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Apatite Froth Flotation Using Pequi's Yellow Pulp Oil as Collector

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Abstract **-**Pequi (Caryocar brasiliense) is a Brazilian oleaginous fruit, rich in fatty acids, with a predominance of oleic and palmitic acids. The fruit is composed of three major parts: the outer mesocarp (or white pulp), the inner mesocarp (or yellow pulp), which is very appreciated in the local cuisine, and the nut. The oil extracted from the nut (43.59 oleic and 43.76% palmitic acid) or from the yellow pulp (55.87 oleic and 35.17% palmitic acid) are used not only for nourishment, but also as a medicinal product and in cosmetic formulations. The white pulp does not have any commercial application being a residue. This paper proposes to use the oil from pequi's yellow pulp as a collector in apatite microflotation, due to its rich fatty acid composition. The oil was saponified with NaOH and then applied in microflotation tests using a modified Hallimond tube and pure samples of apatite. The results indicate that pequi's yellow pulp oil can be used as a collector in the froth flotation of this mineral (recovery greater than 95% for concentrations between 5 and 15 mg/L).

Keywords**:** microflotation; apatite; pequi's yellow pulp oil; flotigan

1. Introduction

Most of the phosphate ores extracted from phosphorus rocks belong to the apatite group ($Ca_5(Cl, F, OH)(PO_4)_3$), a crystalline calcium phosphate fluoride, with a P_2O_5 content ranging from 4 to 15%. The apatite deposits have a complex mineralogy, containing impurities that influence phosphorus recovery in the beneficiation plants. As a result, researches and technological improvements have been made in an attempt to use this apatite (Souza and Fonseca, 2008).

At the same time, the potential of fatty acids as collectors in froth flotation is recognized in literature. Within the group of oxidrilic collectors, there is the carboxylic collector group that has fatty acids as components (Baltar, 2008). In this sense, vegetable oils, rich in fatty acids, have been studied by researchers investigating its potential as collector agents.

As background, it is known that vegetable oils (rich in fatty acids) have drawn the attention of scientists for their potential as collectors. Researches about the application of vegetable oils as reagents in froth flotation have been performed in order to seek alternatives for commonly used collectors that have high costs and can entail high environmental degradation. According to Guimarães et al. (2005) certain vegetables, and animal fat, are capable of reacting self-contained glycerol and fatty acid molecules producing triacylglycerol or oil molecules. Oil extracted from the vegetables is then purified and submitted to a process that combines heat, high pressure and alkalinity, being converted into fatty acids. The fatty acids are saponified with NaOH to produce soluble soaps that act as apatite collector. Some examples are babaçu nut, castor oil plant, corn, olive, rice bran, soybean, tall oil and tallow.

Oliveira et al. (2011) worked with column flotation and samples of tailings from phosphate concentration circuit of Bunge Brazil SA, which processes a phosphate deposit that is part of the Barreiro carbonatite complex located in Araxá, state of Minas Gerais in mid-southern Brazil. The host rocks consist mainly of carbonates and glimmerites. As collector a mixture of the synthetic reagent and rice bran oil soap was used and increased the selectivity of the concentrate considerably. A grade of 29.4% P_2O_5 and a recovery of 46.2% were obtained under selected operating conditions. After testing apatite's microflotation with saponified pure fatty acids as collectors, these authors concluded that linoleic, linolenic and oleic acids, which are unsaturated acids, presented the best performance as collectors for apatite, with linoleic being the best collector. The authors confirmed this result by bench scale froth flotation tests with igneous carbonate ore from Tapira / MG - Brazil using vegetable oils, noting that the soybean oil, rich in linoleic acid, gave the best results.

Costa (2012) analyzed the use of Amazon fruit oils in phosphate ores froth flotation and the found results indicate there is a great possibility of using this oils as collectors. Vieira et al. (2005) analyzed the oil from castor beans, coconut, pequi and sesame. For making the water-soluble oil, the researchers used the procedure of ester hydrolysis or saponification. The authors used calcite samples in and a modified Hallimond tube in the tests. As a result, it was found that the saponified pequi and sesame oils performed well as collectors, producing results similar to those when pure sodium oleate was used.

