Jatropha curcas L. Oil Selectivity in Froth Flotation

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Abstract**—**In Brazil, most soils are acidic and low in essential nutrients required for the growth and development of plants, making fertilizers essential for agriculture. As the biggest producer of soy in the world and a major producer of coffee, sugar cane and citrus fruits, Brazil is a large consumer of phosphate. Brazilian's phosphate ores are predominantly from igneous rocks showing a complex mineralogy, associated with carbonites and oxides, typically iron, silicon and barium. The adopted industrial concentration circuit for this type of ore is a mix between magnetic separation (both low and high field) to remove the magnetic fraction and a froth flotation circuit composed by a reverse flotation of apatite (barite's flotation) followed by direct flotation circuit (rougher, cleaner and scavenger circuit). Since the 70's fatty acids obtained from vegetable oils are widely used as lower-cost collectors in apatite froth flotation. This is a very effective approach to the apatite family of minerals, being that this type of collector is both selective and efficient (high recovery). This paper presents *Jatropha curcas L.* oil (JCO) as a renewable and sustainable source of fatty acids with high selectivity in froth flotation of apatite. JCO is considerably rich in fatty acids such as linoleic, oleic and palmitic acid. The experimental campaign involved 216 tests using a modified Hallimond tube and two different minerals (apatite and quartz). In order to be used as a collector, the oil was saponified. The results found were compared with the synthetic collector, Fotigam 5806 produced by Clariant, which is composed mainly by soy oil. JCO showed the highest selectivity for apatite flotation with cold saponification at pH 8 and concentration of 2.5 mg/L. In this case, the mineral recovery was around 95%.

Keywords**—**Froth flotation, *Jatropha curcas* L., microflotation, selectivity.

I. Introduction

APPROXIMATELY 70% of Brazilian territory is composed by acidic soil, which is capable of reducing crop productive potential by up to 40% [1]. The soil has its natural acidity originated during the soil formation process. Agricultural activity could accelerate the acidification and when the soil is acidic (low pH); we have a lower availability of some nutrients, such as phosphorus and molybdenum, the aluminum toxicity and microbial activity losses are observed with negative reflections on biological fixation and nutrition [2].

Agriculture has had participation in Brazil's trade balance. The country nowadays is one of the most important global players of soy, corn, coffee, poultry meat and beef, among others. During each harvest time, new products and greater quantities are exported to the world supply. When it comes to economic activity, agriculture is subject to greater risks, because it takes as input an uncontrollable factor and hard predictability [3].

Brazilian dependence on fertilizers has been debated for years, but in addition to the question about the existence or not of deposits that can ensure a future production; in this case, one should examine the entire production chain in order to improve mineral processing [4].

Most phosphorus minerals from phosphate rock belong to the group of apatite ($Ca_5(Cl, F, OH)(PO_4)_3$), a crystalline calcium phosphate with carbonate, with P_2O_5 content between 4% and 15%. [5]. Phosphate rock mines in operation and under study in Brazil are, by far, igneous deposits. Apatite ores concentrates reach levels of P_2O_5 above those from sedimentary rocks. Brazilian phosphate originated from igneous deposits has simultaneous occurrence of several minerals of gangue. The most frequent are iron oxides, micas, vermiculites, titanium minerals, carbonates (calcite, dolomite) and other minerals in lower proportion. Currently, the most used technology for processing igneous ores is the froth flotation [6].

The complex mineralogy of our minerals compared to deposits of sedimentary origin, for example those formed in Florida (USA) and Morocco, has led to the definition of a specific reagents system for the froth flotation of phosphates, constituting one of the great achievements of Brazilian mineral engineering, leading to the consecration of Professor Paul Abib Andery [7].

In the 70's in Brazil, occurred the very significant contribution of Prof. Paulo Abib Andery to develop the apatite concentration process from the use of fatty acid as the collector and the use of corn starch as a depressant in the apatite separation process from carbonate gangue. This unique process allowed the economic exploitation of apatite carbonates in Brazilian mines such as Cajati (SP), Araxá (MG) and Catalão (GO) [8].

Currently, the biggest concern about researches that appropriate vegetables and oils, as the unit of analysis, is focused on clean energy production. Nowadays, several researches using these products have gained prominence, particularly in the mineral area, which is one of the national economic pillars [9].

In Brazil, oilseeds are used for human consumption, including soy, corn, sunflower, palm oil and canola oil, and this competition can cause a decrease in food production. Jatropha presents an advantage over the above related seeds, because its commercial production is exclusively for the purpose of oil production [10].

