MACAUBA PULP OIL BLEACHING USING COMMERCIAL ADSORBENT AND ACTIVATED CARBON FROM ENDOCARP OF THE OWN FRUIT

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RESUMO: Macauba Palm (Acrocomia aculeata) is a promising source of vegetable oil with production capacity of up to 5000 kg/ha. The refining process is essential to impurities removal and also to obtain oil with color more appreciated by consumers. Covering a literature failing, the aim of this study was to investigate the Macauba pulp oil refining focusing at bleaching stage by assessing the temperature effect and amount of commercial adsorbent. Further was evaluated the use of activated carbon produced from the endocarp of own Macauba fruit as a partial replacer of bleaching earths. Conventional methods were employed and results were analyzed considering bleaching capacity, acidity index and phosphorus content. The use of 6% commercial adsorbent at 90 °C led to a bleaching capacity about 84% while the use of a commercial adsorbent mixed with activated carbon resulted in a bleaching capacity superior to 90% and with greater percentage of phospholipids removal.

PALAVRAS-CHAVE: oil refining; oil bleaching; Acrocomia aculeata; Macauba pulp oil; activated carbon.

1. INTRODUCTION

Macauba (Acrocomia aculeata (Jacq. Lodd. ex Mart.)) is a palm tree with wide distribution in America and with large populations in Brazilian Cerrado (Silva e Caño Andrade, 2013). The literature suggests that oil productivity from Macauba fruits can range from 1500 to 5000 kg/ha (Mota et al., 2011) and this quantity could be improved by conversion of native culture for the planned, reaching values superior or equal than those obtained by the Oil Palm culture (Elaeis guineensis).

Macauba pulp oil has a yellow-orange coloration due to the presence of carotenoids, especially β-carotene, which corresponds to about 80% of total carotenoid (Ramos et al., 2008). This oil is mainly composed by unsaturated fatty acids, with high percentage of oleic fatty acid (66%), followed by linoleic acid (11%). It also contains significant amounts of saturated palmitic fatty acid (16%) (Rezende et al., 2015). Several studies about the use of this pulp oil for biodiesel production have been carried, but its similar fatty profile to olive oil makes the Macauba pulp oil promising for human consumption. Oils with high
monounsaturated fatty acid profile are desirable for food and biofuels industries due to its nutritional quality and oxidative stability (Cano Andrade et al., 2006; Nunes et al., 2015).

Crude vegetable oils contain minority constituents such as free fatty acids, pigments (chlorophyll, carotenoids, xanthophylls, tocopherol), phospholipids, metals traces and hydroperoxides, limiting the use and preservation of these oils (Zschau, 2001). In general, vegetable oils are sold after undergoing refining process that removes these compounds ensuring products with quality and stability, which results in long shelf life. There are few literature works focusing on refining of the Macauba pulp oil. Bleaching is the most important stage in crude oil refining process that determines the appearance, the flavor and stability of the final product (Nguetnkam et al., 2008). Nowadays the growing search for a low-cost adsorbent in vegetable oil bleaching process introduces as alternative the use of carbonaceous materials in the form of activated carbon (Aishat et al., 2015). Generally the activated carbon is used as a small part of mixtures with bleaching clays, where the ratio of the activated carbon does not exceed 5-10% of the mass of clay (Patterson, 1992).

The aim of this research was to achieve the Macauba pulp oil refining in order to adjust it with the quality standards established by Brazilian legislation, as well as proposing the use of an alternative adsorbent for the bleaching step. To reach this goal, the effect of the temperature and adsorbent amount was evaluated in the conventional bleaching process by commercial adsorbent typically used in industrial bleaching. Further it was introduced the use of activated carbon obtained from the endocarp of own fruit as a partial substitute for commercial adsorbent, therefore proposing a new application for this biomass that is a co-product generated in the processing of the Macauba coconut.

2. MATERIAL AND METHODS

2.1. Raw material and refining procedure

Macauba fruits were collected on Campus of Federal University of Minas Gerais (UFMG). For the extraction in expeller continuous press the pulp was prepared according to the methodology of Pimenta et al. (2012) that includes a previous drying in an oven at 60 °C for 48 h. The obtained oil was centrifuged to remove the solids and stored in dark bottles in a refrigerator at 4°C until utilization. The refining step was performed on a laboratory scale.

