NEW COLLECTORS AND DEPRESSANTS FOR APATITE FLOTATION

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Abstract
The crescent demand for raw material has increase mining activities. Mineral industry faces the challenge of process more complexes ores, with very small particles, and low grade, together with the constant pressure to reduce production costs and environment impacts. Froth flotation deserves special attention among the concentration methods for mineral processing. Besides its great selectivity for different minerals, flotation is a high efficient method to process fine particles. The process is based on the minerals surficial physicochemical properties and the separation is only possible with the aid of chemicals such as collectors, frothers, modifiers, and depressants. In order to use sustainable and eco-friendly reagents, oils extracted from fruits (especially from Brazilian savanna) and an alternative starch source (sorghum) had been tested. Apatite samples were characterized by SEM, EDS, XRD, XRF, and had their zeta potential measured. The results show a great potential for the new collectors, with apatite flotability equal or higher than compared with the reagents industrially adopted nowadays. The results for sorghum were compatible with the results for cornstarch, indicating that this cereal can be a feasible substitute for corn as a starch source.

Keywords: Flotation; Vegetal oils; Starches; Apatite.

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1 INTRODUCTION

Around 80% of the Brazilian phosphate rock deposits are igneous and related with volcanic geological environments with accentuated presence of carbonates and micaceous minerals with low grade of \( P_2O_5 \) [1]. The adoption of fatty acids, specially soy and rice oil, as collectors and cornstarch as depressant on flotation process allowed the economic exploitation of Brazilian phosphate mines, such as Cajati (SP), Araxá (MG), and Catalão (GO) [2].

The Brazilian phosphate rock processing includes stages of comminution (with liberation around 65# Tyler), magnetic separation to remove magnetite and other iron bearing minerals (with ROM grade ranging from 30-35%), desliming of particles < 10 μm using cyclones, and apatite direct flotation in alkaline pH (normally around 11). The phosphate recovery is significantly affected by the presence of slimes in the flotation [3].

Several studies showed that oil extract from vegetable rich in fatty acids have high potential to be used as collectors especially because the presence of carboxylic groups on their structure. The search for cheap, reliable, sustainable, and ecofriendly collectors is consider very important since the most common collectors industrially adopted are synthetic, with high cost, and can contribute to environment degradation. Even better if the collectors can lead to gains in phosphate recovery and/or increase in the process selectivity.

Depressants are fundamental to flotation since these modifiers are responsible for inhibiting the collector absorption on the surface of the minerals whose flotation is not desired. Cornstarch is the most widely used depressant nowadays in Brazil due to its effectiveness for different minerals. However, most of the corn produced in Brazil is used for human and animal feed, to produce ethanol, and exported. This scenario is not favorable for the mining industry. Companies are adopting low quality cornstarch and, in some cases, coproducts of the cornstarch processing in order to reduce production costs.

The Brazilian Cerrado is the largest savanna formation in South America and originally covered approximately 25% of the Brazilian territory, with over than 10,000 species of plants (45% are exclusive to this biome) [4, 5]. Some of this species and especially their fruits have a considerable potential to be adopted as flotation reagents regarding to their chemical makeup. This strategy can help the conservation and preservation of native species with no other economical function and the family farming since many of this species does not have a developed industrial agriculture.

Oils from three oleaginous perennial species, pequi (Caryocar brasiliense) and macauba (Acrocomia aculeata), typical fruits from Brazilian Cerrado, and Jatropha Curcas (Jatropha Curcas L.) were tested as apatite collectors. Pequi is a fruit of strong and distinctive smell largely used in the cuisine of the Midwest, North and part of the Northeast on Brazil. It has many utilities from timber to applications in craft industry, cuisine, popular pharmacy, cosmetics, and has potential to be used in the production of fuel and lubricants [6]. Pequi fruit’s pulp is rich in lipids corresponding to 33.4% of its composition. Macauba is a palm that naturally occurs throughout the tropical zone of Latin America. Their economic exploitation occurs both in extractive systems as for rational cultivation with diverse products and applications as pharmacological, nutraceutical, timber, craft, forage, food, and fuel. Its oil productivity approaches the African Palm (Elaeis guineensis), around 5 tons of oil per ha. African Palm the known
culture with the highest oil productivity per ha cultivated and largest share of vegetable oil produced worldwide [7]. Jatropha Curcas is a species belonging to *Euphorbiaceae* family. With high oil productivity, resistance to hydric stress, soil and weather variations and low production cost, the seeds present good conservation after harvest and can be stored for long periods without any degradation of the oil on them [8]. It was brought to Brazil to be used as hedge and for small-scale oil production and nowadays is cultivated in many areas of the country [9]. Jatropha Curcas’ seeds contain high levels of polyunsaturated fatty acids, which negatively influence the biofuel quality [10]. Table 1 shows the fatty acid profile of the four tested oils.

