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# Study on the use of chitosan as a collector in chalcopyrite flotation

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***Keywords*— Chalcopyrite flotation. Chitosan. Xanthate.**

***Abstract*— *Chalcopyrite is an important ore to obtain copper where in Brazil we have several mines located in all regions. The process of ore separation known as flotation is an efficient process that allows the use of bubbles and a foaming material that with the help of collectors are able to conduct the chalcopyrite as well as other ores for separation through appropriate equipment. Currently in this process are used PH modifiers and collectors that allow the separation of this ore with the use of the pneumatic flotation method. The Chitosan is a biotechnological material produced from the exoskeleton of some arthropod animals that can be used as collector in the flotation process. In this work the performance of the Chitosan was analyzed in relation to a very common collector, the Xanthate, and with this it was verified how in media with different concentrations and levels of PH we can verify the efficiency of the Chitosan in the flotation of the Chalcopyrite. The material used in the microflotation tests was the tailings proceeding from copper mining in São Félix do Xingu-PA, lent by the laboratory of Mining Engineering of CEULP/ULBRA, the tests were made in bench with the use of the modified Hallimond tube. The results showed that there was a considerable recovery where in the solution the most indicated pH is pH 9 for maximum recovery.*

## I. INTRODUCTION

Minerals are of paramount importance for the continuity of the evolution of mankind, every day it becomes essential to think about the development of new ways to treat these materials, due to the growth of the world population that demands an increasingly high consumption of technologies and because these resources in nature are scarce and non-renewable.

As minerals are not a renewable source of raw material, it is necessary that these materials receive appropriate treatment for better use and economic viability. In addition, environmental aspects are an important factor in mining, as it is one of the activities developed by man that produces relevant impacts on nature.

Annually, about 400 million metric tons of mineral are crushed and ground into particles, typically less than 100 µm in diameter, subsequently, in some cases, are subjected to a process called froth flotation, a procedure that isolates the valuable components (YANG; PELTON; RAEGEN; MONTGOMERY; DALNOKI-VERESS, 2011).

The replacement of chemicals by biotechnological materials in ore processing enables the mitigation of environmental impacts, such as chemical bioaccumulation in micro and macro organisms, besides producing effluents with great toxic potential for soil and water bodies.

In this perspective the need of components and biodegradable materials is appearing, where its discard would have less impacts to the environment, having the same functionality of other inorganic compounds, elaborated on organic matrices that form bioproducts and biomaterials as in the case of the Chitosan.

The chitosan is a biopolymer non-toxic, biodegradable, biocompatible and produced by natural renewable sources, whose properties are being explored in industrial and technological applications for almost seventy years, some of the main areas of application of the chitosan is among many the water treatment in the form of flocculants for clarification, removal of metallic ions.

Flotation is employed in the separation of fine mineral particles of iron, copper, molybdenum, nickel, lead, zinc, gold, platinum, phosphate or potassium and related gangue particles such as silica, silicates (argillominerals), carbonates, magnetite, or iron sulfides, among others, thus making this technique one of the most useful in the industry and mineral processing (YIANATO, 2003) (CLARK *et al*, 2005).

The process of ore concentration and classification by flotation is one of the most comprehensive and important in the processes of ore processing, especially metal ores, its great success of the flotation method in the mineral industry is due to its, separation accuracy, wide use and great ability to collect fines in addition to enabling large-scale production.

Studies of the use of nanoparticles in flotation have shown that hydrophobic nanoparticles can obtain advantages as collectors in the flotation process with higher efficiency than conventional collectors (YANG *et al*., 2013). For example, the coverage of polystyrene collector should contain only 10% nanoparticles on the surfaces with the use of glass beads which can promote high flotation efficiency, while the conventional molecular collector requires 25% or more coverage for good recovery (ABARCA *et al*., 2015).

Considering these advantages of nanoparticles as collectors in the flotation process, researchers have exerted substantial efforts to clarify the feasibility of nanoparticles as collectors in a less polluting and effective strategy through still experimental and theoretical approaches (HAJATI *et al*., 2016).

