Ouricuri (*Syagrus coronata*) fiber: a novel biosorbent to remove methylene blue from aqueous solutions

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**ABSTRACT**

In this work, the potential of ouricuri (*Syagrus coronata*) fiber as a novel biosorbent to remove methylene blue (MB) from aqueous solutions was investigated. The fiber was prepared and characterized according to the fundamental features for adsorption. A 2³ experimental design was used to evaluate the effects of adsorbent dosage \((M)\), fiber diameter \((D)\) and agitation \((A)\) on the adsorption capacity. In the more adequate conditions, kinetic and equilibrium studies were performed. The experimental design results showed that \(M = 10 \text{ g L}^{-1}\), \(D = 0.595 \text{ mm}\) and \(A = 200 \text{ rpm}\) were the more adequate conditions for MB adsorption. Based on the kinetic study, it was found that the adsorption process was fast, being the equilibrium was attained at about 5 min, with 90% of color removal. The isotherm was properly represented by the Sips model, and the maximum adsorption capacity was 31.7 mg g\(^{-1}\). In brief, it was demonstrated that ouricuri fiber is an alternative biosorbent to remove MB from aqueous media, taking into account the process efficiency and economic viewpoint.

**Key words** | agro-wastes, color removal, methylene blue, ouricuri

**INTRODUCTION**

The effluents contaminated with dyes and pigments can cause risks to the environment and human health ([Rashidza-deh et al. 2015](#)). These colored compounds are widely used in textile, leather, paper, printing, pigment, solvent, rubber, plastic, food, pharmaceutical, and cosmetic products. When released into water, these contaminants make it difficult for the light penetration and the oxygen consumption, affecting the aquatic life negatively. In humans, dyes can cause eye burns and damage the respiratory system. If ingested, these compounds can lead to nausea, vomiting, sweating, and mental confusion. Further, they can be mutagenic and carcinogenic ([Tan et al. 2008; Chen et al. 2015](#)). As a consequence of all these problems, the environmental laws regarding the discharge of colored effluents are becoming stricter, encouraging the industries to invest more in efficient treatments ([Mahmoodi et al. 2014](#)).

Various treatment technologies can help to remove dyes from industrial effluents, including chemical coagulation, chemical oxidation, precipitation, photo-bleaching, membrane separation, ion exchange, advanced oxidation processes and adsorption ([Guler & Sarioglu 2013; Patel & Hota 2014; Altinisik et al. 2015](#)). Adsorption, a surface phenomenon where a solid surface chemically or physically attracts a gas or liquid multi-component mixture, is one of
the most efficient and promising operations to remove dyes from aqueous effluents. The main advantages are low initial investment, ease of implementation and operation, low energetic requirements and high efficiency (Ahmad et al. 2009; Foo & Hameed 2009, 2010; Tanyildizi 2011).

The use of low-cost adsorbents or biosorbents makes the adsorption process economically more attractive than other treatment processes (Gao et al. 2011). According to Brito et al. (2010), a material is considered inexpensive when it requires little processing and is naturally abundant or consists of an industrial byproduct or residue. In this way, researchers have searched for adsorbents/biosorbents that can make the adsorption process even more economically interesting. Papaya seeds (Paz et al. 2013; Weber et al. 2013), bottle gourd (Foleto et al. 2013), red algae (Vijayaraghavan et al. 2015), municipal solid waste (Berrazoum et al. 2015), okra seed (Lee et al. 2015), bread fruit (Lim et al. 2015), corn fiber (Mallampati et al. 2015), pseudostem banana fibers (Sousa et al. 2014), and many other materials have been evaluated as dye biosorbents. However, based on the best of our knowledge, ouricuri fibers were not tested as biosorbent for dyes. In Brazil, the palm Syagrus coronata is known as ouricuri or licuri. It occurs primarily in semi-arid regions in the states of Alagoas, Sergipe, Bahia, and Minas Gerais. Ouricuri has been used to recover degraded areas; its seeds are employed as an aromatic ingredient in the local cuisine. One of the most important derivatives of these plants is vegetable oils, with an annual production of 99 million tons. Its oil has been used for the manufacture of cosmetics and soaps (Faria et al. 2008). Furthermore, ouricuri oil has application in the kitchen and biodiesel production (Bauer et al. 2013; Belviso et al. 2013; Iha et al. 2014). On the contrary, the potential of ouricuri fibers is little investigated.