Sorghum (*Sorghum bicolor* L. *Moench*) flour and starch were investigated as an alternative depressant to cornstarch. Sorghum is a crop widely grown over the world for production of food and feed. Quantitatively is the world’s fifth most important cereal grain, after wheat, maize, rice, and barley. It is mostly cultivated across the world in the warmer weather areas. Sorghum is the main staple food for the world’s poorest people. Starch is the major storage form of carbohydrate in sorghum making up about 60-80% of normal (non-waxy) kernels. Nowadays sorghum is cultivated in Brazil only for animal food despite the fact of its possible usefulness in different food products [11]. Sorghum is generally considered inferior to corn for food, feed or industrial uses. Sorghum is grown in arid regions since its demands less water than corn. Sorghum is less demanding of soil fertility than other cereals and has a short vegetative cycle (varying from 90 to 130 days) which makes it ideal for production during other crops off-season, such as sugarcane, soy or corn. The same planting, cultivating, and harvesting equipment used for other cereals, such as soybean, rice, wheat, and corn, can be used, although the farming can be conducted manually with good adaptation to systems usually used by small producers [12].

### Table 1. Fatty acid composition (in w %).

<table>
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<tr>
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<tbody>
<tr>
<td>Oleic – ω9 (C18:1)</td>
<td>55.87</td>
<td>58.7</td>
<td>31.60</td>
<td>25.70</td>
</tr>
<tr>
<td>Palmitic (C16)</td>
<td>35.17</td>
<td>19.7</td>
<td>9.09</td>
<td>19.60</td>
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<tr>
<td>Stearic (C18)</td>
<td>2.25</td>
<td>2.0</td>
<td>4.19</td>
<td>9.60</td>
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<tr>
<td>Cis-vaccenic – ω7 (C18:1)</td>
<td>1.90</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Linoleic – ω6,9 (C18:2)</td>
<td>1.53</td>
<td>7.3</td>
<td>3.07</td>
<td>40.00</td>
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<tr>
<td>Palmitoleic – ω7 (C16:1)</td>
<td>1.03</td>
<td>2.8</td>
<td>-</td>
<td>2.40</td>
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<tr>
<td>Linolenic - ω3,6,9 (C18:3)</td>
<td>0.45</td>
<td>1.1</td>
<td>0.15</td>
<td>-</td>
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<tr>
<td>Gadoleic (C20:1)</td>
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<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Arachidic (C20)</td>
<td>0.23</td>
<td>0.2</td>
<td>-</td>
<td>0.30</td>
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<tr>
<td>Myristic (C14)</td>
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<td>1.1</td>
<td>10.60</td>
<td>-</td>
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<td>3.83</td>
<td>-</td>
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<tr>
<td>Capric (C10)</td>
<td>-</td>
<td>0.5</td>
<td>3.29</td>
<td>-</td>
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<tr>
<td>Lauric (C12)</td>
<td>0.04</td>
<td>3.8</td>
<td>34.30</td>
<td>-</td>
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<tr>
<td>Elaidic (C18:1t)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.50</td>
</tr>
</tbody>
</table>

### 2 MATERIALS AND METHODS

#### 2.1 Reagents preparation
Oil extracted from three different vegetable species (pequi pulp, macauba nut and pulp, and Jatropha Curcas) were studied and tested as apatite collectors. Since the oils are not soluble in water, an alkaline hydrolysis (or saponification), was necessary before their contact with the minerals. The saponification was performed at room temperature. A solution with 5.0 g of oil, 20.0 mL of distilled water and 7.5 mL of sodium hydroxide solution (10%) was kept under magnetic agitation until full homogenization. The solution was then weighted and distilled water was added to it until its mass reached 100 g. Graniferous sorghum grains, cultivated in Brazil, were used to produce flour and starch. Straw residues and other impurities were removed by dry sieving. Grains were then oven dried at 35 °C for 30 hours to remove residual moisture. The flour was produced through comminution of the dried grains using two cereal mills operating in series. The methodology proposed by Rupollo et al. [17] was used, with minor modifications, for starch extraction from the flour. A suspension of 500 g of sorghum flour and 2.0 L of sodium bisulfite solution (0.16%) was left in the refrigerator for 24 hours at 4 °C. The supernatant liquid was drained after the starch decantation. To the precipitate was added 600 mL of distilled water. Using an industrial blender the solution was homogenized for 5 minutes. Sieves (38, 75, and 355 μm) were used to remove coarse fraction. Particles under 38 μm were centrifuged using a micro processed centrifuge at 3600 rpm for 5 minutes. The liquid fraction was drained. The not withe solids were manually removed using a stainless steel spatula and rinsed with distilled water. The centrifugation process was repeated until the solids were completely white (between 5 to 8 cycles). The extracted sorghum starch was dried in a forced air oven for 12 hours at 40 °C. The depressant gelatinization was performed by adding 2.7 mL of sodium hydroxide at 10% to a solution of 20.0 mL of distilled water and 1.0 g of starch. The solution was kept under magnetic stirring until complete gelatinization.