Studies with jojoba oil were carried out by Santos and Oliveira (2012) noting the efficiency of this oil as an alternative collector for selective separation between apatite and calcite. Jojoba, which grows naturally in the deserts of northwestern Mexico and southwestern United States, is a shrub that has become more popular in other regions, such as South America. The oil extracted from its seed is 50% of the seed's weight and its main component is gadoleic acid (69.4%) featuring erucic acid (14.3%) and oleic acid (12.4%). The hydrophobicity studies show that the selective separation of calcite and apatite can be obtained by using jojoba oil at a pH below 7.0. In this condition, the apatite is hydrophilic and calcite is hydrophobic, allowing their separation through froth flotation.

Pequi, *Caryocar brasiliense*, is an oleaginous fruit with a strong and distinctive smell used in the cuisine of the Midwestern, Northern and Northeastern parts of Brazil. The fruit and its tree has many utilities from the timber to the fruit, with applications in the craft industry, cuisine, popular pharmacy and cosmetics industry. Also it has potential uses for the production of fuels and lubricants (Oliveira et al., 2008). The tree produces from 100 to 2000 fruits per year depending of the variety and location, with a life expectancy around 50 years. The fruit weight ranges from 30 to 400 g, typically containing one to two seeds and rarely three to four seeds (Lima et al., 2007; Carvalho, 2009). Besides being a typical species of the Brazilian Midwest, the fruit is also found in the southeastern, northeastern and northern states of the country, and may be found in Bolivia and Paraguay (Carvalho, 2009).

Pequi has a large amount of fatty acids. Zuppa (2001) performed the analysis of many Brazilian savanna fruit oils, including the pequi. The oil extraction was carried out with a Soxhlet extractor and hexane as solvent, using dried and crushed seeds and pulp from the fruits. The author noted that the pequi's yellow pulp showed a high viability for oil extraction.

Lima et al. (2007), in his work for characterization of extracted pequi's yellow pulp oil, found that the fruit's pulp is rich in lipids, corresponding to 33.4% of its composition. The results indicate that in the yellow pulp predominate unsaturated fatty acids (61.4% of the total). The highest concentration is oleic acid (55.9%), followed by palmitic acid (35.2%) and the lesser concentrations are gadoleic (0.3%), arachidic (0.2%) and myristic (0.1%) as shown in figure 1.

Brandão et al. (1994) performed microflotation tests in a Hallimond tube with pure apatite, using as collectors the sodium salts of palmitic, stearic, oleic, linoleic and linolenic fatty acids, as a function of pH. The results showed that the unsaturated fatty acids (linoleic, oleic and linolenic) exhibited superior performance compared to the saturated acids. Therefore, the pequi's fatty acid composition suggests its potential as a collector because, as described by Lima et al. (2007), unsaturated fatty acids predominate in pequi's yellow pulp.