The first step was the degumming. The mixture of crude oil with 3.0% of distilled water was heated in rotary evaporator (SL-126, Solab) for 30 min at 60 °C and agitation of 60 rpm. Subsequently, the mixture was centrifuged at 2000 rpm for 10 minutes. The parameters used in this step were defined as described by Moretto e Fett (1998) and Viera et al. (2009).

The neutralization was performed as described by Pimenta et al. (2010), using sodium hydroxide solution (2.0 mol/L) in a volume sufficient to neutralize all free fatty acids present in the degummed oil. In this work, in order to ensure total removal of the free fatty acids, the added volume of base was 10% superior to the calculated value. Initially the oil was maintained for 5 minutes at 60 °C in rotary evaporator to homogenize the temperature, then was added the calculated volume of sodium hydroxide. The mixture was stirred for 15 minutes at 60 °C and 60 rpm. After neutralization, the mixture was centrifuged at 2000 rpm for 15 minutes to remove the soap. At the end of this step, the residue of soap remained in the
bottom of the tubes and the oil from the surface was transferred to a separating funnel for further washing. The washing step consisted on the addition of 10% of cold water in relation to the oil mass, with manual agitation. This step was repeated until the discarded water was clear and with a pH equal to the initial distilled water. The drying lasted for 30 min with temperature at 80 °C and 60 rpm, under vacuum.

Adsorbents used in the bleaching experiments were the commercial earth Pure-Flo®B80 (Oil:Dri Corporation of America), named here B80, and activated carbon produced from the Macauba endocarp in powdered and granular forms. B80 adsorbent is clarifier activated naturally through physical processes, suitable for different types of oils, being composed of a hybrid of hormita and smectite mineral with unique adsorption and filtration characteristics. The activated carbons in granular and powdered form used in this study were produced by chemical activation with ZnCl$_2$ and similar surface area, respectively equal to 419 m$^2$/g and 399.4 m$^2$/g (RIOS, 2015).

Bleaching experiments were carried out in a rotary evaporator at constant speed and under vacuum. In each test, 0.070 kg of neutralized pulp oil was placed into 500 mL flasks and the following procedure was performed: the neutralized pulp oil was heated until the selected temperature. Upon reaching the required temperature, the vacuum was stopped and the adsorbent, previously dried at 110 °C for 3 h, was added. The oil/earth mixture was heated and stirred (60 rpm) in a glycerin bath at selected temperature for 20 minutes. Then, the mixture was centrifuged at 2000 rpm for 15 min and the bleached oil was collected from the supernatant. Until analyzes, the bleached oil was stored in dark bottles in a refrigerator at 4 °C.

2.2. Experimental design

A $2^2$ full factorial design was used to identify the relationship existing between temperature and commercial adsorbent amount in the oil bleaching as well as to determine condition to get the best bleaching capacity without affecting oil quality. The coded values for the levels -1, 0, 1, -α and α chosen for bleaching process are present in Table 1. The α value was calculated from the equation $\alpha = (2^2)^{1/4}$. On this stage it was only used the commercial adsorbent B80. Temperatures and the mass of adsorbent, as well as the time of the process were chosen according to data collected in the literature. The only study about Macauba oil refining (Nunes et al. 2015) indicates that the optimum amount of adsorbent is 10%, however several studies on bleaching of other vegetable oils indicates lower values, which allows to evaluate the effect of smaller adsorbent amounts. Following the guidance of Didi et al. (2009), who reported that the contact time between the oil and the bleaching earth should not exceed 20 minutes at 100 °C to prevent unwanted reactions, in this work, it was decided to fix the contact time at 20 min.

<table>
<thead>
<tr>
<th>Parameter / levels</th>
<th>-1.41</th>
<th>-1</th>
<th>0</th>
<th>+1</th>
<th>+1.41</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C) = $X_1$</td>
<td>75.9</td>
<td>80</td>
<td>90</td>
<td>100</td>
<td>104.1</td>
</tr>
<tr>
<td>Adsorbent amout (%) = $X_2$</td>
<td>0.36</td>
<td>2</td>
<td>6</td>
<td>10</td>
<td>11.64</td>
</tr>
</tbody>
</table>
The dependent variables (responses) were the acid value and the bleaching capacity. A quadratic polynomial model was proposed for each variable response, as shown in Equation 1.

\[
Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{12} X_1 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 
\]  

(1)

where \( Y \) is the dependent variable, \( X_1 \) and \( X_2 \) are the coded independent variables, \( \beta_0 \) is the constant, \( \beta_1 \) and \( \beta_2 \) are the linear coefficient, \( \beta_{11} \) and \( \beta_{22} \) are the quadratic coefficient, and \( \beta_{12} \) is the interaction coefficient.

