Soybean hull as an alternative biosorbent to uptake a reactive textile dye from aqueous solutions

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ABSTRACT

The textile industries are responsible for generating large volumes of effluents containing toxic dyes, harmful to ecosystems if disposed of without prior treatment. The adsorption process stands out due to its simplicity and efficiency in removing a wide variety of contaminants present in effluents, also, it allows the use of residual biomass from agriculture. The soybean hull is a by-product of wide available but made used only for animal feed. Thus, the present study aimed to characterize and evaluate the soybean husk as a biosorbent of the 5G blue reactive dye, widely used in the dyeing processes of the textile industries. The soybean hull was characterized by SEM and FTIR. Kinetic and equilibrium tests were carried out under conditions of pH 2, 40 °C, and 90 rpm. Besides, kinetic and equilibrium mathematical models previously described in the literature were adjusted to the experimental data. Through the morphological characterization of the biosorbent, it was possible to evidence superficial pores in practically all their extension, a characteristic that directly influences the adsorption process. The analysis of FTIR showed, as expected, the presence of functional groups characteristic of lignocellulosic substances. Besides, the results obtained in the kinetic and equilibrium essays in the studied conditions show that the adsorption equilibrium was obtained in about 120 min, with the removal of 88% of the dye. The mathematical modeling indicated that the pseudo-second order and Sips models were the most adequate to represent the kinetic and equilibrium experimental data, respectively. The maximum adsorption capacities calculated experimentally and predicted by the Sips model were 53.33 and 48.13 mg g⁻¹, respectively. In general, the biosorbent studied was effective to remove the reactive dye.

Keywords: textile effluent; biosorption; agroindustrial waste.

1 INTRODUCTION

The dyeing process of textile industries is the major responsibility for the generation of liquid effluents, being chemically complex due to the variety of dyes used, which are classified into: dispersants, acids, bases, salts, detergents, moisturizers, oxidizers, and others [1]. If these effluents are not properly treated before disposal in rivers or lakes, contamination of water bodies will be imminent, causing the reduction of dissolved oxygen in the water, in addition to affecting aquatic ecosystems, as well as the death of aquatic animals [2, 3].

In this context, several technologies have been studied as a method for the treatment of textile effluents, such as ion exchange, coagulation, and coagulation-flocculation, however, present as limitations the large number of reagents used and the generation of post-treatment sludge. Besides, biological treatments such as activated sludge (based on algae and anaerobic-aerobic) require physical space, care with microorganisms,
and their restrictions and relatively long process time [3].

Given the limitations of conventional techniques, adsorption has stood out in the effective removal of color, since there is no generation of sludge, no use of physical spaces or expensive reagents. The efficiency of the process, however, is directly related to the choice of an adsorbent with high selectivity, easy acquisition, and low cost [4]. Thus, soybean hull (Glycine max) is a viable by-product for use as an adsorbent [5].

According to EMBRAPA [6], Brazil's 2018/19 soybean production reached approximately 115 million tons, of which about 10% hulls. While the grains can be used in different processes, the hulls are treated as agricultural waste, being destined only as animal feed, due to the low protein content (11%) high fiber content (36%) [7, 8]. Aiming at a greater utilization of this agro-industrial waste, soybean hulls has been reported as a promising alternative for use as an adsorbent in the removal of textile dye [9] and heavy metals [5]. In this sense, this study aimed to evaluate the adsorption capacity of in natura soybean hull (Glycine max) to remove the 5G blue reactive dye, commonly used in textile dyeing.

2 MATERIALS AND METHODS

2.1 Obtainment and Preparation of Biosorbent
Soybean hulls were collected from a soybean processing industry located in Rondonópolis, Mato Grosso, Brazil. The hulls were dried in a forced-air oven (CienLab CE-220) at 60 ºC for 24h. They were then ground in a hammer mill (SP-33) and packed in polyethylene bags.

2.2 Preparation of 5G reactive blue dye solutions
Initially, a 500 mg L\(^{-1}\) stock solution of 5G reactive blue dye with 98% purity was prepared to be used in the dilutions of the other concentrations studied. Besides, a 100 mg L\(^{-1}\) solution was used to determine the maximum absorption length in a UV/Vis spectrophotometer (Varian, Cary 50 Scan), which was obtained at 610 nm. To obtain the calibration of the curve, dye solutions were prepared with concentrations from 0 mg L\(^{-1}\) to 50 mg L\(^{-1}\) with an interval of 5 mg L\(^{-1}\). The pH of the dye solutions was adjusted by adding solutions of 0.1 mol L\(^{-1}\) HCl or NaOH, when necessary. All chemical reagents used were of analytical standard.

2.3 Biosorbent characterization
The biosorbent was characterized by Electronic scanning microscopy (SEM) (Tescan Vega3 LMU, Czech Republic). The samples were fixed in stub using double-sided carbon tapes and metalized with high vacuum gold. The analyses were performed at 5 kV voltage accelerations, with magnifications of 80 and 1600 times.