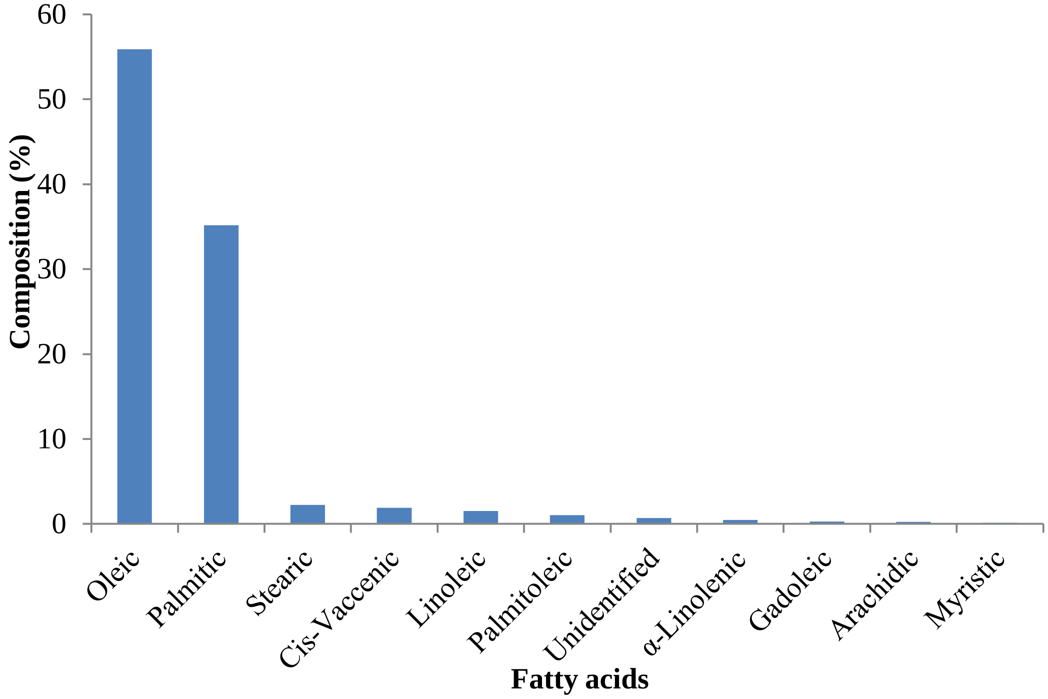

Fig. 1. Composition (%) of pequi's yellow pulp fatty acids (adapted from Lima et al., 2007).

2. Materials and Methods

The apatite samples were comminuted in a ball mill, granulometric classified by wet screening, vacuum filtrated and sent to dry in a drying oven for 8 hours at 80 oC. After the preparation procedure, samples were submitted to optical microscope analysis. The presence of impurities were noted, resulting in a new stage of processing whereby the samples underwent a process of magnetic separation with rare earth magnet, where it was possible to remove the magnetic contaminants presents. Other impurities were remove by elutriation. Figure 2 shows two optical microscopic images from apatite sample used in microflotation tests.

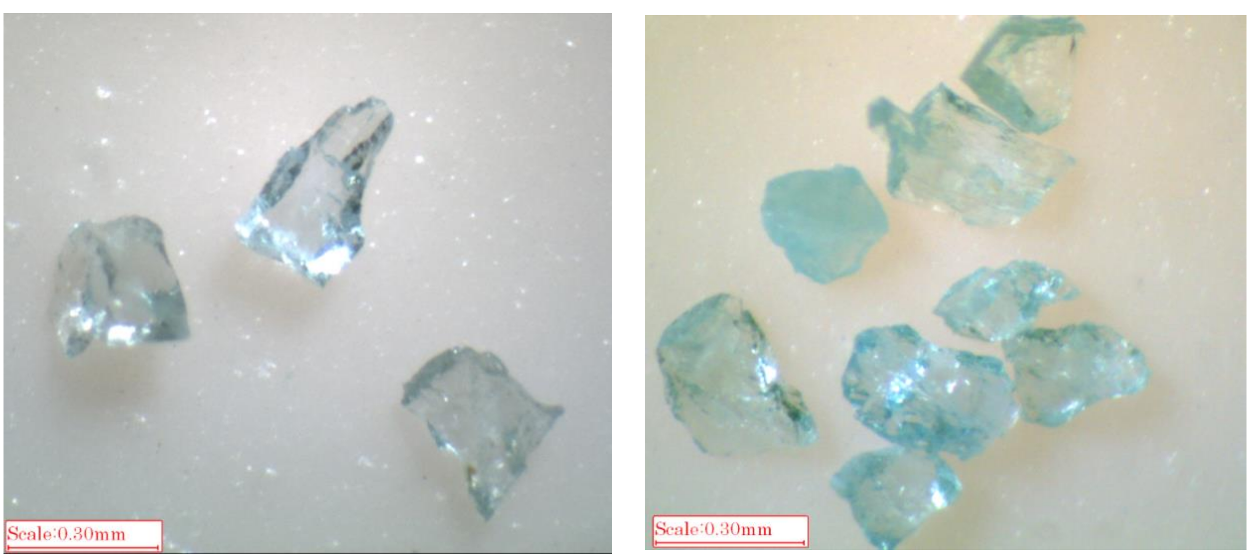

Fig. 2. Apatite samples used in the microflotation tests (-60+80# or -212+180 μm).