All experimental data regression was performed with analysis of variance (ANOVA) and the accuracy and general ability of the above polynomial model was evaluated by the coefficient of determination (\( R^2 \)), using for this the Statistica 7.0 software (StatSoft Inc, Tulsa, Oklahoma, USA).

The oil acid value (acidity index) was determined by titration according to the rules of AOCS, Cd 3-63 method. The color changes in the treated oils were evaluated by the total carotenoid content, determined by spectrophotometry (equipment model E-225D, Celm), diluting oil with spectrophotometric grade hexane and reading the absorbance at 450 nm (Rodriguez-Amaya and Kimura, 2004). For this purpose, the bleaching capacity was determined by the Equation 2.

\[
\text{Bleaching capacity (\%)} = (\text{C}_0 - \text{C}) \times 100 / \text{C}_0 
\]

(2)

where \( \text{C}_0 \) is the concentration (µg/g) of total carotenoid content in the neutralized oil and \( \text{C} \) is concentration (µg/g) of total carotenoid in the bleached oil.

## 2.3. Activated carbon effect used as adsorbent

To evaluate the effect of the use of activated carbon produced from the Macauba endocarp in the pulp oil bleaching, it was used the experimental design condition that reached the highest bleaching capacity (90 °C and 6% of adsorbent). In this step it was used mixtures of commercial adsorbent and activated carbon, with the ratio of the activated carbon ranging between 5 and 100% of the total mass of the adsorbent, but keeping the total amount of adsorbent equal to 6% of the oil mass. After bleaching, the mixture was centrifuged for 30 min and the supernatant oil was filtered. Only in the tests which were used 100 and 50% pulverized activated carbon, the oil was filtered twice.

The effect of the use of activated carbon was also evaluated through of both properties: oil acid value and bleaching capacity.

## 2.4. Oil characterization during refining steps

Samples of crude oil and oils after all refining steps were characterized as acid value (expressed in mg KOH/g and % acid oleic), total carotenoid content by spectrophotometry and phosphorus content. The phosphorus content was expressed by the total phosphorus, measured using an Inductively Coupled Plasma (ICP) according to the ASTM D5185.
2.5. Statistical analysis

All analyses in the oils were performed in triplicate, except to the phosphorus content that were made in duplicate. The results were subjected to analysis of variance (ANOVA) and differences between the means were evaluated by the Tukey test at 5% probability using the software Minitab, version 16.

3. RESULTS AND DISCUSSION

3.1. Experimental design

The experimental results were shown in Table 2. The results indicate a considerable variation in the bleaching capacity under different process conditions. The highest values of the bleaching efficiency, around 84%, were obtained in the central point region, where the temperature was equal to 90 °C. Regarding acidity index response, the results indicate that the bleaching process using the adsorbent B80 presented no negative effect of raising the oil acidity. The acid index of the oil after neutralization was 0.29 mg KOH/g and the values obtained after the bleaching was in the range between 0.19 and 0.27 mg KOH/g, with the minimum value obtained in test 5 where it used the lowest temperature (75.9 ºC) and an intermediate amount of adsorbent. It is noteworthy that the central point for both answers showed little variation, indicating good process repeatability.

Table 2 - Experimental design results.

