Dyeing of matrinxã (*Brycon amazonicus*, Spix Agassiz) leather with pigments from crajiru (*Arrabidaea chica* Verlot) leaves

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ABSTRACT

Natural dyes made from fruit peels, seeds, flowers and other parts of the plant, which preserve the Amazonian flora and are not harmful to health and the environment, can be used as an alternative for dyeing fish leather. The objective of this work was to evaluate the use of dye from the leaves of the crajiru (*Arrabidaea chica* Verlot) in the dyeing of matrinxã leather (*Brycon amazonicus*, Spix Agassiz). Crajiru leaves were oven dried at 65 ºC, ground and evaluated for moisture, dry matter, phenolic compounds, water-soluble pigments and pH. Aqueous solution of leaves (dry and ground) in proportions of 5, 10 and 15% (w/v) were used in the dyeing of matrinxã leather. After dyeing and finishing, the leather samples were evaluated for coloration, scanning electron microscopy, lightfastness and washability test. The dye showed resistance to the action of light (fluorescent and solar) and water. Due to the proportion of the dye, the color varied from red-purple to wine. Although there was no statistical difference between the proportions of 10 and 15%, the highest concentration (15%) resulted in a more intense coloration. Under the conditions and proportions adopted, both proved to be adequate. The choice of proportion depends on the desired color, shade and availability of crajiru. Therefore, crajiru can be an excellent source of natural coloring, since in the Amazon this plant is quite common, easy to grow and has a rapid growth cycle.

**Keywords:** Fish Residue, Chica Cricket-Vine, Dyeing, Lightfastness, Washability.
INTRODUCTION

Since the dawn of civilizations, man has tried to reproduce the colors present in the world, seeking the necessary elements in nature (Ferreira, 1998). Dyeing with vegetable dyes is an ancient practice. In Brazil, the production of dyes has been around since its discovery, mainly motivated by the Pau Brazil wood, from which deep red colored pigments were extracted (Dallogo & Smaniotto, 2005).

Currently, around 10,000 synthetic dyes are produced on an industrial scale, of which 2,000 are available for the textile industry. In Brazil, the textile industries consume around 20 t year-1 annually. Of this total, 20% is disposed of as effluents (Guaratini & Zanoni, 2000). From an environmental point of view, the removal of these dyes from effluents is one of the major problems faced by the textile sector. Due to the risks synthetic dyes can cause, those of vegetable origin have been gaining market share in recent years, especially in the food and beverage industries, encouraging the global trend of consumption of natural products (Constante et al., 2002). Despite this, it is estimated that only 0.5% of terrestrial plants are exploited as sources of vegetable dyes (Ferreira, 1998).

Dye extraction techniques vary depending on the type of plant and the composition of the product to be dyed. The dyeing process is one of the fundamental factors in the commercial success of products. In addition to the standardization and beauty of the color, the consumer usually requires some basic characteristics of the product, such as a high degree of fixation in relation to light and washing (Ferreira, 1998; Guaratini & Zanoni, 2000). In Brazil, there is a great diversity of native plants as potential sources of natural dyes (Ferreira, 1998). Crajiru (Arrabidaea chica Verlot) is a species of the Bignoniaceae family, occurring naturally from southern Mexico to southern Brazil (Bobbio et al., 1984). This plant is made up of colored, polar substances called deoxyanthocyanins and 3-Desoxyanthocyanidins (Zorn, et al., 2001), similar to the anthocyanins found in leaves, flowers and fruits. Because it is fast growing and easy to plant, it is widely cultivated in the Amazon (Oliveira, 2001). Due to its biological properties, this plant has been used as a dye in the cosmetics industry, and in home medicine as an anti-inflammatory, astringent and in the treatment of iron deficiency anemia. The crajiru (Arrabidaea chica), is also known as: chica, carajuru, cajuru, oajuru, paripari, pariri, puca panga, piranga, cipó-pau, cipó-cruz and chica cricket-vine (Oliveira, 2001; Lorenzi & Matos, 2002).

Because it is exotic, innovative, basic to the leather artifacts industry, and has acceptability in specific market niches, tanning fish skin is a tool that adds value (Ingram & Dixon, 1994). The skin has resistance, by protective coverslips on insertion, resulting after tanning, in leather with a typical appearance, difficult to imitate, guaranteeing an exclusive pattern with a high visual impact (Almeida, 1998; Adeodato, 1995; Souza et al., 2003). Honczaryk (1994),
Melo et al. (2009) and Pizango-Paima et al. (2001) report that matrinxã reaches 4 to 5 kg (adult stage), has wide distribution (Central and South America) and potential for commercial exploitation, due to its easy adaptation to food, high growth rate, wide food spectrum, and tolerance to high creation density.