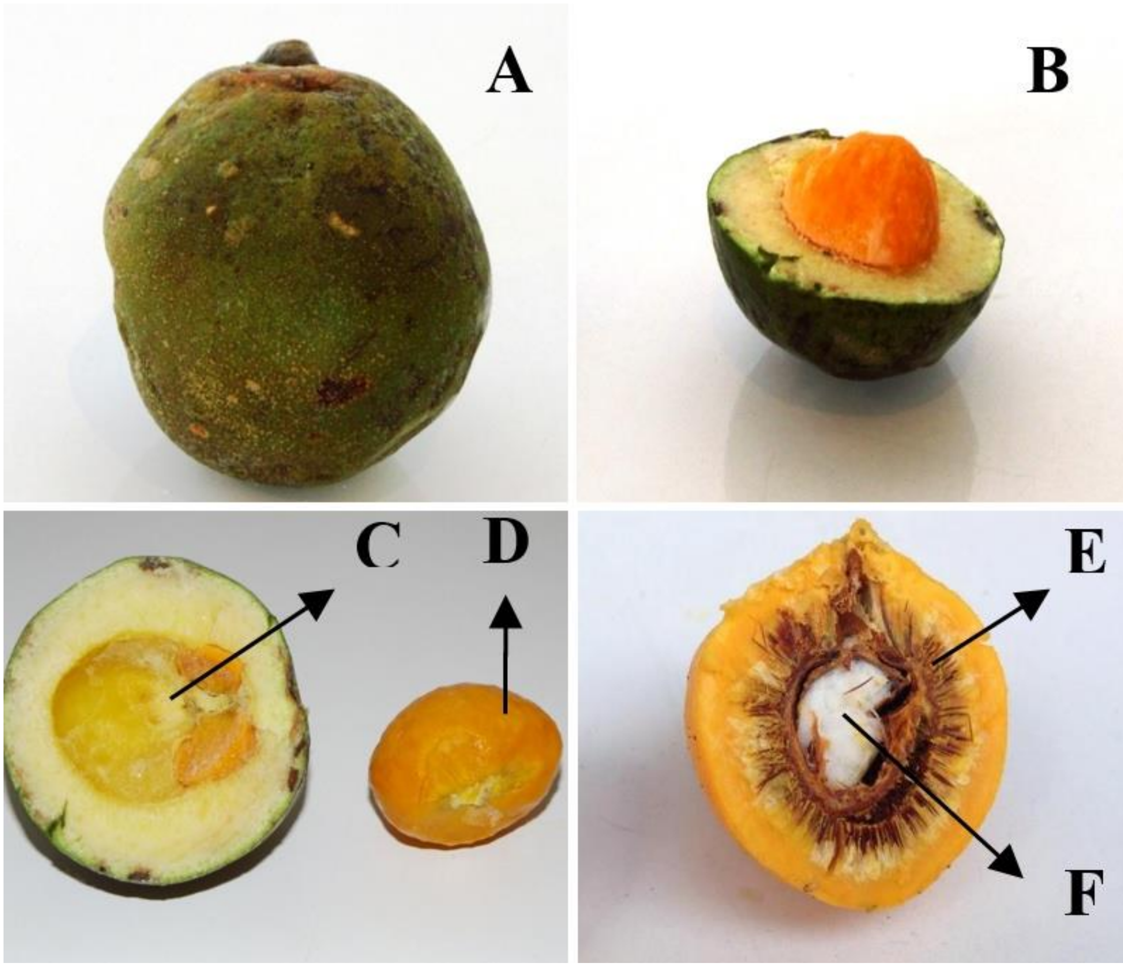

Fig. 3. Pequi's parts: (a) whole fruit; (b) fruit cut in half; (c) outer mesocarp (white pulp); (d) inner mesocarp (yellow pulp); (e) endocarp and (f) nut.