The *Jatropha curcas* L. is an oilseed crop not used in the human or animal food chain yet, but is considered a potential raw material. The species *Jatropha curcas* L. or Jatropha has several comparative advantages for the production of its oil: it

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is a perennial plant, rustic, easy-to-use, containing quality oil for biodiesel production, with high content in the seeds (about 38%), and is suitable to be mixed with other crops, for being a bush and able to grow in wide areas [11].

In studies with samples of Jatropha seeds from three different locations were obtained income from oil extraction ranging to 54% to 64%. The chemical composition of the extracted oil presented the following fatty acids: oleic (42.3%), linoleic (35.5%), palmitic (14.7%), stearic (7.0%), Palmitoleic (0.4%) and Arachidic (0.1%), being the content of unsaturated fatty acids equal to 78.2% [12].

A large variety of plant species can be found in Brazil. Some have few study and applicability. The Jatropha is a perennial plant that does not require an annual renewal planting and is adapted to low fertility soils, it is a non-food crop, which does not present direct competition with food farming. The Jatropha stands out for its raw potential that presents contents of oil coming up to 48%, its seeds are used for oil production, its leaves and latex for medicinal uses. Several Brazilian States have the cultivation of *Jatropha curcas*; on this account in 2005, the Brazil's Government had encouraged small and medium-sized producers in planting as an extra form of income. This article proposes to evaluate the technical feasibility of using Jatropha oil, hot saponified as the microflotation collectors of apatite, and quartz, in a modified Hallimond tube. The laboratory results showed that the JCO presents potential as a collector for phosphate rock froth flotation.

II. Materials and Methods

The minerals samples used in the microflotation tests in the Hallimond tube were comminuted in a ball mill and sieved for subsequent separation in particle size -150+106 μm (-100+150 #). The sieving stage was performed wet. After the screening, the minerals underwent vacuum filtering and drying in a heater. For the removal of any eventual contamination of magnetic material in the comminution stage, the samples were subjected to magnetic separation using a rare earth magnet with a field of 2000 G.

In order to identify the components of the mineral, which was purchased and used in the microflotation tests, chemical analysis of the samples was carried out in an X-ray Fluorescence Spectrometer from Panalytical, AXIOX MAX model, Series DY and number 5001, in Anglo American Brazil Phosphates.

Image analysis of different aliquots of the samples in the scanning electron microscope (SEM) coupled to an x-ray spectrometer in energy dispersive (EDS) was important for the characterization of the samples with very fine minerals and commonly heterogeneous, allowing a description of the particles morphology, liberation and chemical composition.

The microstructural characterization was performed using a SEM, Jeol KAL-6610, equipped with EDS, Thermal scientific NSS Spectral Imaging. Apatite and quartz samples were analyzed, in the particle size of -150+106 μm (-100+150 #).

The Jatropha oil characterization became necessary for the interpretation of the results in the froth flotation, relating the oil's features that can influence the performance of the oil as a collector. The chemical characterization of the Jatropha oil was developed from the Adolfo Lutz Institute procedures [13], which are based on the methods of the American Oil Chemists' Society (AOCS). The following indexes were determined: saponification index (SI), acid index (AI) and the iodine index (II).

Jatropha oil was used in the microflotation tests as the collector, provided by Embrapa Agroenergia located in Brasília-DF. A helical mechanical baler performed the chestnut oil extraction. Moreover, the purpose of determining the fatty acids present in the oil was characterized using the gas chromatograph with FID-Detector by ionization in flame (Flame Ionization Detector). Capillary column for gas chromatography model HP-88 (60 meters long, 0.250 mm internal diameter and 0.20 μm film thickness), Agilent brand (part number 112-8867).

To be used as the collector, Jatropha oil was subjected to alkaline hydrolysis (saponification) evaluating the technical feasibility for its application as saponified oil using alcoholic solution 95% and NaOH 4% in a heating blanket and reflux [14].

Microflotation tests in Hallimond tube were run with apatite and quartz samples in a particle size of -150+106 μm (-100+150 #). The samples conditioning was carried out for a period of seven minutes in a more concentrated way, that is, 1 g of mineral placed at the end of the tube. A collector amount that ensures the desired final concentration (2.5; 5.0; .10 7.5 mg/L) and the tube was completed with water up to the limit of 50 ml of solution for conditioning. At the end of the conditioning, the remainder of the water needed for the proceedings was added, coming to a solution with 320 ml, starting the flotation of one minute duration. All tests were performed in triplicate.