Approximately 2 billion tons of ores are beneficiated and concentrated using the flotation method per year, including almost all copper, lead, zinc, nickel and molybdenum produced in the world.

The xanthate salt is used as the main collecting reagent of the most widely used in flotation operations for both simple metallic minerals and sulphide minerals. However due to its toxicity to aquatic living beings, its effluents must be treated after the end of the process and before discharge into rivers.

The xanthate as industrial waste presents, mainly, high toxicity when found in aqueous media (GARCÍA-LEIVA *et al*, 2017). The greatest risk of toxicity is related to its derivative carbon disulfide (CS2). Which could cause a potential pollutant to the environment, which is why it constitutes the interest to study possible alternatives of organic and biodegradable materials for the replacement of xanthate as an ore collector and one of the main wastewater effluents in sulfide mining.

Mining wastewater from the flotation process collected in tailings dams or tailing ponds can contain both residual xanthate and dissolved metals and non-metals, including some types of acid mine drainage.

When they come into contact with the external environment, they can cause pollution of surface water and groundwater, since xanthate is highly toxic when found in an aqueous medium.

However this research had for objective to verify the potential of the Chitosan as collector in ultrafines of chalcopyrite ore in the flotation process to verify the viability of the addition of this biodegradable material in comparison to the Xanthate, as potential collector and as generator of effluent of minor environmental impact.

## II. MATERIAL AND METHODS

The experimental procedures were carried out in the Mining Engineering Laboratory of the Palmas Lutheran University Centre (CEULP/ULBRA). The mineral sample used in the flotation tests came from Garimpo of Matuto, a copper mine in the municipality of São Félix of Xingu-PA.

For the accomplishment of the research it was necessary the execution of some steps such as: comminution, particle size classification in sequence the flotation with concentration variation and pH variations, as demonstrated in Figure 9 presents a flowchart of the steps performed.

2.1 - Sample Processing

During the processing of the chalcopyrite samples, primary and secondary processes of crushing, grinding and granulometric classification were used. The preparation of the samples had as objective to comminute the same so that it possesses appropriate granulometry to suffer the process of pneumatic flotation in precise degree for industrial performance, besides counting on the use of the collector Xantato and of the foaming Lauril, having as modifier of PH, solutions of NaOH and H2SO4. This process was developed on a laboratory scale using small equipment.

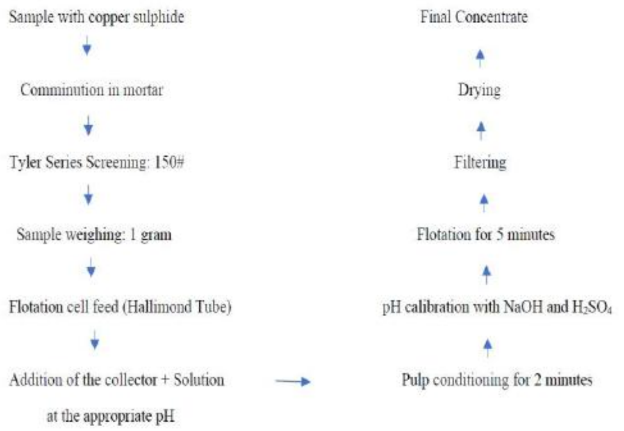


*Fig. 1: Process Flowchart*

2.2 – Sample Preparation

The sample in question was obtained in its raw state and went through a crushing process, which was performed by a mechanical process based on blows with a common hammer.

In the search for material in appropriate granulometry for the flotation process, it was necessary to fragment the chalcopyrite-based material so that the particles could undergo the flotation process.

*Fig. 2: Sulphide copper massif containing chalcopyrite*

For this, a common hammer was used on an iron table appropriate for the type of impact generated by the breakage of the material. This process was done at the CEULP-ULBRA Mineral Processing Laboratory.

*Fig. 3: Iron table and hammer used for chipping*

Figure 3 shows the place where the material was fragmented, a kind of concrete tank with a grid consisting of iron plates approximately 10cm wide, spaced 1.5 mm apart, where the finer material falls into a container and the thicker material is retained on top.