<table>
<thead>
<tr>
<th>Test</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>$Y_1$ (mg KOH/g)</th>
<th>$Y_2$ (%)</th>
<th>Predicted $Y_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>0.25 ± 0.02</td>
<td>51.04 ± 0.15</td>
<td>52.86</td>
</tr>
<tr>
<td>2</td>
<td>+1</td>
<td>-1</td>
<td>0.27 ± 0.02</td>
<td>72.54 ± 0.06</td>
<td>52.86</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>+1</td>
<td>0.24 ± 0.02</td>
<td>76.03 ± 0.65</td>
<td>79.23</td>
</tr>
<tr>
<td>4</td>
<td>+1</td>
<td>+1</td>
<td>0.24 ± 0.02</td>
<td>77.15 ± 0.33</td>
<td>79.23</td>
</tr>
<tr>
<td>5</td>
<td>-1.41</td>
<td>0</td>
<td>0.19 ± 3E-4</td>
<td>82.18 ± 0.93</td>
<td>84.70</td>
</tr>
<tr>
<td>6</td>
<td>+1.41</td>
<td>0</td>
<td>0.21 ± 0.02</td>
<td>82.79 ± 0.19</td>
<td>84.70</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>-1.41</td>
<td>0.24 ± 0.02</td>
<td>17.43 ± 0.84</td>
<td>29.03</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>+1.41</td>
<td>0.20 ± 0.02</td>
<td>71.07 ± 0.26</td>
<td>66.20</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0.27 ± 0.02</td>
<td>83.88 ± 0.54</td>
<td>84.70</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>0.25 ± 0.02</td>
<td>84.04 ± 0.46</td>
<td>84.70</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0.23 ± 2.E-4</td>
<td>84.31 ± 0.35</td>
<td>84.70</td>
</tr>
</tbody>
</table>

$X_1$ = temperature (°C); $X_2$ = the total commercial adsorbent/oil ratio (wt%); $Y_1$ = Acidity index (mg KOH/g); $Y_2$ = Bleaching capacity (%).

The statistical analysis results allowed to determinate the coefficients regression, as showed in Table 3, and the establishment of the equations that represent the models for each response. For the acidity index, no linear coefficient, quadratic or interaction between variables were statistically significant ($p < 0.05$), i.e. it was not possible to fit a model and generate surface for the response acidity index as a function of these variables. As there is little variation in the repetitions of the central point (Table 2), the non-significant coefficients...
only indicates that the temperature and the amount of adsorbent did not affect the values of acidity index in the bleached oil. Regarding bleaching capacity, the only statistically significant parameter (p<0.05) was the amount of adsorbent (linear and quadratic coefficient). Neither the temperature nor the interactions between the two variables affect this response.

**Table 3 - Coded second-order regression coefficients.**

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Bleaching capacity (%)</th>
<th>Acidity index (mg kOH/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mean</td>
<td>84.08</td>
<td>0.25</td>
</tr>
<tr>
<td>T (L)</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>T (Q)</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>% Ad (L)</td>
<td>13.18</td>
<td>NS</td>
</tr>
<tr>
<td>% Ad (Q)</td>
<td>-18.45</td>
<td>NS</td>
</tr>
<tr>
<td>T x %Ad</td>
<td>NS</td>
<td>NS</td>
</tr>
</tbody>
</table>

T: Temperature; % Ad = amount of adsorbent; L = linear; Q = quadratic; NS: non-significant (p>0.05)

The proposed model for bleaching capacity with the variables coded taking into account only the significant coefficients is shown in Equation 3:

\[ Y_2 = 84.70 + 13.18x_2 - 18.65x_2^2 \]

Table 4 presents the analysis of variance (ANOVA) for response bleaching capacity, as suggested by Rodrigues and Iemma (2005). The proposed model was statistically significant at 95% confidence level: the correlation coefficient (R²) was 86.14%; the F calculated was higher than F table and the calculated probability value (p-value) was 0.0004. Figure 1 shows the experimental Y-values versus the values predicted by the equation developed, observing a good agreement between them.

**Table 4 – Analysis of variances for bleaching capacity.**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Sum of Squares</th>
<th>Mean square</th>
<th>F calculated</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
<td>2</td>
<td>3540.767</td>
<td>1770.384</td>
<td>24.86</td>
<td>0.0004</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>569.774</td>
<td>71.222</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>10</td>
<td>4110.541</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

R²(%) = 86.14 e F₂,₈,0.05 = 4.46.

Figure 2 contains the surface response for the bleaching capacity. Values greater than 80% was observed in a range of quantity of adsorbent between 6 and 10% for any temperature between of 75.9 to 104.1 °C. This result indicates that it is possible to obtain high values of bleaching capacity with temperatures around 80 °C that provides an energy saving in the process. In the present study the highest efficiency (84%) was obtained for the concentration of 6%, a lower value when compared with the 10% value reported by Nunes et
al. (2015). It is noteworthy that the largest concentrations of earth, besides representing a higher cost to the process, can also result in a greater loss of oil. According to Souza (2002), bleaching earths retains oil in the amount of 20 to 35% of its mass.