TABLE I
Operational Variables Adopted in Microflotation in Hallimond Tube Tests

Operational variable	Value
Airflow (cm^3/min)	40
Air pressure (psi)	10
Mass of the mineral (g)	1
Conditioning time (min)	7
Flotation time (min)	1
Collecting solution (mL)	320
pH	8; 9; 10
Particle size range (μm)	-150+106
Collector concentration	2.5; 5.0; 7.5; 10

Hydraulic entrainment tests in the Hallimond tube revealed a low recovery (approximately 0.7% at 40 cm^3/min airflow). In this way, the microflotation data will be presented regarding hydraulic entrainment tests values.

In order to compare the Jatropha oil's performance the industrial collector Flotigam 5806 made by the Clariant company, was used, which is a collector developed for phosphate rock froth flotation, composed of a Brazilian formulation of fatty acids. The Flotigam 5806 was submitted to the same saponification process and microflotation tests in the Hallimond tube used for JCO.

III. Results and Discussions

Characterization analysis of the apatite sample revealed the presence of small quantities of Barite and iron. However, the P2O5 and CaO concentrations are high, representing 92.54% of its composition, matching with a sample of high purity degree. Table II presents these results.

TABLE II
CHEMICAL ANALYSIS OF APATITE SAMPLE BY X-RAY FLUORESCENCE

Oxides	P_2O_5	Fe_2O_3	SiO_2	BaO	Al_2O_3	CaO
%	40.50	0.07	0.94	0.06	0.38	52.04

Fig. 1 shows morphology images of the apatite grains obtained in SEM. It can be observed in Fig. 2 that the quartz sample used in this study is solid with conchoids fractures, and so the image indicates a good release in this particle size range, as it is virtually free of mixed particles that can highlight in another color, like grey darker or lighter. A chemical analysis by X-ray Fluorescence (XRF) proves this apparent purity degree.

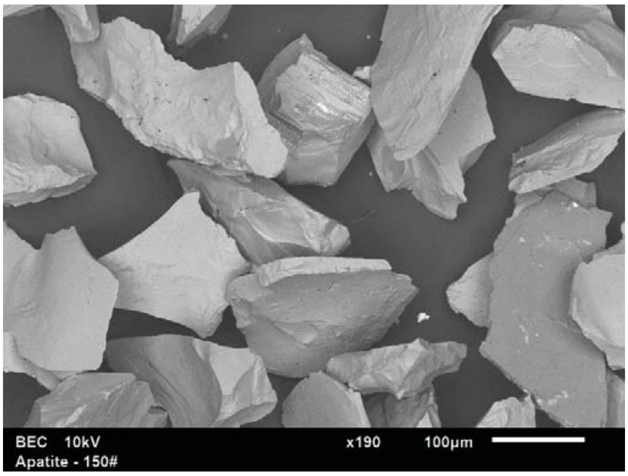


Fig 1 Apatite sample analysis by SEM

The AI of JCO found was 7.67 mg KOH/g, which according to [15] and [16], the (AI) in the raw material should not exceed 2.0 mg KOH/g, which means, 1% w/w. In this case, the JCO should go through a neutralization process in order to reach the ideal acidity.

The Jatropha oil presented (SI) of 182.57 mg KOH/g, a close value according to the author [18], which his tests showed an average value between 197.90 mg KOH/g and 199.56 mg KOH/g oil. The author explains that the larger the size of the fatty acid chain, the lower the oil saponification value, which may explain the (SI) found.

The SI presented a result of 72.75 mg of oil, showing that microflotation tests of apatite had the SI within the parameters. As stated by [17], industrial practice seeks to work with a range of saponification between 55% and 75%. Therefore, the saponification's grade of the microflotation tests were performed according to industrial practice.