Based on the aforementioned, this work aimed to investigate, for the first time, the ouricuri (S. coronata) fiber as an alternative biosorbent to remove methylene blue (MB) from aqueous solutions. MB is a cationic dye molecule, extensively used in dyeing processes and not strongly hazardous. However, it is harmful if swallowed, inhaled or comes in contact with skin or eyes. The contact can cause increased heart rate, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Bulut & Aydin 2006; Sharma et al. 2010; Rahimidokht et al. 2016). At first, the fibers were characterized by ash content, moisture content, pH, scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Then, the effects of adsorbent dosage (M) (10 and 50 g L⁻¹), fiber diameter (D) (0.595 and 0.841 mm) and agitation (A) (50 and 200 rpm) on the adsorption capacity were investigated by a 2⁵ experimental design. Finally, kinetic and equilibrium studies were performed under the more adequate conditions.

MATERIALS AND METHODS

Preparation and characterization of ouricuri fiber

The ouricuri fibers were obtained from a farm located in northeast Brazil, washed several times with distilled water and placed in an oven at 60 °C for 24 h. After drying, the fibers were ground in a knife mill (Wiley Mill Standard, 03, USA) using sieves, in order to obtain particles with 0.595 and 0.841 mm. No oil was present in the fibers, but oil occurred in the almond fruit.

The ashes and moisture content were determined by the standard methods (AOAC 1995). The pH was measured by stirring 2.0 g of the fibers material in 50 mL of distilled water for 10 min. The surface morphology was analyzed by SEM (Shimadzu, SSX-550 Superscan, Japan) (Goldstein et al. 1992). The thermal profile was obtained by thermal analysis (TGA) (Shimadzu, DTG-60H, Japan) (Haines 2002). The functional groups of ouricuri fibers were identified by FTIR (Perkin Elmer, Model IR 660, USA) (Silverstein et al. 2007). XRD (Shimadzu, XRD-6000, Japan) was used to verify the structure of ouricuri fibers (Brindley & Brown 1980).

Batch assays

The potential of ouricuri fibers as biosorbent was evaluated using batch experiments with MB, a common dye found in textile effluents (Hessel et al. 2007). MB dye (color index 52,015, molar weight of 319.8 g mol⁻¹, λmax = 664 nm) was obtained from Plury Chemical Ltda., Brazil. All other reagents were of analytical grade. Distilled water was used to prepare all solutions.

The batch assays were performed in three steps using a thermostated shaker (Marconi, MA 093, Brazil) at 25 °C and initial pH of 5.5 (according to Hessel et al. 2007), these conditions are common for textile effluents. (i) In the batch assays for experimental design, a determined adsorbent dosage (10 or 50 g L⁻¹) with specific fiber diameter (0.595 or 0.841 mm) was added in 50 mL of MB solution with 100 mg L⁻¹ and the solutions were agitated (50 or 200 rpm) for 180 min (established from previous experiments). At 180 min, an aliquot was removed for
quantification. (ii) The kinetic experiments were performed in the more adequate conditions (determined from the experimental design), with initial MB concentration of 100 mg L\(^{-1}\) and contact time from 0 to 210 min. Samples were removed at different time intervals for quantification. (iii) The equilibrium experiments were obtained in the more adequate conditions (determined from the experimental design) by varying the initial dye concentration from 5 to 450 mg L\(^{-1}\). At equilibrium, aliquots were removed for quantification.

For all experiments, the remaining MB concentration in liquid phase was determined by spectrophotometry at the maximum wavelength, using a spectrophotometer Biospec-tro SP-22 (Brazil). The experiments were randomly performed in duplicates \((n = 2)\) and blanks were performed. The MB removal percentage \((R, \%)\), adsorption capacity at any time \((q_t, \text{ (mg g}^{-1})\)) and at equilibrium \((q_e, \text{ (mg g}^{-1})\)), were determined as follows:

\[
R = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

\[
q_t = \left( \frac{C_0 - C_t}{M} \right) \times V
\]

\[
q_e = \left( \frac{C_0 - C_e}{M} \right) \times V
\]

where \(C_0, C_t, C_e\) (mg L\(^{-1}\)) are the MB concentrations at \(t = 0\), at any time and at equilibrium, respectively, \(M\) (g) is the adsorbent mass and \(V\) (L) is the volume of the solution.