The pequi's yellow pulp oil was analyzed by a wet method for determining the acidity index. A sodium hydroxide standard solution of 0.01 N, a phenolphthalein solution 1% in an ethanol solution of 99%, and, a solvent, ether ethyl – alcohol solution (2:1) were used in the experiment. In a beaker, were added: 1.6 mL of phenolphthalein in solution 1% and 100 mL of ethyl ether – ethanol solution (2:1), neutralized with NaOH solution until pale pink coloration. Subsequently, this neutralized solution was inserted into an Erlenmeyer flask containing 5 g of oil sample. Then, titration method was performed with the NaOH solution until the appearance of first permanent pink color. The calculation of the acidity index was performed using the equation 1, proposed by Oliveira (2005):

$$A.I. = \frac{56.105 \times V_{NaOH} \times N_{NaOH}}{M_{sample}} \quad (1)$$

Where:
V_{NaOH} is the NaOH solution volume (in mL) spent in the titration;
N_{NaOH} is the NaOH solution normality;
M_{sample} is the oil sample mass (g).

The oil saponification index was determined using hydrochloric acid standard solution of 0.5 N, alcoholic solution of potassium hydroxide 4% and a phenolphthalein solution 1% in ethanol 99%. The procedure consisted of adding to 2 g of the oil sample to 25 mL of the alcoholic solution of potassium hydroxide. A blank test must be performed simultaneously. The solution was heated to maintain gentle boiling for 1 hour or until complete saponification. After leaving the solution cool, 0.5 mL of phenolphthalein solution was added and titrated with hydrochloric acid standard solution 0.5 N until the solution pink color complete disappeared. The equation 2 was used to calculate the oil saponification index (Oliveira, 2005):

$$S.I. = \frac{56.105 \times (V_B - V_S) \times N_{HCl}}{M_{sample}} \quad (2)$$

Where:
V_B is the HCl solution volume (in mL) spent in the blank test;
V_S is the HCl solution volume (in mL) spent in the sample test;
N_{HCl} is the HCl solution normality.

To be used as collector the pequi's yellow pulp oil was subjected to alkaline hydrolysis, also called saponification, which made the oil soluble in water. Its saponification was performed adding a sample of 5 g of pequi's yellow pulp oil in 20 g of water under magnetic agitation. On agitation, 7.5 mL of sodium hydroxide solution 10% was added to saponify the solution. Water was then added until the solution reached 100 g and magnetic agitated for homogenization.

Microflotation tests were conducted with pure apatite samples (with granulometry between -60+80# or -212+180 µm), at pH 9 (as usual in the industrial process for phosphate rock in Brazil) and varying the concentration of the collector. The modified Hallimond tube was the equipment used in these tests because it is an easy method for determination of mineral hydrophobicity or hydrophilicity, defining if the used collector is effective in recovering the analyzed mineral. Hydraulic entrainment tests were performed to quantify how much apatite was hydraulic carried up the tube. All tests were carried out in triplicate.

The mineral conditioning time was established as 7 minutes in a more concentrated form, i.e., the mineral was placed in the final part of the tube with the amount of collector that ensures the desired final concentration and to it was added water at pH 9 until the maximum volume for the conditioning solution, 50 mL. Towards the end of the 7 minutes, the remainder of the water required for the procedure, coming to a solution of 320 mL, was added and then the flotation started. This procedure was performed for a stronger contact between the mineral and the collector. Preliminary tests showed that the flotation is most effective when the conditioning is more concentrated, and therefore, this methodology was adopted. The flotability of apatite under the collector action was measured as a function of floated mass, i.e., the recovery of the mineral was calculated from the ratio between the floated mass and the total mass of the apatite sample.

To compare the pequi's yellow pulp oil recovery in apatite microflotation additional tests were carried out using Flotigam 5806 from Clariant, which is a highly used collector for phosphate rock froth flotation worldwide. Table 1 summarizes the conditions of microflotation tests using pequi's yellow pulp oil and Flotigam 5806.

Table. 1. Test conditions for apatite's microflotation using pequi's yellow pulp oil and Flotigam 5806.

Conditions	**Values**
Air flow rate	40 cm^3/min
Conditioning time	7 min
Flotation time	1 min
Mass of the mineral	1 g
Size range	-60+80# (or -212+180 µm)
Collector concentration	1, 2.5, 5, 7.5, 10, 15 mg/L (Pequi) 1, 2.5, 5, 7.5 mg/L (Flotigam 5806)
pH	9

3. Results and Discussions

The X-Ray fluorescence spectrometry of the apatite sample revealed the presence of barite and iron in small amounts. However, concentrations of P_2O_5 and CaO are high, consistently with a high purity sample (over 95% of purity), as shown in Table 2.