2.2 Apatite samples preparation and characterization

Apatite samples were comminuted in a jaw crusher followed by a ball mill, and granulometric separated through wet sieving using a Tyler sieving series during 15 minutes to produce samples with granulometry -100+150#. The samples were then dried in an oven for 24 hours at 60 °C. A ferrite magnet with field of 2 kG was used to remove and possible contamination from the previous stages. The mineralogical phase characterization was performed using an X-ray Diffractometer with graphite monochromator, operating at 30 kV/15 mA, angular step of 0.02˚ and acquisition time of 2 seconds. Chemical composition was determined by X-ray Fluorescence. Images were acquired with a SEM JSM-6610 from Jeol coupled with EDS probe from Thermo Scientific NSS Spectral Imaging at Labmic /UFG. Particle size analyze was performed with addition of Na$_2$P$_2$O$_7$ (1 g/L) as dispersant agent and tap water at IFAD/TUC using a HELOS laser diffraction particle size analyzer from Sympatec. The zeta potential was measured at LPI/EM/UFOP with pH ranging from 3.5 to 12.5 with distillate water and having KCl at 10$^{-3}$ mol/L as indifferent electrolyte using a ZS90 Zetasizer Nano from Malvern.

2.3 Microflotation tests
Microflotation tests were performed in Hallimond modified tube (addition of an extender between the bottom and upperparts of the tube in order to reduce the effects of hydraulic entrainment) with 320 mL of internal volume, at room temperature and 1 g of apatite sample. To minimize the hydraulic entrainment the airflow was kept at 40 cm$^3$/min and pressure at 10 psi, as suggested by Guimarães Júnior et al. [18]. The adopted flotation time was 1 min, the condition time was 7 min for the collector and 5 minutes for the depressant. The tests with the new collectors were carried out at pH 9 and Flotigam 5806, a synthetic mix of fatty acids industrially adopted as apatite collector manufactured by Clariant, was used as benchmark. The tests with the new depressants were carried out at pH's 9.5, 10.0, 10.5, and 11.0 and Flotigam 5806 (300 g/t) were used as collector (reverse flotation of apatite).

3 RESULTS AND DISCUSSION

Table 2 shows the results of X-ray fluorescence of apatite sample used on microflotation tests. Since pure apatite contains amounts CaO and P$_2$O$_5$ of 55.07 and 41.82%, respectively, it is possible to estimate that the apatite sample has 95.5% of purity, regarding its chemical composition.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>P$_2$O$_5$</th>
<th>K$_2$O</th>
<th>SiO$_2$</th>
<th>SO$_3$</th>
<th>I</th>
<th>Na$_2$O</th>
<th>ThO$_2$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>BaO</th>
<th>SrO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>54.02</td>
<td>38.49</td>
<td>4.20</td>
<td>1.10</td>
<td>0.63</td>
<td>0.39</td>
<td>0.34</td>
<td>0.27</td>
<td>0.18</td>
<td>0.11</td>
<td>0.11</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 1 shows scanning electron microscope images for apatite samples using backscattered and secondary electron imaging. It is possible to notice the association of apatite with an acicular mineral phase. Energy-dispersive X-ray spectroscopy (EDS) results are shown for two points, one on the acicular phase and the other on the apatite phase. The main mineral phase is composed by Ca, P and O, as expected for apatite (Ca$_5$(PO$_4$)$_3$). Since Cl and F was also observed this could be an indication of the existence of fluorapatite and chlorine apatite in the sample (Ca$_5$(PO$_4$)$_3$(F,Cl)). The acicular phase (figure 1f) could not be correctly identified based only on this result.

Figure 2 shows the results of the apatite sample characterization. The XRD objective was confirm the mineral phases present in the sample and a simple search in the Bragg peaks allowed the confirmation of the apatite phase. Nevertheless, a refinement step of the results was performed to check the sample composition and the results did not indicate the presence of other mineral phase. Zeta potential measurements (figure 2b) showed that the electronegativity of the apatite surface increased with the pH. According to Oliveira [19] apatite has negative superficial charge at alkaline pH and the adsorption of anionic collectors on its surface is due chemisorption. The isoelectric point was not found, which agrees with the sample high purity. Even though the samples had been wet sieved (+106-150 μm) it was possible to notice that the presence of particles below 106 μm (68%) and above 150 μm (20%). This fact can be explained by the imperfection of the sieving process.