**Experimental design**

A full factorial experimental design \(2^3\) (Myers & Montgomery 2002) was employed to verify the effects of adsorbent dosage \((M)\) (10 and 30 g L\(^{-1}\)), fiber diameter \((D)\) (0.595 and 0.841 mm) and agitation \((A)\) (50 and 200 rpm) on the adsorption capacity \((q_e)\). The factors and levels were determined on the basis in preliminary tests and literature, being presented in Table 1 (real and codified forms). The statistical analysis was carried out with 95\% confidence level.

**Kinetic and equilibrium models**

From the kinetic viewpoint, the MB adsorption onto ouricuri fibers was investigated using the common models of pseudo-first order (Lagergren 1898) (Equation (4)) and pseudo-second order (Ho & McKay 1998) (Equation (5)):

\[
q_t = q_1(1 - \exp(-k_1t))
\]

\[
q_t = \frac{t}{(1/k_2q_2^2) + (1/q_2)}
\]

where \(q_t\) (mg g\(^{-1}\)) is adsorption capacity at any time, \(k_1\) and \(k_2\) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively, in (min\(^{-1}\)) and (g mg\(^{-1}\) min\(^{-1}\)), \(q_t\) and \(q_2\) are the theoretical values for the adsorption capacity (mg g\(^{-1}\)) and \(t\) is the time (min).

Regarding the equilibrium, Langmuir (Langmuir 1918) (Equation (6)), Freundlich (Freundlich 1906) (Equation (7)), Sips (Sips 1948) (Equation (8)) and Redlich–Peterson (Redlich & Peterson 1959) (Equation (9)) models were used:

\[
q_e = \frac{q_mK_LC_e}{1 + (K_LC_e)}
\]

\[
q_e = KC_e^{1/\nu_F}
\]

\[
q_e = \frac{q_S(K_SC_e)^{m_S}}{1 + (K_SC_e)^{m_S}}
\]

\[
q_e = \frac{K_{RP}C_e}{1 + (a_{RP}C_e^2)}
\]

where \(q_m\) is the maximum adsorption capacity (mg g\(^{-1}\)), \(K_L\) is the Langmuir constant (L mg\(^{-1}\)), \(K_F\) is the Freundlich constant (mg g\(^{-1}\) mg L\(^{-1}\)\(^{-1/\nu_F}\)), \(1/\nu_F\) is the heterogeneity factor, \(q_S\) is the maximum adsorption capacity from the Sips model (mg g\(^{-1}\)), \(K_S\) is the Sips constant (L mg\(^{-1}\)), \(m_S\) is the
exponent of the Sips model, $K_{RP}$ (L mg\(^{-1}\)), $a_{RP}$ (L mg\(^{-1}\))\(^\beta\) and $\beta$ are the Redlich–Peterson constants. Another important aspect of the Langmuir model is the equilibrium factor, $R_L$:

$$R_L = \frac{1}{1 + (K_L C_t)} \quad (10)$$

For $R_L = 1$, the isotherm is linear, $0 < R_L < 1$ indicates a favorable process and $R_L = 0$ indicates an irreversible process (Langmuir 1918).

The parameters of the kinetic and equilibrium models were determined by nonlinear regression, minimizing the least squares function, using the Quasi-Newton estimation method. The calculations were realized using the Statistic 9.1 software (Statsoft, USA). The fit quality was verified through determination coefficient ($R^2$) and average relative error ($ARE$) (El-Khaiary & Malash 2011).

RESULTS AND DISCUSSION

Characteristics of ouricuri fiber

The ouricuri fiber presented ash content of 2.23%, showing that the material is mainly composed of an organic fraction. This fact can facilitate the dye adsorption. The moisture content was 6.99%, obtained after the drying at low temperature; and this value also favors adsorption, as the fiber pores contains less water and more free space. The pH of the fiber suspension was 4.4, whereas the pH of the MB solution was about 5.5.

