the range of 400 to 600 kPa. A needle valve was used to adjust the outlet of the supersaturated water portion.

2.1. FTIR (Fourier-Transform infrared)
Infrared spectra were performed on the Scientific Nicolet 6700 FT-IR FTIR spectrophotometer and followed the KBr pellet method. The spectra were performed to identify the functional groups present in the polymer, pure mineral and mineral after interaction with the polymer. In order to obtain the pellets, particle or bioreagent size reduction was first performed using mortar and pestle in order to obtain a homogeneous mixture between the sample and the KBr. The proportion of sample and KBr was 1/100 (w/w). Then, the homogeneous mixture pellet was obtained by compression. Finally, the obtained tablet was analyzed in the FTIR apparatus. Spectra were obtained at a resolution of 4 cm\(^{-1}\) using 120 scans.

2.2. Zeta Potential
Zeta potential measurements were made for polymer and mineral sample. These studies were performed on a Malvern Zetasizer Nano-type microelectrophoresis device at PUC-RIO mineral and environmental technology laboratory. The measurements aimed to study the possible mechanisms of interaction between the polymer and the mineral surface. Zeta potential measurements were made for polymer, mineral and mineral after interaction with the polymer. All Zeta potential measurements were performed within a pH range of 2 to 10.

2.3. Contact Angle
Contact angle measurements were performed for mineral samples before and after interaction with the biosurfactant. These studies were done on the Surface Electro Optics DCA 200 SERIES device at PUC-Rio mineral and environmental technology laboratory. Washburn method was used to obtain contact angle values in pH range from 7.0 to 8.0 in duplicate with the powder samples. The solvent used to determine Washburn constants was Toluene.

2.4. Flotation
Firstly, coagulation and flocculation tests were performed to verify flake formation. The working range of pH was between 5.0 and 11.0 and the biosurfactant concentration was between 35 and 200 mg L\(^{-1}\), maintaining a fixed iron ore mass of 4.0 g. At the end of each test, with the highest biosurfactant concentration, the mixture was floated to preliminarily assess the flotability of each pH. This test is illustrated in figure 5.

Based on these preliminary coagulation and flocculation results, flotation tests were performed to evaluate ore recovery at each fixed pH with the Tanfloc SG concentration variation.

First, water and iron ore are added, which are placed under agitation. Then the biosurfactant was added and vigorously stirred for 5 minutes. After this interval, stirring was reduced and maintained for 10 minutes to keep the solid material suspended for flake formation. At the end of these 10 minutes the flotation was performed and the flotated material was scraped and filtered.

3. Results

3.1. FTIR (Fourier-Transform infrared)
One of the important aspects of infrared spectroscopy analysis is the possibility of identifying the functional groups of the collector and their structure. With this, one can understand more about how the polymer interacts with the mineral.

These characteristics can be observed by the FTIR spectra. Table 1 shows the main characteristic peaks of Tanfloc. The absorption band is preserved around 3369 cm\(^{-1}\) which corresponds to the stretch vibration of the O-H and N-H groups present in the polymer. Other important factors are strong carbonyl bands near 1713 cm\(^{-1}\).
This band is in the range of carbonyls attached to alkyl groups or carboxylic acids. Due to the interval, it is difficult to confirm with infrared spectroscopy alone. The bands in 1609, 1233, 1021 and 830 cm\(^{-1}\) refer to aromatic groups. At 1609 cm\(^{-1}\) there are stretches of conjugated alkenes or the aromatic ring itself. At 1233 cm\(^{-1}\) the strong bands may refer to the \(\nu\) (C-N) or \(\nu\) (Ph-O) stretches of alkyl amines or aromatic ethers. The bands at 1021 and 830 cm\(^{-1}\) refer to the \(\delta\) (C-H) folds both inside and outside the plane of the aromatic ring. Finally, the 1111 cm\(^{-1}\) band refers to the stretching of aliphatic cyclic ethers directly linked to the aromatic ring and at 1300 cm\(^{-1}\) there is evidence of the presence of alcohols, with phenol grouping being the most likely. Thus, one can assume which are the major functional groups present in the tanfloc structure, being similar to the tannin structure as expected.