Figure 3 shows the results of microflotation tests. For dosages below or equal to 5 mg/L the macauba pulp oil was able to floated more than 91% of all apatite, superseding all other oils and Flotigam 5806. However, for dosages above 5 mg/L pequi oil floated approximately 99% of the apatite. The macauba pulp oil was, by far, the oil with lower apatite flotability. The flotability peak (84%) was obtained at 10 mg/L.
Jatropha Curcas' oil, which was the cheaper oil tested, presented similar results to Flotigam 5806 for dosages above 2.5 mg/L, with apatite flotability above 90%.

Figure 1. SEM images: (a) BEC and (b) SEI image at x190 magnification and (c) BEC and (d) SEI at x750 magnification. EDS results for apatite samples (e) point 1 and (f) point 2.
Figures 4 to 7 show the apatite flotability using sorghum (starch and flour) and cornstarch as depressants. It was expected that the depressant acted against the apatite flotation, forcing the mineral particles to depress. As expected, apatite flotability decreased with the increase of the depressant dosage. This result was expected once there was no other mineral present to react with the depressant. Sorghum (starch and flour) showed superior results when compared with cornstarch. Sorghum flour had lower flotability than the other two depressants for dosages equal or higher than 800 g/t. The best results for apatite reverse flotation were found at pH 9.5 and 11. The dosage of 400 g/t of sorghum starch flotated 3.23 ± 0.49% at pH 9.5 and 2.11 ± 1.14% at pH 11.5, around 42 and 90% lower than cornstarch, respectively. Very similar results were obtained for sorghum flour. Despite this values not being the lower apatite flotability obtained, they were produced with the lower dosage of depressant, which can be industrially more cost effective. Sorghum starch flotated more apatite than cornstarch only in two occasions: at pH 10 and pH 10.5 with dosage of 400 g/t. For all other tests, the sorghum starch results were lower, or similar, to cornstarch.
**Figure 3.** Apatite flotability as a function of the collector concentration at pH 9.

**Figure 4.** Apatite flotability as function of the depressants dosage at pH 9.5.
Figure 5. Apatite flotability as function of the depressants dosage at pH 10.

Figure 6. Apatite flotability as function of the depressants dosage at pH 10.5.
The found results evidence the pH influence over flotation systems, as proposed in the literature. In the absence of depressants, an increase in the pH from 10 to 10.5 reduced the apatite flotability from 87.49 ± 8.41% to 72.11 ± 9.59%. At pH 11, which is the pH industrially adopted by mining companies in phosphate rock flotation, the apatite flotability was only 23.18 ± 3.07%.

4 CONCLUSIONS

The microflotation tests using oils extracted from pequi, macauba and Jatropha Curcas’ proved their potential as fatty acids source to be used as apatite collectors. It is possible to highlight that for dosages equal or higher than 7.5 mg/L, pequi oil flotated almost all apatite particles. In one hand macauba pulp oil showed excellent results for all dosages, with more than 90% of apatite flotated, but in the other hand with the nut oil the higher flotability found was around 84%. Jatropha Curcas’ was second best oil tested and at a dosage of 7.5 mg/L more than 90% of the apatite particles were flotated. These results represent a good alternative to synthetic collector industrially adopted, since the oils are natural, sustainable, and biodegradable. Some of them, like macauba and Jatropha Curcas are cheaper than most of the synthetic collectors based on fatty acids. Another important contribution that the adoption of these alternative oils can bring is related to the preservation of the Brazilian Cerrado by creating an industrial demand for this species.

Regarding the new depressant the lower apatite flotability with sorghum starch were found for a dosage of 1,200 g/t and pH 11, resulting in a flotability of 1.99 ± 0.52%. Sorghum flour, on the other hand, produced at the same conditions an apatite flotability of 1.40 ± 0.36%, approximately 30% lower than sorghum starch and 91% lower than cornstarch (15.44 ± 2.41%).

Figure 7. Apatite flotability as function of the depressants dosage at pH 11.
The results indicate that sorghum, no matter if milled as a flour or purified as a starch, can be used in apatite flotation as a depressant and its depressant action is similar, or higher, than observed for cornstarch. Since sorghum price is lower than corn, the flotation results can be seen not only technically but also economically important.

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REFERENCES

5  The Nature Conservancy. Available from: https://www.nature.org/ourinitiatives/regions/latinamerica/brazil/placesweprotect/cerrado.xml
6  Oliveira M, Guerra NB, Barros LDM, Alves RE. Aspectos Agronômicos e de Qualidade do Pequi. Documents, 113, Embrapa Agroindústria Tropical, Fortaleza, Brazil; 2008. (in Portuguese)
7  REMAPE: Rede Macauba de Pesquisa. Available from: http://www.macauba.ufv.br/.