The grinding was performed manually with the use of a porcelain mortar and laboratory pistil, up to 0.075 mm, a particle size appropriate for the flotation process to which the samples will be subjected later.

The choice of particles of 0.075 mm was aimed to verify if the chitosan would reach ultrafine materials.

The material based on crushed chalcopyrite was placed in mortar of the adequate numbering laboratory type so that it can be manually reduced to smaller particles by mechanical force.

*Fig. 4: Grinding of copper chalcopyrite ore in mortar and pestle*

After milling, the material was sieved with openings in millimeters (sieves of 2.0, 1.0, 0.6, 0.3, 0.15, 0.075 and <0.075).

The sieving was performed by a set of sieves and manually agitated in the laboratory as shown in the figure below.

Sieves with aperture up to 150# were used with agitation performed manually and the material was sorted by laboratory size 8x2 sieves along with manual agitation.

The sieving process makes use of a set of laboratory sieves that together with a sieve shaker allows to classify the grains in a standardized and uniform way to the point of producing appropriate particles for flotation being these particles equal or smaller than 0.075 mm which is the appropriate granulometry for flotation.

*Fig. 5: Sieve set*

With the sieving it was possible to classify the samples having a material that with micrometric particles can adhere to the bubble and with the necessary adjustments has the capacity to float.

2.3 – Flotation Test

After the process of sieving the samples the material obtained was weighed on precision scales using 1g of chalcopyrite-based material taken to the Hallimond tube to be flotted with the Xanthate-based collector in tests with 0.3, 0.6, 0.9, and 1.2 ml of solid Xanthate dissolved in distilled water. In the flotation process the pH was changed in 9, 10 and 11 to verify the ideal pH. The flotation process was developed in a specialized equipment called Modified Hallimond Tube.

In the process was used a foaming agent of the Lauryl type that was placed the measure of a drop in each test. After the development of three samples for each one of the concentrations of Xanthate in each one of the pH alterations (9, 10 and 11) we obtained the averages of flotation in each battery of samples, thus accounting for four averages of twelve samples, which were dried in an oven and then weighed. In a second moment the process was repeated having now as collector the Chitosan in concentrations of 1.2, 2.4, 3.6 and 4.8 ml in the same levels of pH (9,10,11), with the addition 1g of NaOH, where the comparison of the processes and of the results obtained with Xanthate and of the results with the Chitosan was made to verify the performances in each process.

In the flotation process were weighed in precision balance 1g of material already processed.

*Fig. 6: Precision Balance*

The use of the precision balance consists in the exact verification of the initial content having in sight the content of the floated material at the end of the process.

Subsequently the material was placed in a Modified Hallimond Tube of the laboratory type where the flotation process was performed.

*Fig. 7: Modified Hallimond tube of the laboratory type*

To develop the flotation process in the Hallimond Tube it was necessary the use of foaming agents of the type Lauryl or Sodium Ether Sulphate 27%) besides pH modifiers that with the gauging of a digital peagameter we reached the desired pH's of 9, 10, and 11. Still in the Hallimond Tube we added in distinct stages the collectors based on Xanthate and Chitosan. The development of the flotation was made during 5 min where part of the flotation material was collected with the help of a glass beaker, as shown in the figure 8.

*Fig. 8: Flotation being carried out in the modified Hallimond tube*

During the flotation process the floated material was collected and put in filters to be drained in a way not to lose any part of the floated material. After the preparation of the samples and the obtaining of the results of the floated material 24 samples of flotation of the chalcopyrite material were produced, being 12 results with the use of Xanthate and 12 results with the use of Chitosan. The samples taken from the Modified Hallimond Tube were filtered on filter paper.

*Fig. 9: Material being filtered through filter paper*

After filtering the samples of float material they were classified according to the collector dosages and pH levels. After classification, the samples were taken to an oven at 100°C for drying, as shown in figure 10.

*Fig. 10: Samples after removal from the oven*

Once the samples were dry, they were weighed and thus the masses of the float material were computed with the use of the different collectors in this case Xanthate and Chitosan.