Table. 2. Composition of apatite samples after comminution and classification (-60+80#).

Oxide	Nb_2O_5	P_2O_5	Fe_2O_3	SiO_2	BaO	Al_2O_3	CaO
Composition (%)	-	40.50	0.07	0.94	0.06	0.38	52.04

The pequi's yellow pulp oil characterization by wet procedures were performed in triplicate. The average value of the acidity index was 0.03 mg KOH / g of sample. Costa (2012) worked with oils from Brazilian native fruits used as collector in froth flotation and obtained the acidity indexes: passion fruit 1.0 mg KOH / g, inajá 2.8 mg KOH / g, buriti 6.5 mg KOH / g and açaí 10.2 mg KOH / g. Therefore, the acidity index found for the pequi's yellow pulp oil is lower than the values reported in literature for other Brazilian native fruits oils. For the saponification index the average value obtained was 191.98 mg KOH / g. Costa (2012) obtained values between 196 and 212 mg KOH / g.

The tests with the modified Hallimond tube revealed a low rate of hydraulic entrainment (less than 1% at airflow rate of 40 cm3/min) for apatite samples with granulometry between -212+180 µm (or -60+80#). Thus, the microflotation results will be presented disregarding values of hydraulic entrainment. All tests (hydraulic entrainment and microflotation) were performed triplicate. In total 30 microflotation tests were carried out (18 tests with pequi's yellow pulp oil and 12 tests with Flotigam 5806).

The results of microflotation tests are shown in Figure 4. Pequi's yellow pulp oil obtained excellent results (apatite recovery higher than 95%) as a collector in apatite's froth flotation. Concentrations between 5 and 15 mg/L had similar results, all above 95% of recovery. Thus, the concentration 5 mg/L is a good alternative and more economically viable than concentrations above this value, obtaining similar results using less reagent. The results show that the pequi's yellow pulp oil had similar results to the Flotigam 5806 at concentrations above 5 mg/L. At lower concentrations, Flotigam 5806 produced higher recoveries than pequi's yellow pulp oil (around 3.6 times more).

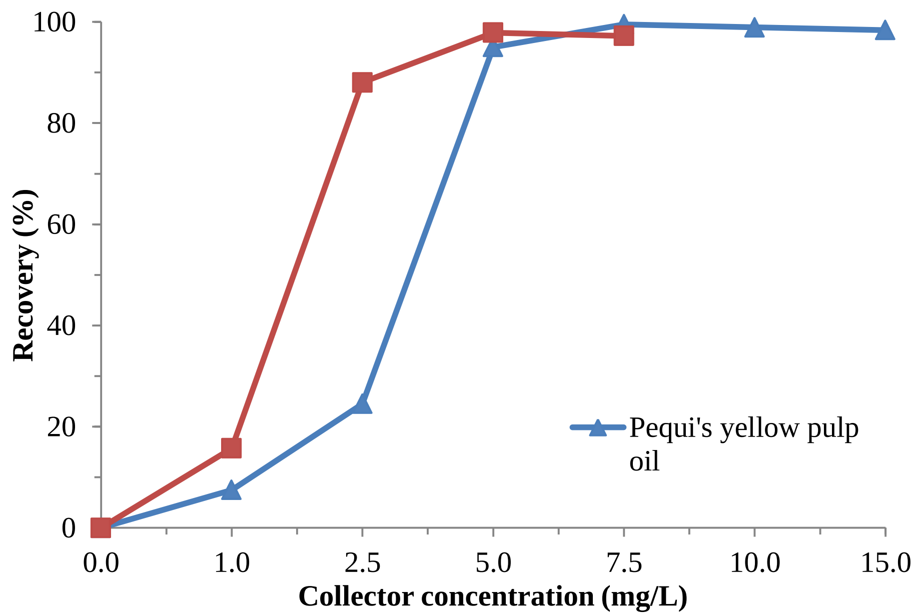

Fig. 4. Recovery results in function of the collector concentration (pequi's yellow pulp oil and Flotigam 5806).