### 3.2. Activated carbon effect used as adsorbent

Table 5 shows the results of acid value and bleaching capacity of each test measured after centrifugation and filtration steps. The assay in which was used only powdered activated carbon achieved a lower capacity bleaching (5.88%). In all other tests, the bleaching capacity resulted in higher values (88.32% to 94.76%) compared with the ones obtained when only commercial earth B80 was used. The activated carbon effect as bleaching agent depends on four factors that will play an essential role: the type of raw material (in this case was Macauba endocarp), the activation process, surface properties and porosity and chemical characteristics (Omar et al., 2003). According to the same author, the activated carbon is highly selective for phospholipids, leaving the free adsorption sites for the adsorption of pigments.
### Table 5 - Acidity index and bleaching capacity after bleaching with a mixture of commercial adsorbent and activated carbon.

<table>
<thead>
<tr>
<th>Test</th>
<th>Adsorbent</th>
<th>Acidity index (mg KOH/g)</th>
<th>Bleaching capacity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>B80</td>
<td>0.23&lt;sup&gt;bc&lt;/sup&gt; ± 2.E-04</td>
<td>84.31° ± 0.35</td>
</tr>
<tr>
<td>12</td>
<td>100% AC powered</td>
<td>0.26&lt;sup&gt;a&lt;/sup&gt; ± 4.E-04</td>
<td>5.88&lt;sup&gt;e&lt;/sup&gt; ± 0.23</td>
</tr>
<tr>
<td>13</td>
<td>50% AC powered</td>
<td>0.19&lt;sup&gt;d&lt;/sup&gt; ± 1.E-03</td>
<td>88.32&lt;sup&gt;d&lt;/sup&gt; ± 0.32</td>
</tr>
<tr>
<td>14</td>
<td>10% AC powered</td>
<td>0.25&lt;sup&gt;ab&lt;/sup&gt; ± 3.E-02</td>
<td>94.12&lt;sup&gt;ab&lt;/sup&gt; ± 0.29</td>
</tr>
<tr>
<td>15</td>
<td>5% AC powered</td>
<td>0.19&lt;sup&gt;d&lt;/sup&gt; ± 1.E-03</td>
<td>94.76&lt;sup&gt;a&lt;/sup&gt; ± 0.27</td>
</tr>
<tr>
<td>16</td>
<td>50% AC granulated</td>
<td>0.23&lt;sup&gt;bc&lt;/sup&gt; ± 1.E-03</td>
<td>90.16&lt;sup&gt;c&lt;/sup&gt; ± 0.53</td>
</tr>
<tr>
<td>17</td>
<td>10% AC granulated</td>
<td>0.20&lt;sup&gt;cd&lt;/sup&gt; ± 2.E-02</td>
<td>93.96&lt;sup&gt;ab&lt;/sup&gt; ± 0.05</td>
</tr>
<tr>
<td>18</td>
<td>5% AC granulated</td>
<td>0.26&lt;sup&gt;a&lt;/sup&gt; ± 3.E-04</td>
<td>92.98&lt;sup&gt;b&lt;/sup&gt; ± 2.E-04</td>
</tr>
</tbody>
</table>

% AC = amount of activated carbon in relation to the total mass of adsorbent with the total adsorbent/oil ratio (wt %) equal to 6%. Values are expressed as the mean ± standard deviation. Means, in the same column, followed by the same letters do not differ by Tukey test (p<0.05).

The bleaching capacity achieved by mixing commercial adsorbent and activated carbon containing 10% and 5% of powdered activated carbon no differ statistically (p<0.05). These results indicate that the use of only 5% of this activated carbon, in relation with the total mixture of adsorbent, is enough for removing carotenoids around 94%. The same behavior was observed when it was employed 10% and 5% of granular activated carbon, but only bleaching capacity obtained for the concentration of 10% granular carbon can be considered equal to that achieved with 10% and 5% powdered activated carbon. Considering the same surface area of both activated carbons and also the higher ease of the filtration process when using granular activated carbon this would be recommended for an industrial application situation.

It cannot be established any relationship between the amounts of activated carbon and oil acidity index (Table 5). The same result was observed in the experimental design, where the amount of commercial adsorbent used did not affect this response. There was a small variation in the oil acidity index of 0.19 until 0.26 mg KOH/g, which correspond respectively to 0.095 until 0.13% of oleic acid.