## III. RESULTS AND DISCUSSION

3.1 – The Drag Test

Results of the flotation tests (drag) made with copper ore using only foaming reagent where firstly distilled water was placed in the Hallimond tube, after that we added 1g of material 0.0211g, and left conditioning the pulp for 2 minutes with the aid of magnetic stirrer. After that we turned on the compressor to start the flotation that lasted 5 minutes. After that we removed the floated material to the filter paper and put it to dry in oven at 100°C for 24 hours.

The calculation of the drag values obtained in the test is done as follows:

$$\text{Drag (\%)} = \frac{Float\ Mass}{(Floating\ mass) + (Sinking\ mass)} \times 100 \quad Eq.\ 1$$

*Table.1: Results obtained*

After that we get the following results:

| TESTS | FILTER WEIGHT (g) | TOTAL WEIGHT (g) | FLOAT MATERIAL (g) | RECOVERY (%) |
|---|---|---|---|---|
| 1 | 0,820 | 1,119 | 0,299 | 29,9 |
| 2 | 0,836 | 1,234 | 0,398 | 39,8 |
| 3 | 0,849 | 1,413 | 0,564 | 56,4 |
| 4 | 0,829 | 1,214 | 0,385 | 38,5 |
| 5 | 0,830 | 1,314 | 0,484 | 48,4 |
| 6 | 0,839 | 1,395 | 0,556 | 55,6 |
| 7 | 0,841 | 1,254 | 0,413 | 41,3 |
| 8 | 0,827 | 1,249 | 0,422 | 42,2 |
| 9 | 0,824 | 1,351 | 0,527 | 52,7 |
| 10 | 0,836 | 1,295 | 0,459 | 45,9 |
| 11 | 0,832 | 1,287 | 0,455 | 45,5 |
| 12 | 0,835 | 1,256 | 0,421 | 42,1 |
| AVERAGE | | | 0,439 | 43,9 |

Therefore, with the obtaining of this average related to the drag, it was possible to disregard the material that is naturally levigated in the process and thus have the parameters for better verification of the performance of the chitosan collector, without the interference of the drag.

The subtraction of the average values of the drag is important because it brings the full verification of the potential of the collector and exposes only the values acquired by flotation with the use of collectors without the contribution of the materials that are dragged by the flow.

3.2 – Flotation with the Xanthate Collector

To compare the chitosan with the xanthate in the performance as collector it was necessary that initially we can verify the performance of the same in the process of flotation of chalcopyrite being made in the same proportion and with the instrumental means such as it was made with the Chitosan.

Once developed in the modified Halimond tube we obtained the following results with the variation of concentration and pH, according to figure 11.

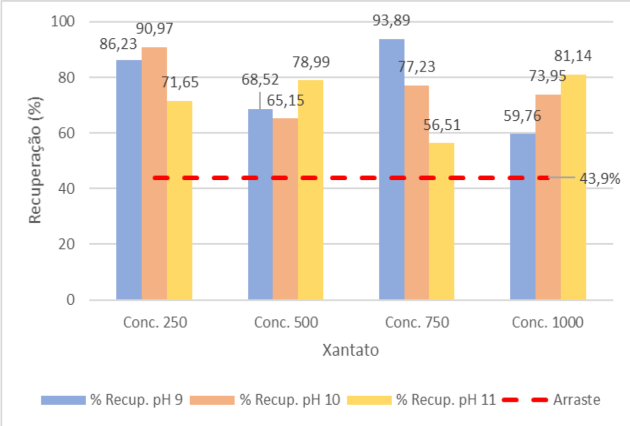


*Fig. 11: Recovery*

It was verified that in conditions where the concentration of xanthate was equal to 750 mg with an aqueous medium where the pH in 9 we had an optimal recovery of 93.89% of the floated chalcopyrite. According to Nogueira, Osti, Pereira and Lopes (2017) in their experiment in bench test it was possible to verify similar recovery with the use of Xanthate.

Also according to Nogueira, Osti, Pereira and Lopes (2017) With the results of the bench flotation it was possible to state that the best set of reagents used was the test with the use of Xanthate that allowed to constitute a floated material (oversize) with differentiated recoveries from the sunk (undersize). Besides, it was the one that obtained higher recoveries of Zn, Pb and Ag.