4. Conclusions

The microflotation tests using saponified pequi's yellow pulp oil indicate that this oil can be used satisfactorily as collector apatite microflotation. In the concentrations from 5 mg/L, the oil presents similar recovery results to the collector industrially used (Flotigam 5806). The found results agree with other works using oils extracted from fruits. Results of microflotation tests performed by Costa (2012) shows that Amazon fruit oils showed apatite recoveries near 100% at concentrations 2.5 mg/L (for buriti, inajá, andiroba and açaí oils) and 5 mg/L (for passion fruit and Brazil nut oils). Therefore, the results for pequi's yellow pulp oil (composed by 55.9% oleic acid and 35.2% palmitic acid) approach these results, reaching recoveries above 95% at concentrations from 5 mg/L, similar to passion fruit oil (composed by 48.8% linoleic acid, 28.9% oleic acid and 12.6% palmitic acids) and Brazil nut oil (composed by 47.0% oleic acid, 18.1% palmitic acid, 15.2% linoleic acid and 13.2% stearic acids).

More work still need to be done to test the selectivity of the pequi's yellow pulp oil in phosphate rock froth flotation.

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References

Baltar, C. (2008). Flotação No Tratamento De Minério. *Recife, Brazil, UFPE.*

Brandão, P.R.G., Caires, L.G., & Queiroz, D.S.B. (1994). Vegetable Lipid Oil-Based Collectors In The Flotation Of Apatite Ores. *Minerals Engineering,* 7(7), 917-925.

Carvalho, P. (2009). Pequizeiro - Caryocar Brasiliense. *Technical Communication 230,* Embrapa, Colombo-PR, Brazil.

Costa, D.S. (2012). Uso De Óleos Vegetais Amazônicos Na Flotação De Minérios Fosfáticos. *Thesis (Doctorate),* School of Engineering, Federal University of Minas Gerais, Belo Horizonte, Brazil.

Guimarães, R.C., Araujo, A.C., & Peres, A.E.C. (2005). Reagents In Igneous Phosphate Ores Flotation. *Minerals Engineering,* 18(2), 199-204, 2005.

Lima, A., Silva, A.M.O., Trindade, R.A., Torres, R.P., & Mancini-Filho, J. (2007). Composição Química E Compostos Bioativos Presentes Na Polpa E Na Amêndoa Do Pequi (Caryocar Brasiliense, Camb.). *Revista Brasileira de Fruticultura*, 29(3), 695-698, 2007.

Oliveira, J. (2005). Grau De Saponificação De Óleos Vegetais Na Flotação Seletiva De Apatita De Minério Carbonatítico. *Dissertation (Master),* Programa de Pós-graduação em Engenharia Mineral, Federal University of Ouro Preto, Ouro Preto, Brazil.

Oliveira, M.E.B., Guerra, N.B., Barros, L.M., & Alves, R.E. (2008). Aspectos Agronômicos E De Qualidade Do Pequi. *Documents 113,* Embrapa Agroindústria Tropical, Fortaleza.

Oliveira, M.S., Santana, R.C., Ataide, C.H., & Barrozo, M.A.S. (2011). Recovery Of Apatite From Flotation Tailings. *Separation and Purification Technology,* 79(1), 79-84.

Santos, E., & Oliveira, J. (2012). Utilização De Óleo De Jojoba Como Coletor Alternativo Na Flotação Seletiva Entre Apatita E Calcita. *In: Painel PEMM 2012*, Rio de Janeiro.

Souza, A., & Fonseca, D. (2008). Fosfato. *DNPM*.

Vieira, M., Lédo, P.G.S., Lima, R.F.S., Paulo, J.B.A., & Brandão, P.R.G. (2005). Flotação De Calcita A Partir De Óleos Vegetais Regionais Saponificados Como Agentes Coletores. *In: VI Congresso Brasileiro de Engenharia Química em Iniciação Científica.* Campinas, SP.

Zuppa, T. (2001). Avaliação Das Potencialidades De Plantas Nativas E Introduzidas No Cerrado Na Obtenção De Óleos E Gorduras Vegetais. *Dissertation (Master),* Institute of Chemistry, Federal University of Goiás, Goiânia, Brazil.