**OBJECTIVE**

Considering the biotechnological potential, and the environmental benefit of the combination of technologies, the use of fish residue for tanning with the use of natural dye for dyeing, this study aimed to evaluate the use of crajiru dye in the dyeing of matrinxã leather.

**MATERIAL AND METHODS**

**Obtaining and physical-chemical analysis of crajiru leaves**

After being collected on Campus III (V-8) of the Instituto Nacional de Pesquisas da Amazônia (INPA), the crajiru leaves were dried in an oven (forced air circulation, at a temperature of 65 °C). Then, the sheets were ground in a mill (Tecnal® brand, mod WILLE PE 680), packed in medium density plastic bags and stored at a temperature of 23 °C, without light. In this study, the matrinxã skins consisted of filleting residue with an average size of 25cm. For greater conservation, before being washed, salted and stored in the freezer, the skins were carefully treated, removing meat residues still attached to them.

Moisture content was determined by weight loss in an oven regulated at 105 °C, until constant weight was obtained, and dry matter by difference. The pH of the supernatant was determined using a pH meter, brand Labmeter®, and model, PHS-3B, with the addition of distilled water at a ratio of 1:2. (Instituto Adolfo Lutz, 1985). The water-soluble pigments were evaluated according to Melo et al. (2006), with modifications, mixing 1.0 g of vegetable sample in 25 mL of distilled water. After one hour of rest, the material was filtered, measuring the volume to 50 mL, centrifuging it (6000 rpm for 15 minutes) at room temperature. The results obtained at 450 nm were expressed in absorbance units.

Phenolic compounds were determined according to the methods described by Goldstein & Swain (1963). For the determination, pure methanol, 50% methanol and water (1:5 w/v) extractors were used, according to the Folin Denis method (Cliffe et al., 1994). The resulting color was measured using a UV-VIS spectrophotometer, mod. Meter, at 760 nm. The standard curve was made with tannic acid at concentrations ranging from 20 to 100 µg mL⁻¹, and the blank with distilled water. The concentration of total phenolic compounds was expressed in mg 100 g⁻¹ of dry matter.
Skin tanning processes

In these processes, the methodology used was the traditional one for skins of large animals (adapted from MELO, 2007). The steps of the tanning process were: In the soaking process, the skins were immersed in a solution of 200% water, 0.5% surfactant (eusapon BR®), 10% bactericide (preventol WB®) and 10% kelp (carbonate sodium). After 4 hours, the solution was exhausted and the skins were placed in the drum. For degreasing, 1:200 of water and 1% of surfactant (eusapon BR®) were used for 30 minutes (8 rpm). Afterwards, the skins were exhausted and washed. In the lime, 1:200 of water, 20% of common salt, 10% of surfactant (eusapon BR®), 10% of ash (“barrilha”) and 10% of hydrated lime (calcium hydroxide) were used for 4 hours, with constant agitation. Then, a solution of Koramin MK® (5%) was added for 2 hours. After this period, the drum was turned off and the skins remained immersed in the same solution for 12 hours. The next day, upon verifying that the epidermal layer (the scales) had been completely eliminated, the bath was drained. In deliming, 1:200 of water and 2% of ammonium sulphate were used (movement in the drum at 8 rpm) for 40 minutes. Then, a solution of 0.25% batan 100® (proteolytic enzyme) was added, followed by stirring for 30 minutes. This was repeated with the inclusion of 0.36% formic acid with stirring for 40 minutes until pH 7.0. The skins were exhausted and washed in running water. In the pickle of the drum, the skins were shaken for ten minutes at a ratio of 1:100 of water, 8% of sodium chloride and 10% of calcium formate. Subsequently, 1.5% sulfuric acid was added and the movement proceeded for 2 hours. The evaluation of acid penetration into the skin was performed through cross-sections and with the addition of the green indicator of bromocresol. At the end of this period, the drum was turned off and the skins remained immersed in the solution for 12 hours. For the tanning, 8% of chromosal mineral tanning agent B® and 3% of implenal UR® were added. In this solution, the skins were moved for 2 hours. For neutralization, solutions of 1.7% of ash and 1:20 of water were added to the hides, added four times at intervals of ten minutes during 2 hours, until pH 4.5. After the boiling test, the hides remained in the solutions for another 12 hours. The next day, the hides were removed from the drum, stacked in a plastic tray and covered with a moistened cloth for 24 hours. In retanning, 1:200 of water at 40 °C, 3.5% of syncotan wsb® and 0.7% of grassan ES® were applied, under agitation for 30 minutes. 3.5% syncotan wsb®, 0.7% grassan ES® and 3.5% syntac FL® (stirring for 1 hour) were added. Then, 3.5% syncotan wsb®, 0.7% grassan ES® and 3.5% syntac FL® were added, followed by stirring for 1 hour and 20 minutes. After this time, it was drained and washed with running water. For fatliquoring, the hides were transferred to a drum containing 1:200 of water at 50 °C, 4.5% of SLW® and 2.3% of BZN®. After 1 hour of stirring, 1.5% MK® fixative and 7.5% of water were added, followed by stirring for 1 hour. After exhaustion and washing, the leather samples were stacked in a plastic tray and kept...
at rest for 24 hours. Finally, for drying the leather samples were attached to nylon ropes in a protected and ventilated place.