3.3 – Flotation with the Chitosan Collector

In the flotation test using chitosan as collector having variations of concentration and pH we can verify its performance as shown in figure 12.

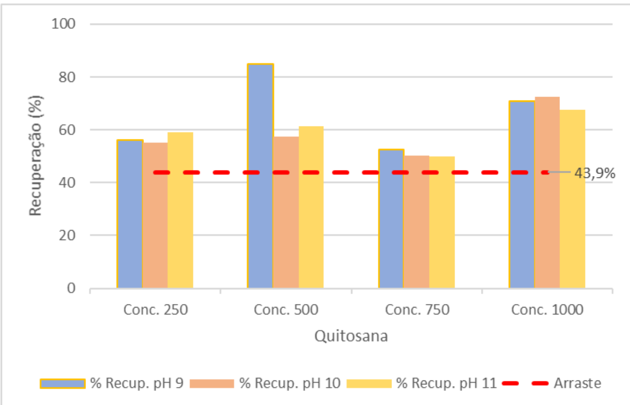


*Fig. 12: Flotation test using chitosan*

The use of the chitosan as only collector glimpses the collecting capacity of this material where with the use of a PH altered to 10 the best result is reached with about 72.34% of the material to be floated. With this we can verify the potentiality of this material in the recovery of fines in the flotation of chalcopyrite because alone it reached 72.34% of the material of interest.

3.4 - Chitosan x Xanthate

It was verified that with the pH 9 and with concentration of 500 mg of chitosan, it was possible to obtain the maximum concentration 84.86 mg of chalcopyrite recovered. What is a lower value than that obtained by Xanthate (93.89%), but should be considered that the benefits in the use of biocolector are high, such as low cost in its production, the environmental gain due to the reduction of tons of pollutants due to its biodegradation properties, biocompatibility and non-toxicity as explained (SILVA *et al.*, 2016).

In verification of the performance and behaviour of the xanthate in comparison with the chitosan it could be concluded that the chitosan has inferior performance to the xanthate as a chalcopyrite collector in flotation, because its capacity as a chalcopyrite collector was functional, but inferior to the xanthate, as shown in figure 13.

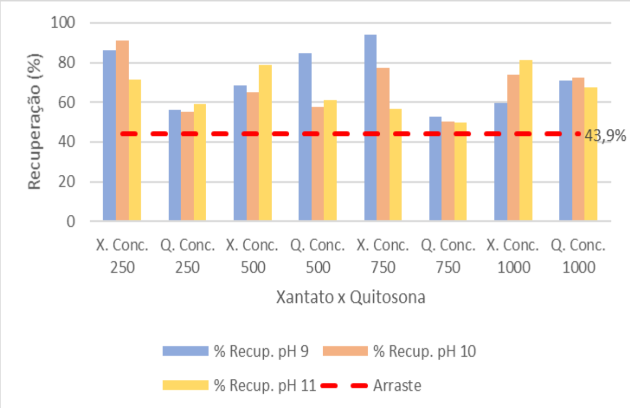


*Fig. 13: Performance and behaviour of xanthate compared to chitosan*

## IV. CONCLUSION

The results obtained in this study, the processing and discussion of the data allow establishing the following conclusions:

The microflotation tests with the xanthate collector presented higher value of flotability of the copper ore, always higher than 55%. The highest values of recovery with the xanthate were: 81.14 % with pH 11 and concentration 1.2 mg, 90.97% with pH 10 and concentration 0.3 mg and 93.89% with pH 9 and concentration 0.9 mg. In relation to the collector with chitosan the highest values of flotability were equal to 67.53%, 72.34% and 84.86% for the tests performed at pH 11, 10 and 9. The results of this work confirm that the chitosan possesses efficiency in the process of recovery in the flotability of the chalcopyrite, however it possesses minor performance that the Xanthate in relation to the recovery, all the way in environmental aspects becomes a sustainable alternative in the process of reduction of environmental impacts what occurs of contrary form with the Xanthate.

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