#### 3.3. Oil characterization during refining steps

The crude oil characteristics and after degumming, neutralization and the best conditions of bleaching are shown in Table 6. The crude oil acidity index was equal to 4.11 mg KOH/g, corresponding to 2.06% of oleic acid. The values found in the literature for Macauba crude oil vary significantly, mainly due to the degree of ripeness and storage time before oil extraction. The acidity index obtained in this study was similar to that found by Ferrari and Azevedo Filho (2012) who obtained acidity of 2.10%. However, in different pulp oil samples extracted from fruits stored for 3-6 months, Navarro-Díaz et al. (2014) found elevated values, ranging from 37.4 to 65.4% free fatty acids. According to the Technical Regulation for vegetable oils, vegetable fats and cream (RDC no270 of September 22th 2005) the maximum amount of acid value allowed for cold pressed oils and unrefined is 4.0 mg KOH/g (ANVISA, 2005). Therefore, the oil of this work exceeded this limit, indicating
the need to carry out the refining process for food use.

<table>
<thead>
<tr>
<th>Refining steps</th>
<th>Acidity index (mg KOH/g)</th>
<th>% oleic acid</th>
<th>Phosphorus content (mg/kg)</th>
<th>Carotenoid content (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude oil</td>
<td>4.11 ± 4.6 ± 4.02</td>
<td>2.06 ± 0.02</td>
<td>82.55 ± 1.91</td>
<td>111.28 ± 0.21</td>
</tr>
<tr>
<td>Degumming</td>
<td>3.55 ± 8.6 ± 0.02</td>
<td>1.78 ± 0.04</td>
<td>53.20 ± 1.98</td>
<td>39.36 ± 0.19</td>
</tr>
<tr>
<td>Neutralization</td>
<td>0.29 ± 2.6 ± 0.02</td>
<td>0.14 ± 0.01</td>
<td>23.35 ± 0.21</td>
<td>35.43 ± 0.16</td>
</tr>
<tr>
<td>Bleaching 1</td>
<td>0.23 ± 2.6 ± 0.04</td>
<td>0.11 ± 1.6 ± 0.04</td>
<td>14.85 ± 0.50</td>
<td>5.56 ± 0.12</td>
</tr>
<tr>
<td>Bleaching 2</td>
<td>0.19 ± 1.6 ± 0.03</td>
<td>0.09 ± 1.6 ± 0.03</td>
<td>11.59 ± 0.06</td>
<td>1.86 ± 0.10</td>
</tr>
<tr>
<td>Bleaching 3</td>
<td>0.20 ± 3.6 ± 0.02</td>
<td>0.09 ± 1.6 ± 0.04</td>
<td>ND</td>
<td>2.14 ± 0.02</td>
</tr>
</tbody>
</table>

1 test using only 6% commercial adsorbent; 2 test using 6% of mixtures of commercial adsorbent and activated carbon, with 5% of powdered activated carbon; 3 test using 6% of mixtures of commercial adsorbent and activated carbon, with 10% of granular activated carbon; ND = not determinated; Values are expressed as the mean ± standard deviation.

During the refining process it was observed a significant reduction in the acidity index, particularly in the neutralization stage. The neutralization process promotes the removal of free fatty acids by the addition of alkali (sodium hydroxide solution), which in contact with the free fatty acids form sodium salts (soap), removed by centrifugation. There was also a reduction in the acid value with the bleaching. The maximum acid value permitted by ANVISA (2005) for refined oils and fats (except olive oil) is 0.6 mg KOH/g, so the refined oil obtained in this work fits the standards required by Brazilian legislation.

The control of the phospholipid content is crucial to ensure the oil stability during storage. These constituents must be removed because they are prone to hydrolysis and also may precipitate during storage (Vaisali et al., 2015). Phospholipid content can be indirectly measured by quantification of phosphorus expressed in mg/kg. In this work, the phosphorus content in the crude oil (82.55 mg/kg) was higher than those found by Ferrari and Azevedo Filho (2012) who obtained values of 14.6 mg/kg.