**Leather dyeing**

The dyeing of crajiru leaves was carried out at concentrations of 5, 10 and 15%, with monitoring of pH, temperature and relative humidity. The previously weighed hides were immersed in a water solution at 40 °C (1:20), remaining at rest for 24 hours. Afterwards, 1% formic acid was added for 2 hours. After dyeing, drying was carried out at room temperature.

**Coloring and light resistance**

The experiments on resistance to fluorescent and sunlight were carried out based on the work of Ferreira (1998), with modifications. The dyed and unfinished leathers (application of water-based lacquer) were cut (2.5 x 5.0 cm) and the samples of each treatment (5, 10 and 15%) were divided into two parts, half wrapped in carbon paper and the other without the paper. Unfinished leather samples were incubated in a dark room, adapted on the laboratory counter. The fluorescent lamp (Portable Light Box®, model LB 101) was fixed on top of the chamber with a distance (height) of 27 cm, with the leather samples remaining in the cabin for 84 hours in the presence of light. Light intensity was measured with the aid of a porometer (Steady State Porometer®, mod LI – 1600). At the end of the exposure, a visual assessment of the difference in color was evaluated.

For resistance to sunlight, leathers with lacquer finish were used, in plastic trays (30 x 60 cm) covered with white paper. The hides were exposed to the sun from 8:00 to 16:00 h, for one week. Light intensity was determined as mentioned above. During the experiment, readings were taken in the morning, at noon and in the afternoon, in the four corners and in the central part of the tray. At the end of each day, a daily average was obtained and at the end of the seven days, an overall average of light incidence on the hides. At the same time, the temperature and relative humidity of the exhibition site were monitored. After this step, samples were evaluated for coloration using a portable colorimeter (mod Micromatch Plus®), developed by Judd and Hunter (Hunter, 1975). Calibration was performed prior to black and white standard readings.

**WATER RESISTANCE**

For this study, the methodology described by Ferreira (1998) was adopted, with modifications, using, in triplicate, 1.0 cm² of leather without lacquer finish. The leather samples were immersed in 10 mL of distilled water, resting for six hours at a temperature of 23±1
°C. After this period, the material was filtered and the absorbance read at 535 nm. After the readings, 10 mL of acidified alcohol was added to the filtered material, followed by rest (two hours) and another reading. The results obtained were compared with those recorded in the absence (before adding) of acidified alcohol. Microscopic analysis was performed to verify the collagen fibers of the leathers. For this, pieces of leather samples were mounted on a support and electron-micrographed in a Scanning Electron Microscope (mod MEV-LEO® 435 VP).

**Statistical analysis**

The data obtained were evaluated by ANOVA, with the significant treatments being compared by the Tukey test, at 5%. All analyzes were processed in triplicate, using the statistical program ASSISTAT version 7.4 beta (Silva & Azevedo, 2006).