| Tanfloc SG | Attribution            |
|-----------|------------------------|
| 3369      | \(\nu\) (O-H) + \(\nu\) (N-H) |
| 1713      | \(\nu\) (C=O)          |
| 1609      | \(\nu\) (C=C)          |
| 1463      | \(\delta\) (C-H\(_2\)) |
| 1354      | \(\nu\) (C-N)          |
| 1300      | \(\nu\) (C-O)          |
| 1233      | \(\nu\) (C-N) + \(\nu\) (Ph-O) |
| 1111      | \(\nu\) (C-O-C)        |
| 1021      | \(\delta\) (C-H)       |
| 830       | \(\delta\) (C-H)       |

Table 2 shows that the pure hematite mineral and after conditioning with the biosurfactant. The bands below 1000 cm\(^{-1}\) correspond to the iron oxide stretching modes, with the bands around 673, 539, 458 and 439 cm\(^{-1}\) corresponding to the Fe-O bond stretching modes [1][7].

| Hematite | Hematite + Tanfloc SG | Attribution |
|----------|-----------------------|-------------|
| 439      | -                     | \(\nu\) (Fe-O) |
| 447      | -                     | \(\nu\) (Fe-O) |
| 458      | 453                   | \(\nu\) (Fe-O) |
| 519      | -                     | \(\nu\) (Fe-O) |
| 522      | -                     | \(\nu\) (Fe-O) |
After the interaction of hematite with the biosurfactant, it is possible to observe the overlapping of the bands below 1000 cm\(^{-1}\) by two bands at 532 and 453 cm\(^{-1}\). This is probably due to the interaction of Tanfloc with hematite, so that there is no significant difference in the different vibrational stretching modes of Fe-O bonds, integrating with the different existing rotational modes. Thus, there is formation of the two predominant bands. Not enough resolution to observe Tanfloc bands.

Table 3 shows that the pure quartz mineral and after conditioning with the biosurfactant. The bands around 465 and 692 cm\(^{-1}\) correspond to the asymmetrical folding of Si-O-Si and symmetrical folding of Si-O bond. The bands around 792 and 1090 cm\(^{-1}\) correspond to the symmetrical Si-O and asymmetrical stretching of the Si-O bond [3].

It is not possible to observe the same phenomenon of band overlap as in the hematite spectrum after conditioning, as well as the Tanfloc bands.

### Table 3. Pure quartz mineral and with Tanfloc SG

| Quartz     | Quartz + Tanfloc SG | Attribution     |
|------------|---------------------|-----------------|
| 465        | 468                 | \(\delta\) (Si-O-Si) |
| 692        | 691                 | \(\delta\) (Si-O)  |
| 792        | 792                 | \(\nu\) (Si-O)   |
| 1089       | 1092                | \(\nu\) (Si-O)   |

3.2. Zeta Potential

Figure 2 shows the results obtained from the Tanfloc SG zeta potential measurements in the presence of potassium chloride (KCl) as electrolyte at concentrations of \(10^{-3}\) mol/L and \(10^{-4}\) mol/L at different pHs. The biosurfactant presented an isoelectric point (IEP) at pH around 8.5, observing that for pH values below 8.5 the zeta potential is positive and for values higher than this the potential measured is negative. At both concentrations, the same IEP was identified without major differences in the magnitude of the Tanfloc SG potential associated with the compression effect of the electric double layer.

![Figure 2. Tanfloc SG zeta potential](image)

Figure 3 shows the hematite potential zeta profiles before and after interaction with the biosurfactant. Prior to interaction, hematite zeta potential values are close to 10 mV in the acid range and around -20
mV. These values show how hematite can interact with an acidic anionic surfactant and basic cationic surfactant.