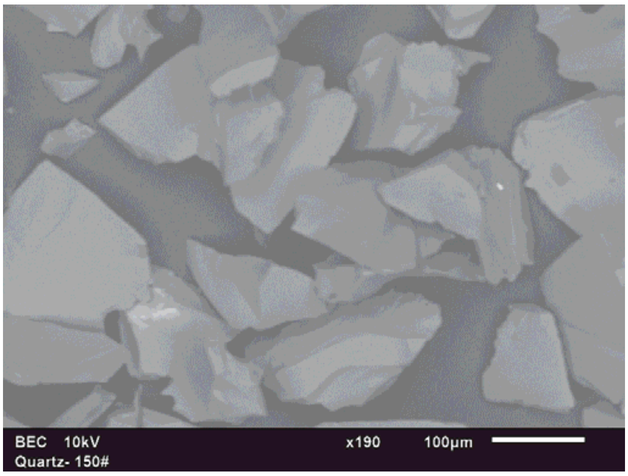


Fig. 2 Quartz sample analysis by SEM

TABLE III
FATTY ACID COMPOSITION OF THE *JATROPHA CURCAS* NUT OIL

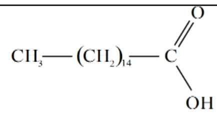
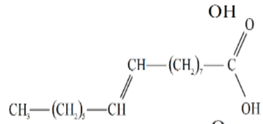
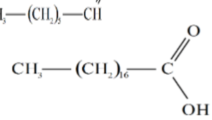
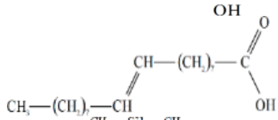
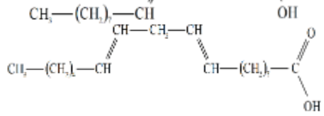
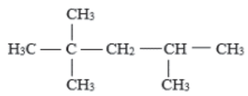
Fatty Acids	Jatropha oil (%)	Chemical structural formulas
Palmitic (C16:0)	15.15	
Palmitoleic (C16:1)	1.06	
Stearic (C18:0)	5.18	
Oleic (C18:1n9t)	33.96	
Linoleic (C18:2n6t)	42.88	
Linolenic (C18:3n3)	0.22	

Table III shows the percentage of fatty acids present in the JCO found by chromatography, note that the JCO has predominance in linoleic acids at 42.88% and oleic at 33.96%. The authors [19] identified the fatty acids in the oil extracted from the seeds of Jatropha; the major fatty acids were linoleic acid with 40.0% followed by oleic acid with 25.7% and Palmitic acid with 19.6%, showing that the results attained were similar to the literature. However, the saturated and unsaturated level of fatty acids found in the Jatropha oil was 82.24% and 16.21%, respectively. Similarly, in [20], the content of unsaturated fatty acids in the oil from Jatropha is greater than 75%.

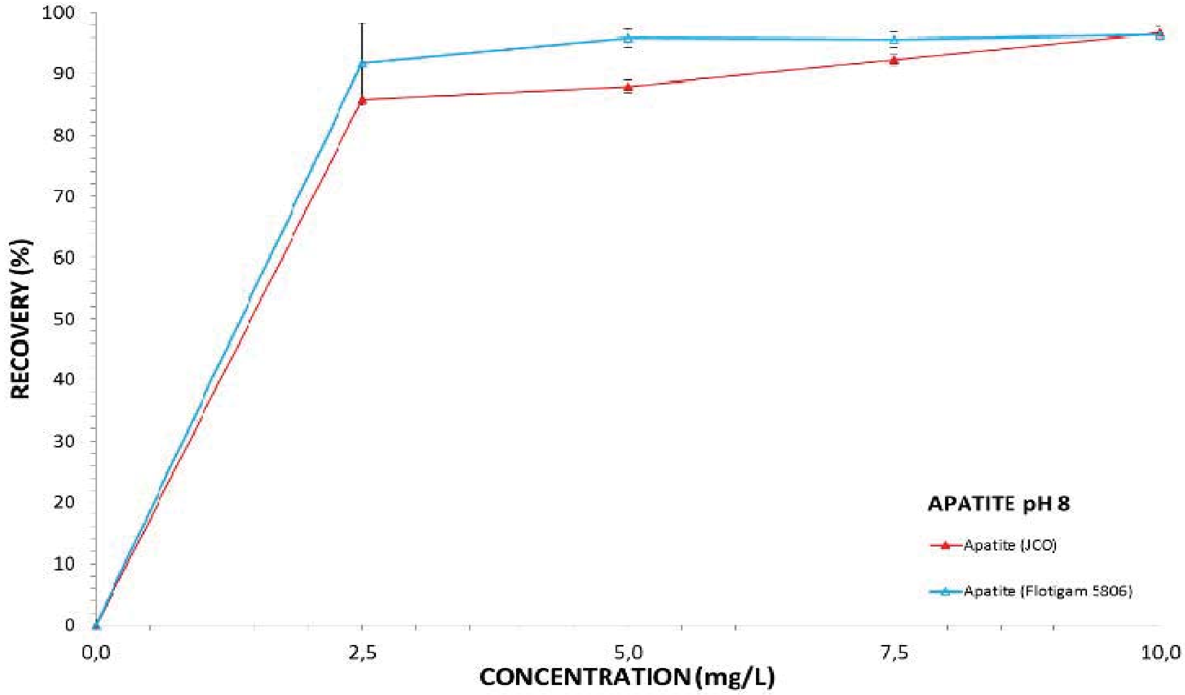


Fig. 3 Apatite recovery variation with collectors' concentration (Flotigam 5806 and JCO) at pH 8