Figure 1 shows the SEM of the ouricuri fibers. This figure revealed that the fiber displayed a heterogeneous surface with many cracks, protuberances and cavities. These surface features can probably lead to the increase in fiber area, consequently increasing the area available for dye adsorption.

Figure 2 shows the thermogravimetric curve (TGA) of the ouricuri fiber. It was found in TGA curve that the water loss occurred from 25 to 100 °C, corresponding to the little peak in the DrTGA curve at around 80°C. The organic material present in the fibers started to degrade at 250 °C and the weight loss lasted until 500 °C. This weight loss is evidenced by the intense peak around 340°C in DrTGA curve. In brief, these curves revealed that the ouricuri fibers maintained their organic fraction until 250 °C.

Figure 3 shows the vibrational spectrum of the ouricuri fibers. The FTIR spectrum of ouricuri fibers was compared with the literature (Yang et al. 2007; Troedec et al. 2008; Spinaçé et al. 2009). The main intense bands were found at 3,560, 2,920, 1,640, 1,247, 1,052 and 620 cm\(^{-1}\). The broad

Figure 1 | SEM images of ouricuri fibers: (a) \( \times 300 \) and (b) \( \times 3,000 \).

Figure 2 | TGA and DrTGA curves of ouricuri fibers.
band at 3,360 cm$^{-1}$ can be assigned to the $\cdot$OH bonds of polysaccharides, typical of cellulose. At 2,920 cm$^{-1}$ the C-H stretching of alkanes present in cellulose and hemicellulose can be observed. The stretchings of C-O of acetyl and C-N of amine can be seen around 1,640 cm$^{-1}$. The bands between 1,247 and 1,052 cm$^{-1}$ could be assigned to the anti-symmetric stretching of the C-O-C bond of lignin, hemicellulose, and cellulose. The band at 670 cm$^{-1}$ is related to the C-OH bond out of plane of cellulose. These results demonstrated that the ouricuri fibers contain several functional groups, which can be possible binding sites for MB.

Figure 4 shows the XRD pattern of the ouricuri fiber, which consists primarily of lignin, hemicellulose and cellulose (as discussed in Figure 3). The lignin and hemicellulose macromolecules are amorphous and the cellulose molecules are semi-crystalline. Despite interference of the amorphous regions of cellulose observed in Figure 4, peaks related to the fiber constituents were evident. The peak in the region of 2 theta $= 25^\circ$ reveals the crystalline portion of the fiber.

### Experimental design results

Table 1 shows the experimental design matrix $2^3$ with the average values of the response variable ($q_e$) obtained for each combination of input variables.

The results depicted in Table 1 were fit to a linear model, which provided an empirical correlation to describe the capacity of the ouricuri fiber to adsorb MB. Analysis of the effects provided the empirical model. Equation (11) corresponds to the empirical model with the statistically significant parameters obtained by linear regression of the experimental data.

\[
q_e = 4.95 - 2.4M + 0.09A - 0.18MA
\]  

(11)

To verify if the proposed model represents with accuracy the experimental results, analysis of variance (ANOVA) was used. Table 2 summarizes the model evaluation by the ANOVA method. It was found that the model was statistically significant. The determination coefficient ($R^2$) was 0.99, close to the unit, and the values of lack of fit and pure error were low, indicating that the model can successfully predict experimental data. In addition, the $F$ test (95% of confidence level) showed that $F_{calculated}$ for the regression (51.4) was higher than the standard $F$ (3.49). The ratio between calculated $F$ and standard $F$ was higher than 1 ($F_{calculated}/F_{standard} = 14.7$), confirming the model validation.

Based on Equation (11), the influence of each factor ($M$, $D$ and $A$) on the adsorption capacity can be verified in Figure 5.