Following interaction with the biosurfactant, a change in the surface properties of the mineral is observed. There is a shift in the pH value corresponding to the IEP pH around 5.3 to 6.5 after interaction. This result may be due to the adsorption on the surface of the mineral caused by electrostatic forces, since hematite has a less positive charge than Tanfloc.

Figure 3 shows the zeta potential profiles of quartz before and after interaction with the biosurfactant. Prior to interaction, the quartz zeta potential values are close to the EIP in the acid range and around -20 and -30 mV for 10^-4 and 10^-3 mol/L electrolyte concentration, respectively. These values show that quartz particles are negatively charged and how quartz can interact with cationic surfactant throughout the pH range. In the literature, there are reports in which IEP is around pH 2.0 [2]. After interaction with the biosurfactant, the pH corresponding to the PIE pH around 4.2 is observed.

Figure 4. Quartz potential zeta
3.3. Contact angle

Contact angle measurements were performed to prove the hydrophobicity of minerals before and after interaction with Tanfloc SG biosurfactant. Both pure mineral and biosurfactant interacting mineral (140 mg/L) measurements were performed at pH 7.0, 7.5, and 8.0 and are shown in Table 4.

| Sample          | pH 7.0     | pH 7.5      | pH 8.0      |
|-----------------|------------|-------------|-------------|
|                 | C (x10^-3) | θ (°)       | C (x10^-3)  | θ (°)       | C (x10^-3)  | θ (°)       |
| Hematite        | 3.43       | 72.5 ± 4.5  | 3.4         | 72, ±4.0    | 3.43        | 81, ±1.0    |
|                 | E-03                   | 3E-03       | 0           | E-03        | 0           |
| Hematite + Tanfloc | 3.80       | 85.0 ± 1.0  | 3.1         | 88, ±3.8    | 4.00        | 62, ±1.2    |
| Quartz          | 3.13       | 65.0 ± 7.0  | 3.1         | 66, ±2.5    | 3.13        | 63, ±1.0    |
|                 | E-03                   | 3E-03       | 5           | E-03        | 0           |
| Quartz + Tanfloc | 2.67       | 70.0 ± 2.0  | 3.9         | 81, ±1.5    | 3.74        | 89, ±1.0    |
| Tanfloc         | E-03                   | 2E-03       | 0           | E-03        | 0           |

Prior to the interaction with the biosurfactant, hematite and quartz surfaces presented lower values than interacted minerals. Quartz presented a value below hematite, around 65° and 72°, respectively. It is noted that the contact angle at pH 8.0 is much higher for hematite.

Regarding interacted minerals, their contact angle values are generally higher than pure minerals. Hematite samples show values above 80° for pH 7.0 and 7.5, decreasing at pH 8.0.

Quartz samples, on the other hand, have increasing values of pH 7.0 to 8.0, ranging from 70° to 89°. Thus, the biosurfactant would have attributed a hydrophobic character to the minerals after interaction, with values varying in relation to the pH of the measurement. These contact angle values for pure minerals are high compared to literature reports [2].

One factor that may have interfered with these higher values is the particle size of the mineral samples (<20μm). There are reports of decreased contact angle due to increasing particle diameter, happening exactly the opposite in this case. It is possible that smaller particles may generate smaller capillaries compared to larger sample sizes, leading to an increase in water mass in the samples during measurement [10].

The larger contact angle may also be due to less efficient packaging and possible higher porosity of the system, as the preparation method used only contemplates pipe impacts on the table.

The values obtained for the minerals after interaction are also high, and it is possible that the combination of low particle size and increased hydrophobicity by Tanfloc may be responsible. Nevertheless, the increase in contact angle is observed with the interaction of the mineral with the biosurfactant.