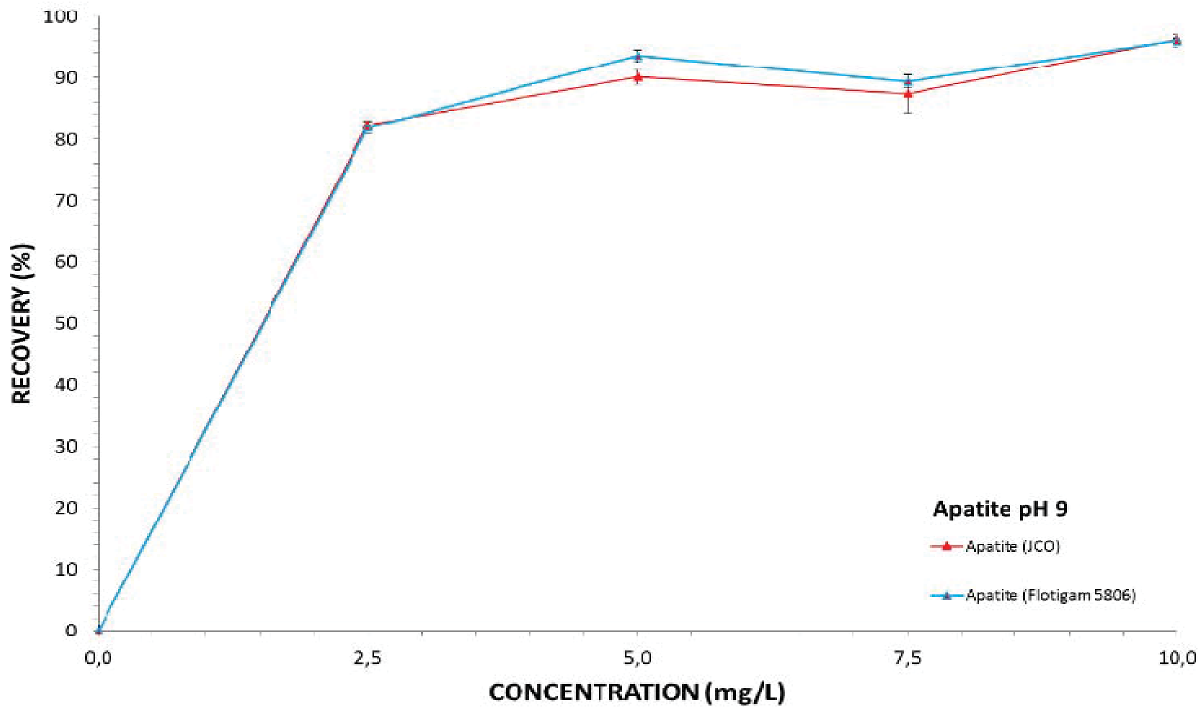


Fig. 4 Apatite recovery variation with collectors' concentration (Flotigam and JCO) at pH 9

Microflotation tests in Hallimond tube were performed with apatite using as collectors sodium salts of fatty acids (palmitic, stearic, oleic, linoleic and linolenic) as a function of pH [21]. The authors noted that unsaturated fatty acids salts had higher performance compared to the saturated. Among the unsaturated, the one, which presented high recovery, in a wide range of pH was the salt obtained from linoleic acid. The oleic acid collector presented high recovery on a narrow range of pH and the obtained from linolenic acid presented intermediate behavior to the previous ones.

Fig. 3 shows the recovering variation of apatite with increase at concentration of the two collectors tested at pH 8. A comparison of the two collectors with the mineral apatite, shows that JCO has submitted a recovery similar to Flotigam 5806 at a concentration of 10.0 mg/L and in other concentrations the recoveries were close and over 90%.

Fig. 4, which shows the apatite recovery variation with increase at concentration of the two collectors tested at pH 9, notes that the apatite results in concentrations of 5.0 mg/L and 7.5 mg/L the collectors achieved a recovery next and over 90% and the concentrations of 2.5 mg/L and 10.0 mg/L, both collectors had similar recovery. However, in the results with quartz, both collectors at pH 9 showed a low selectivity, which the maximum recovery was presented by the collector Flotigam 5806 at a concentration of 10.0 mg/L with approximately 18% recovery.