**RESULTS AND DISCUSSION**

The drying of leaf samples facilitated the analysis of quantification, use in dyeing, in addition to reducing weight and volume, also facilitating packaging and storage. In this study, the moisture and dry matter contents were 6.7 and 93.3%, respectively. As for the water-soluble pigments, an average absorbance of 1.9 was noted, with a pH of 5.6. In turn, the concentration of phenolic compounds varied between the different extractors. The most efficient extraction was obtained with 50% methanol, as it is constituted by intermediate molecular weight compounds (Goldstein & Swain, 1963) that are soluble in both water and organic solvent (Table 1).

The skinning and brine treatments allowed the storage of the skins for later use. In the soaking stage, the skins obtained complete and uniform hydration, with the fibers showing the appearance of fresh skin. Leathers tanned with mineral tanning agent showed a blue (wet-blue) color, with stability of the entire collagen system of the skin, making matrinxã leather flexible and elastic, desirable characteristics in the finished product. The retanning and grease operations resulted in a softer and more resistant leather. After transforming the skin into leather, it was found that the natural design of the lamella insertion of the scales had no changes that devalued the leather, presenting a pattern that resembles a mosaic (Souza et al, 2006).
Table 1. Physicochemical characteristics of crajiru (*Arrabidaea chica* Verlot) leaf samples.

<table>
<thead>
<tr>
<th>Constituents in crajiru leaves</th>
<th>Quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)</td>
<td>6.7±1.2</td>
</tr>
<tr>
<td>Dry matter (%)</td>
<td>93.3±1.2</td>
</tr>
<tr>
<td>pH</td>
<td>5.7</td>
</tr>
<tr>
<td>Water-soluble pigments (absorbance units)</td>
<td>1.9</td>
</tr>
<tr>
<td>Phenolics extracted with water (mg%, in dry matter)</td>
<td>83.5</td>
</tr>
<tr>
<td>Phenolics extracted with 50% methanol (mg%, in dry matter)</td>
<td>105.3</td>
</tr>
<tr>
<td>Phenolics extracted with methanol (mg%, in dry matter)</td>
<td>71.6</td>
</tr>
</tbody>
</table>

Electron microscopy revealed that in matrinxã skin the thickness of the fiber layers increases as it approaches the hypodermis (Figure 1). This is because the dermis is composed of overlapping layers of collagen fiber bundles, which are thinner and closer to the epidermis, and it increases in thickness as it moves away from it (Souza et al., 2006).

**Figure 1.** Increased thickness of collagen fibers in the leather of matrinxã (*Brycon amazonicus*, Spix Agassiz) as it approaches the hypodermis.

**Leather dyeing**

The dyeing treatments resulted in shades ranging from red-purple to wine, as a function of the increase in dye concentration (Figure 2). The drying process was important, as it favored the elimination of water that was not chemically combined with the leather, thus providing color stabilization. The values of temperature and relative humidity of the air were 34.25 °C and 64.5% respectively.

In the dyeing process without constant movement, leathers dyed with 5% showed less uniformity in coverage. The water used in the dyeing stage (without chlorine and coming from the artesian well on the INPA Campus) presented a pH of 6.4, decreasing to 5.7 with the addition of the dye (Table 1). The pH of the solution also decreased during the process. This reduction is due to the sulfuric acid residue applied during the tanning process (Table 2).
Color stability

In the darkroom experiment, the leather samples did not show visual differences in color when compared to covered and uncovered ones. However, the same behavior did not occur in the presence of sunlight, when exposed to an average temperature of 31.7 °C and relative humidity of 74.04%. This is due to the difference in light intensity between the two environments, as the fluorescent light intensity was $21 \mu\text{mol} \times \text{m}^{-2} \times \text{s}^{-1}$, and $1,870 \mu\text{mol} \times \text{m}^{-2} \times \text{s}^{-1}$ for sunlight. Melo et al. (2006) observed that time and luminosity influence the stability of pigments, and that the presence of light reduces the lifetime of the dyes.

Figure 2. Coloring of matrinxã (*Brycon amazonicus*, Spix Agassiz) leather with crajiru (*Arrabidaea chica* Verlot) leaf dye in proportions of 5% (A), 10% (B) and 15% (C).

<table>
<thead>
<tr>
<th>Proportion (%)</th>
<th>Process sequence</th>
<th>When dissolving the dye*</th>
<th>At the beginning of the process**</th>
<th>At the end of the process***</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td></td>
<td>5.7</td>
<td>3.0</td>
<td>2.7</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>5.7</td>
<td>3.1</td>
<td>2.9</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>5.7</td>
<td>3.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* Dye and water; ** Dye, water and leather; *** Dye, water, leather and acid.