3.4. Flotation Tests

Prior to the flotation tests, some coagulation and flocculation tests were performed to verify the pH range that flakes form with Tanfloc. Flake formation occurred that the pH range between 6.5 and 9.0 (Figure 5). From these results, flotation tests were performed at the best pHs.
The effect of Tanfloc concentration on the flotability of fine iron ore particles is shown in Figure 6. The study was performed at a concentration of 30 to 200 mg/L, a particle size range of -20 µm and at a pH of 6.5 up to 9.0.

First, preliminary results of flotability were sought in order to observe the best conditions to perform the tests. According to the results obtained, the maximum buoyancy values for a concentration of 175 mg/L at pH 7.0 with also high results at pH 8.0. A considerable result at pH 9.0 is also observed with 140 mg/L Tanfloc.

It was not possible to verify the decrease in flotability at high biosurfactant concentrations, which may be due to the formation of aggregates during the biosurfactant adsorption on the mineral surface, resulting in the decrease of the effective adsorption area.

From the preliminary results, flotability tests were performed at pH 7.0, 7.5 and 8.0 with a concentration of 175 mg/L of Tanfloc SG, and this range presented the best preliminary results. These results are presented in Figure 7.
In order to obtain selectivity in iron ore flotation, sodium metasilicate (Na$_2$SiO$_3$) was used in an attempt to depress the quartz present in the iron ore sample. The effect of depressant concentration on the flotability of fine iron ore particles is shown in Figure 8.

The study was performed at a concentration of 0.04 to 200 mg/L at pH 7.0 and biosurfactant concentration of 140 mg/L. These conditions were chosen based on the previous results because it is one of the conditions with the highest flotability.

It can be seen that the flotability decreases considerably with increasing depressor concentration, converging to between 40 and 30% flotability at higher concentrations. A decrease in flotability is expected as the quartz ore particles present are not expected to float under these conditions. Depreciation with the increase is also justified by the possible depreciation of the hematite particles as there is a large excess of depressor in the flotation cell.

The iron content was analyzed in some selected results to observe if there is concentration of the mineral of interest with the use of this depressant. The results of the analyzes are shown in Table 5. It was possible to concentrate iron ore from 54 to 60% with a single flotation step, and concentrations above 4.00 mg/L depressor showed no significant differences in iron recovery.

**Table 5.** Concentration of depressor in the mineral.

| Depressor Concentration (mg/L) | Iron % (% p/p) |
|-------------------------------|----------------|
| 0.00                          | 53.76          |
4. Conclusion
Possible functional groups present in Tanfloc SG and minerals were identified by infrared spectroscopy, identifying the Fe-O clusters of hematite and Si-O of quartz. In addition to O-H, N-H, C-N, Ph-O groups, conjugated alkenes, aromatic groups and aliphatic cyclic ethers present in tannin-based structures.

Zeta potential profile measurements for biosurfactant, mineral and mineral / biosurfactant interaction showed the following isoelectric points (IEP): close to pH 8.5 for Tanfloc, while the hematite EIP was close to pH 5.3 and quartz below pH 3.0. The hematite / Tanfloc interaction shifted the EIP from the hematite from pH 5.3 to pH 6.5. The quartz / Tanfloc interaction also showed a change in the quartz IEP to pH around 4.2, which indicated interactions of an electrostatic nature.

Contact angle measurements identified that the hematite surface has a more hydrophobic character compared to quartz before interaction with biosurfactant, ranging from 72 to 80° for hematite and around 63° for quartz. After interaction with Tanfloc SG hematite presented higher contact angle values at pH 7.0 and 7.5 (85 and 88°) compared to quartz (70 and 81°), being the value obtained at pH 8. The largest for quartz, 89° for quartz and 62° for hematite.

The dissolved air flotation of iron ore using Tanfloc SG depends on the biosurfactant concentration and the pH of the mixture, with the best flotability results at pH 7.0 with Tanfloc concentration between 140 and 175 mg/L for 4 g. ore with flotation values above 50% for a single flotation step. Besides concentrating the ore from 54 to 60% with sodium metasilicate as a quartz depressant.

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