Fig. 5 shows the recovery variation of apatite with increase at concentration of the two collectors tested at pH 10. It shows that the results of apatite with JCO had a recovery higher than Flotigam 5806 at concentration of 2.5 mg/L and 10.0 mg/L. At other concentrations, the results of the two collectors had a recovery higher than 80%. The results with quartz showed a similar recovery; close in some concentrations and showing low selectivity with maximum 10% recovery.

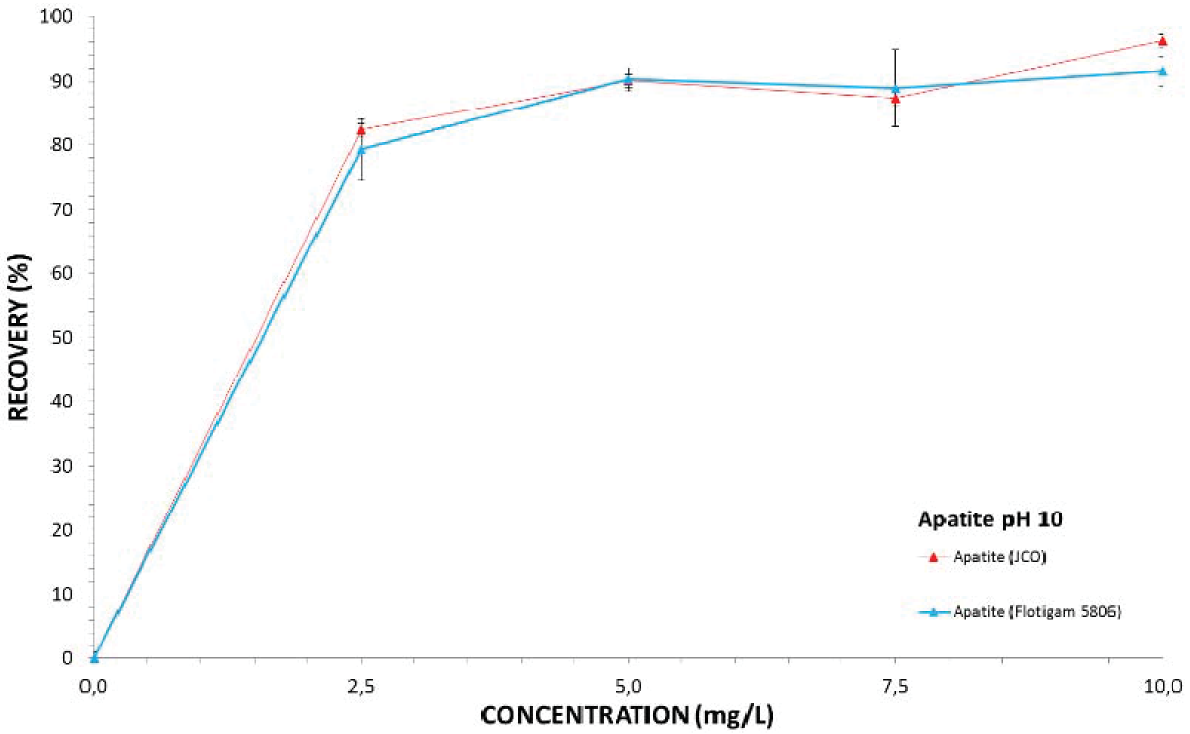


Fig. 5 Apatite recovery variation collectors' concentration (Flotigam 5806 and JCO) at pH 10

Fig. 6 shows the recovery variation of quartz with increase at concentration of the two collectors tested at pH 8. The two collectors showed low quartz selectivity reaching a maximum recovery of 48% and a minimum of approximately 12% with the Flotigam 5806; however, the JCO results showed the maximum recovery as 12% and 4% minimum, which shows that the JCO and the Flotigam 5806 are low selective to quartz.

Fig. 7 shows the recovery variation of quartz with increasing concentration for the two collectors tested at pH 9; the results reveal a low selectivity to the mineral. The maximum mineral recovery was with the collector Flotigam 5806 at concentration 10.0 mg/L with approximately 18% recovery and at concentration 7.5 mg/L, both collectors (JCO and Flotigam 5806) had a similar recovery showing low selective with approximately 5% recovery.

Fig. 8 shows the recovery variation of the quartz with the increase at concentration for the two collectors tested at pH 10. The results with quartz showed a similar recovery and close in concentrations 5.0 mg/L and 7.5 mg/L showing low selective to the mineral, and in the other concentrations shows a near recovery and low selectivity for the two collectors.