It can be seen in Figure 5 that the variable $M$ (adsorbent dosage) presented the most pronounced effect in relation the

### Table 2 | ANOVA

<table>
<thead>
<tr>
<th>Sum of squares (SQ)</th>
<th>Degree of freedom</th>
<th>Mean of squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression</td>
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</tr>
<tr>
<td>Residue</td>
<td>0.69</td>
<td>12</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.54</td>
<td>4</td>
</tr>
<tr>
<td>Pure error</td>
<td>0.15</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td>93.85</td>
<td>15</td>
</tr>
<tr>
<td>$R^2$</td>
<td></td>
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</tr>
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adsorption capacity, followed by the linear interaction adsorbent dosage ($M$) and agitation ($A$). The fiber diameter presented no significant influence on the adsorption capacity (Figure 5(b)). The second term in Equation (11) and Figure 5(a) showed that an increase in adsorbent dosage ($M$) led to a decrease in the adsorption capacity, indicating that the adsorbent material was not saturated at the upper level of the $M$ parameter (30 g L$^{-1}$). A reason for this behavior might be the particle interaction when more adsorbent was used. The interaction could cause aggregation decreasing the surface area (Deng et al. 2011). The third term of Equation (11) and the Figure 5(c) revealed that the agitation ($A$) increase caused an increase in the adsorption capacity. The experimental design presented consistent results, which resembled the data published by Rocha (2012). Based on the experimental design, the maximum adsorption capacity was obtained under the following conditions: adsorbent dosage ($M$) = 10 g L$^{-1}$, fiber diameter ($D$) = 0.595 nm and agitation ($A$) = 200 rpm. These operating conditions were used for the kinetic and isotherm studies.

**Adsorption kinetics**

Figure 6 shows the adsorption kinetic curve for the adsorption of MB onto ouricuri fibers ($M$ = 10 g L$^{-1}$, $D$ = 0.595 nm and $A$ = 200 rpm). Pseudo-first-order and pseudo-second-order models were fitted with the experimental data, and the results are presented in Table 3.

The kinetic curve (Figure 6) showed that the adsorption of MB onto ouricuri fibers was a fast process, where 90% of saturation was attained at 5 min. A similar trend was found by Hameed et al. (2008), using coconut fiber as adsorbent. The high values of the coefficient of determination ($R^2 > 0.98$) and the low values of the ARE (<1.0%) (Table 3)
demonstrated that both pseudo-first- and pseudo-second-order models were suitable to fit the experimental data.

**Adsorption isotherms**

Figure 7 shows the adsorption isotherm curve for the adsorption of MB onto ouricuri fibers. Langmuir, Freundlich, Sips and Redlich–Peterson models were fitted with the experimental data aiming to obtain information about the adsorption process. These results are shown in Table 4.

It can be seen in Figure 7 that the equilibrium curves presented a typical behavior of a L2 type isotherm (Giles et al. 1960). The high values of the coefficient of determination and the low values of the ARE (Table 4) revealed that the Sips model was the more adequate to represent the adsorption equilibrium. The Langmuir and Redlich–Peterson also were suitable. It was verified that $0 < R_L < 1$, indicating that the adsorption of MB onto ouricuri fibers was a favorable process. The maximum adsorption capacity from Sips (31.7 mg g$^{-1}$) was compared with other adsorbents used in the literature to remove MB (Hameed et al. 2008; Tan et al. 2008; Paz et al. 2015; Rashidzadeh et al. 2015; Vijayaraghavan et al. 2015). The above mentioned studies presented adsorption capacities ranging from 28.9 to 637.3 mg g$^{-1}$. Then it is possible to affirm that ouricuri fibers presented suitable adsorption capacity.

**CONCLUSION**

This work investigated the potential of ouricuri fibers as biosorbent to remove MB dye from aqueous solutions. The process variables like adsorbent dosage, fiber diameter and agitation were studied using the experimental design. It was found that the maximum adsorption capacity was achieved with 10 g L$^{-1}$ of ouricuri fiber, fiber diameter of 0.595 mm and agitation of 200 rpm. Pseudo-first- and pseudo-second-order models were suitable to represent the experimental kinetic data. A fast kinetics was observed, where around 90% of saturation was attained at 5 min. The adsorption was favorable and the experimental equilibrium data fitted very well the Sips model. The maximum
adsorption capacity was 31.7 mg g\(^{-1}\). These results showed that ouricuri fibers are an alternative biosorbent to remove MB from aqueous media, taking into account the process efficiency and economic viewpoint.

REFERENCES


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