The phospholipids composition in the Macauba pulp oil is not yet established. In this work was performed aqueous degumming, a simpler method that eliminates only hydratable phospholipids. After the degumming step the phosphorus content decreased of 35.4%, a result that indicates that the water degumming process was not efficient in the removal of all phosphorus or phospholipids content. Further studies should be done by assessing parameters such as the amount of water added and the process temperature or even to identify the need to perform the acid degumming to removal of the hydrophobic phospholipids.

However, it was observed that with the neutralization step there was a phosphorus removal of approximately 56%, indicating that some of the non-hydratable phospholipids were removed during the neutralization of free fatty acids. According to Morais et al. (2012) in terms of cost-effective parameters, it is advisable treat the oil by water degumming
technique, since the neutralization of free fatty acids have been done with the consequent removal of hydrophobic phospholipids in draff. Further, the phosphorus content after the bleaching process using a mixture of commercial adsorbent and powered activated carbon (11.59 mg/kg) was lower than the one obtained when it was used only commercial adsorbent (14.85 mg/kg), indicating a higher affinity of the activated carbon with the phospholipids. This beneficial characteristic of activated carbon was previously described in this work.

The carotenoid content in crude oil (111.28 µg/g) was lower than the one that was found by Nunes et al. (2015) who obtained values of 378.0 µg/g. However, Pereira et al. (2009) found values of 117, 120, 173 and 283 ppm for oils extracted from different Macauba genotypes in the Minas Gerais state. The lowest amount of carotenoids found in this study may be associated to the drying treatment carried out for the oil extraction, since carotenoids are sensitive substances to temperature and light, as well as easily oxidized in the presence of oxygen. Other factor that can cause this difference in the quantification of total carotenoids is the regional variability. According Ciconini (2012), total carotenoids determined in Macauba pulp oil from fruits of different biomes in Brazil showed high variability intra and inter-regional with average values between 312.34 to 425.50 µg/g.

The degumming process removes a certain amount of oil pigments and the neutralization with alkali also displays a whitening effect due to chemical coagulation (Oeterrer et al., 2006). In this work it was noted that the degumming process promoted a reduction of about 64.3% in total carotenoids. The neutralization step also promoted a slight reduction in carotenoid content, resulting in the amount of 35.43 µg/g. Table 6 shows that the use a mixture of commercial adsorbent and activated carbon, in its two forms, promoted greater removal of carotenoids.

4. CONCLUSION

The refining process of Macauba pulp oil was efficient in the removal of free fatty acids, with values below the limit required by Brazilian legislation. This result is very promising, taking into consideration that Macauba fruits are still obtained through extractivism often generating oils with high levels of acidity. Although degumming stage has not been efficient for phosphorus removal, the posterior steps provided a significant reduction of the initial phosphorus content. The interaction of activated carbon with commercial adsorbent during the bleaching promoted increased phosphorus removal compared with the use of only commercial adsorbent. Therefore, the use of mixtures containing activated carbon from Macauba endocarp can be recommended for the refining of oils with high phospholipids content. Besides, the use of the mixture with commercial adsorbent and activated carbon also promoted greater bleaching capacity if compared to the bleaching process that utilizes only commercial adsorbent.

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CLARIFICAÇÃO DO ÓLEO DA POLPA DA MACAÚBA USANDO ADSORVENTE COMERCIAL E CARVÃO ATIVADO PRODUZIDO DO ENDOCARPO DO PRÓPRIO FRUTO

RESUMO: O Macauba (Acrocomia aculeata) é uma fonte promissora de óleo vegetal com capacidade de produção de até 5000 kg /ha. O processo de refino é essencial, não só para a remoção de impurezas que reduz a qualidade do óleo, bem como para fornecer ao consumidor uma cor mais apreciada. O objetivo deste estudo foi desenvolver o refino de óleo da polpa Macauba com o foco na fase de clarificação, onde foi investigado o efeito da temperatura e da quantidade de adsorvente comercial. Além disso, avaliou-se o uso de carvão ativado produzido a partir do endocarpo de Macauba como um substituto parcial econômico de adsorventes. A utilização de 6% adsorvente comercial a 90 ºC promoveu uma capacidade de branqueamento de cerca de 84%. A utilização de uma mistura adsorvente comercial e carbono ativado promoveu uma maior capacidade de branqueamento (acima de 90%) e aumentou a remoção de fosfolípidos.

PALAVRAS-CHAVE: Refino de óleos, clarificação, óleo da polpa da macaúba, Acrocomia aculeata, carvão ativado.