IV. Conclusion

Jatropha curcas L. collector presented a higher selectivity among the apatite and low selectivity of quartz when compared with the collector Flotigam 5806, the apatite and quartz recovery did not suffer significant influence of pH variation. The collector obtained from the Jatropha's oil showed better performance than the collector Flotigam 5806 at all pH's and some concentrations suggesting that unsaturated fatty acids are responsible for the greatest power particle collection.

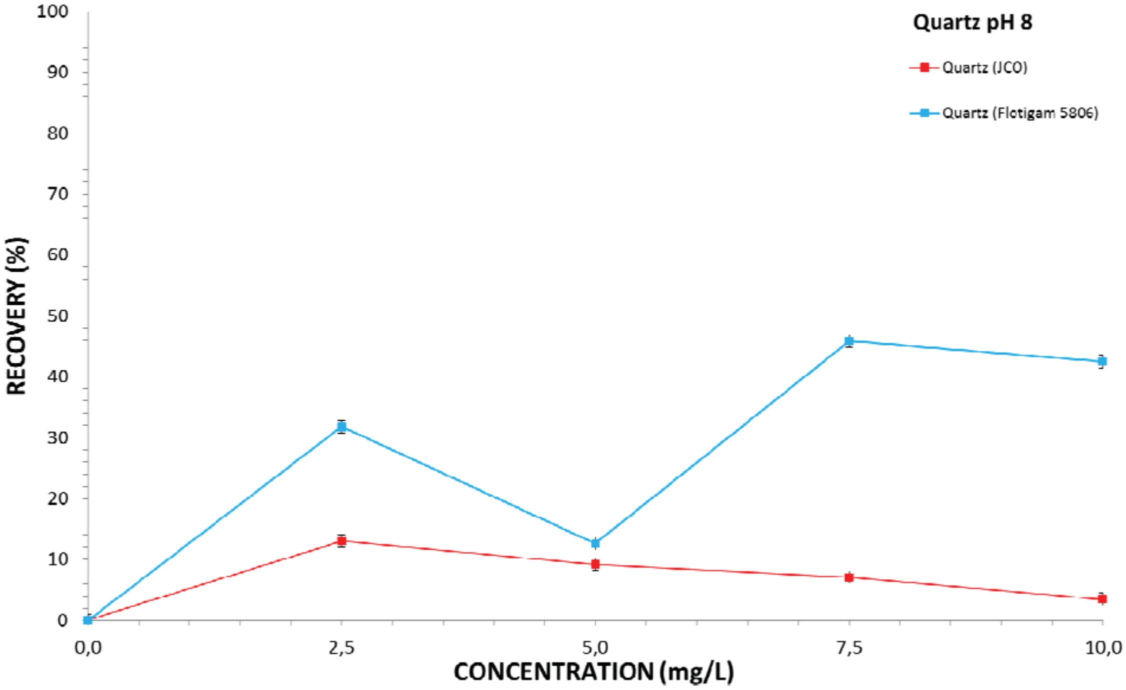


Fig. 6 Quartz recovery variation with collectors' concentration (Flotigam 5806 and JCO) at pH 8