There was a significant difference between the samples with and without coverage for the parameters luminosity and chromaticity $a^*$ (Table 3). In the proportions of 10 and 15%, the losses caused by the action of light were greater for the uncoated samples. On the other hand, luminosity did not result in significant variations between the covered samples, regardless of the concentrations evaluated. The same behavior was observed for those without coverage. The presence of the coating allowed for greater stability of the pigment and lower
luminosity, when compared to leather samples exposed to sunlight without coating, in the proportions of 10 and 15% of pigment (Table 3).

In the $a^*$ chromaticity, there was no significant difference for the uncoated leather samples. This can be explained by the non-variation of the hue (red-purple) during exposure to the sun. The same did not occur for the coated samples, with the use of 15% in the dyeing, providing a more intense and stable shade (Table 3).

### Table 3. Effect of dye proportion and luminosity on the color of matrinxã leather (*Brycon amazonicus*, Spix Agassiz).

<table>
<thead>
<tr>
<th>(%)</th>
<th>Coloring</th>
<th>No covered</th>
<th>Covered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$L^*$</td>
<td>$a^*$</td>
<td>$b^*$</td>
</tr>
<tr>
<td>5</td>
<td>39,31±3,16$^{aA}$</td>
<td>16,10±1,14$^{aA}$</td>
<td>11,16±0,89$^{aA}$</td>
</tr>
<tr>
<td>10</td>
<td>27,97±2,86$^{bA}$</td>
<td>15,74±2,48$^{bA}$</td>
<td>6,45±1,48$^{bA}$</td>
</tr>
<tr>
<td>15</td>
<td>29,20±0,42$^{bA}$</td>
<td>18,93±0,50$^{bA}$</td>
<td>5,70±1,50$^{bA}$</td>
</tr>
</tbody>
</table>

Note: The means followed by the same letter do not differ from each other by the Tukey test, at 5%; lowercase averages comparison between columns; capitalized averages comparison between lines.

In $b^*$ chromaticity, there was no significant difference between the samples with and without coating. However, all samples visibly tended to hue changes. For coated leathers, the use of 15% dye provided a purer color when compared to 5% and 10%, demonstrating that the greater the amount of dye, the more stable the color becomes. Among the other pigments, 3-deoxyanthocyanidins from *Arrabidaea chica* were detected (Zorn et al., 2001).

In the washability tests with water and acidified alcohol, the release of pigments from the leathers was not visually observed; however, when the reading (absorbance) of the samples was performed, low values were detected, suggesting the presence of pigments. Although there was no significant variation between washability tests, it was observed that pigment release was proportional to the amount of dye used (Table 4).

### Table 4. Resistance to washability in leather from matrinxã (*Brycon amazonicus*) dyed with crajiru leaves (*Arrabidaea chica* Verlot) in proportions of 5, 10 and 15%.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Crajiru (%)</th>
<th>5</th>
<th>10</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.004a</td>
<td>0.0057a</td>
<td>0.0087a</td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td>0.005a</td>
<td>0.0067a</td>
<td>0.0097a</td>
<td></td>
</tr>
<tr>
<td>Overall average</td>
<td>0.00467</td>
<td>0.00617</td>
<td>0.00917</td>
<td></td>
</tr>
<tr>
<td>DMS</td>
<td>0.00185</td>
<td>0.00131</td>
<td>0.00131</td>
<td></td>
</tr>
<tr>
<td>C.V. (%)</td>
<td>17.50</td>
<td>9.36</td>
<td>6.30</td>
<td></td>
</tr>
</tbody>
</table>

Note: The means followed by the same letter do not differ statistically from each other by the Tukey Test, at 5%. Minimum significant deviation (DMS); Coefficient of variation (CV).
CONCLUSION

When looking for the use of natural dye for the dyeing of fish leather, it was observed that the crajiru leaves presented constituents and behavior of interest for the dyeing of matrinxã leather. Under the experimental conditions adopted, the stains exhibited resistance to the action of light and water. The hue was intensified due to the increase in the dye concentration, with the proportions of 10 and 15% being the most efficient. Depending on the proportion of dye, the color varied from red-purple to wine. Therefore, crajiru can be an excellent source of natural coloring, since in the Amazon this plant is common, easily cultivated and has a rapid growth cycle.

ACKNOWLEDGEMENTS

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REFERENCES