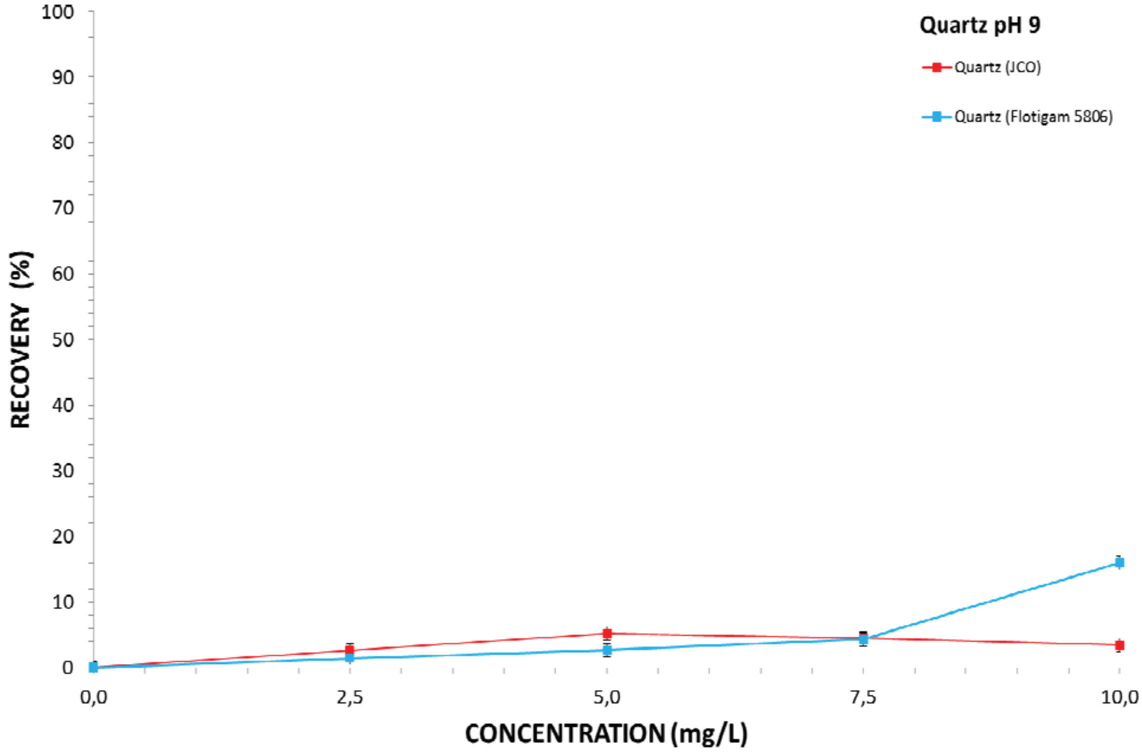


Fig. 7 Quartz recovery variation with collectors' concentration (Flotigam 5806 and JCO) at pH 9

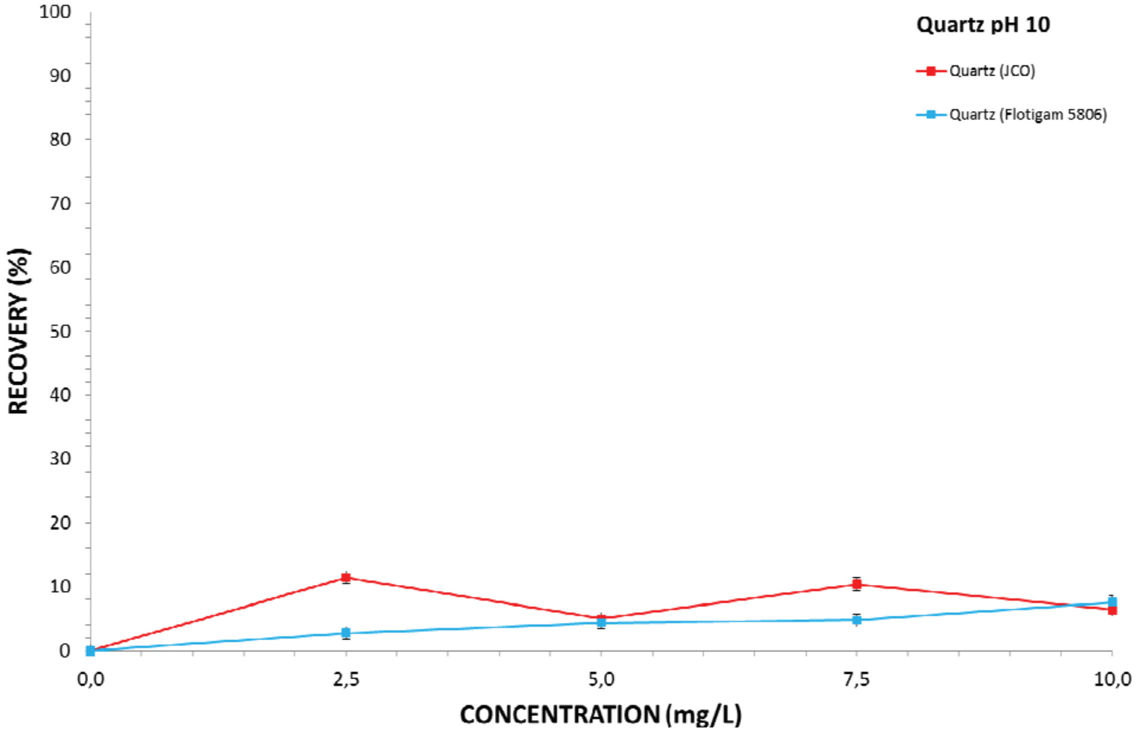


Fig. 8 Quartz recovery variation with collectors' concentration (Flotigam 5806 and JCO) at pH 10

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