To identify the functional groups, present in the biosorbent, the infrared analysis with Fourier (FTIR) transform was used. The samples were submitted to spectroscopic determination in the infrared region (450-4500nm) (Prestige 21, 210045, Japan) using the total attenuated reflectance technique (ATR). The samples were submitted to drying in a greenhouse of forced air circulation at 60 ºC for 24h, to perform the analysis.

2.4 Adsorption kinetics and isotherms
The isotherms and adsorption kinetics were conducted under the better preliminary conditions (pH 2, 90 rpm and 40 ºC), according to suggested by RIGUETO et al. [9]. The kinetics were performed with 50 mL of 5G blue reactive dye solution at a concentration of 100 mg L\(^{-1}\) and 0.3 g of biosorbent in 125 mL conical flasks. The equilibrium isotherms were constructed using 50 mL blue reactive dye solution of 5G at a concentration of 250 mg L\(^{-1}\), varying the biosorbent mass from 0.02 to 0.60 g.

At the end of the kinetic and equilibrium assays, the samples were submitted to the centrifugation process, followed by spectrophotometric reading (Bel, SP-2000), and the dye concentration was determined by Equation 1.

\[
q = \frac{V(C_0-C)}{m} 
\]

Where, q the amount of dye adsorbed per gram of water bath root (mg g\(^{-1}\)), C\(_0\) and C dye concentration in the initial and final aqueous solution respectively (mg L\(^{-1}\)), V the volume of dye solution (L), and m the mass of biosorbent (g).

The equilibrium was defined when the concentration of the dye showed standard error between its measurements of less than 5% in 3 measurements at 1h intervals.
2.5 Mathematical modeling

The equilibrium kinetics and isotherms were analyzed according to the models shown in Table 1. The pseudo-first-order and pseudo-second-order models were applied to represent the adsorption kinetics, according to Equations 2 and 3. The adsorption isotherms were evaluated by the Langmuir, Freundlich, Temkin, and Sips models, according to Equations 4 to 7. The parameters of the models were calculated using the software Origin® version 15, by minimizing the objective function sum of the squares [10].

Table 1: Equations of kinetic and equilibrium models.

| MODEL | EQUATIONS |
|-------|-----------|
| **KINETIC MODELS** | |
| Pseudo-first order | \( q(t) = q_1(1 - e^{-k_1t}) \) (2) |
| Pseudo-second order | \( q(t) = \frac{t}{(1/k_2q_2^2) + (t/q_2)} \) (3) |
| **ISOTHERM MODELS** | |
| Langmuir | \( q_e = \frac{q_m K_L C_{eq}}{1 + K_L C_{eq}} \) (4) |
| Freundlich | \( q_e = K_F C_e^{1/n_F} \) (5) |
| Temkin | \( q_{eq} = B \ln(K_T C_{eq}) \) (6) |
| Sips | \( q_e = \frac{q_m K_S C_e^m}{1 + K C_e^n} \) (7) |

Where: \( k_1 \) (min\(^{-1}\)) rate constant of pseudo-first-order, \( q_1 \) (mg g\(^{-1}\)) theoretical value of adsorption capacity, \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) rate constant of pseudo-second-order, \( q_2 \) (mg g\(^{-1}\)) theoretical value of adsorption capacity, \( q_m \) (mg g\(^{-1}\)) maximum adsorption capacity, \( K_L \) (L mg\(^{-1}\)) Langmuir constant, \( K_F \) (mg g\(^{-1}\)) (mg L\(^{-1}\))\(^{-1/n_F}\) Freundlich constant, \( 1/n \) (-) heterogeneity factor, \( B \) (kJ mol\(^{-1}\)) Temkin isotherm constant, \( k_T \) Temkin constant (L mg\(^{-1}\)), \( q_m \) (mg g\(^{-1}\)) maximum adsorption capacity, \( K_S \) (L mg\(^{-1}\)) Sips constant, and \( m \) (-) heterogeneity factor.

3 RESULTS AND DISCUSSION

3.1 Biosorbent characterization

Scanning electron microscopy has been a very important tool to characterize the surface morphology and physical properties of the adsorbent. It is used to analyze porosity, particle shape, and appropriate size distribution [11]. Soybean hull scanning electron micrographs are shown in Figure 1.

The considerable number of pores present in the soybean hull, as shown in Figure 1, indicates the great possibility of dyes getting trapped and adsorbed in these pores. Besides, the surface morphology is irregular and rough. Similar morphology was also found by ARAMI et al. [11] and WEI et al. [12], who studied the surface characteristics of soybean hulls for adsorption of direct and acid dyes and Pb (II), respectively. Based on this morphology, it is observed that the soybean hull presents an adequate morphological profile to retain dyes like 5G reactive.
To determine the vibration frequencies of possible functional groups, present in the soybean hull, the infrared spectroscopy technique was applied. Each group has a characteristic frequency, so it is possible to propose through this analysis the presence of the groups that are part of the soybean hull, characteristics of which directly influence the adsorption process. Figure 2 shows the FTIR spectrum of the soybean hull.

Figure 2 presents a set of characteristic bands of lignocellulosic substances, as expected. According to ALEMDAR and SAIN [13], the wideband located at 3412 cm\(^{-1}\) is attributed to the symmetric stretching vibrations of OH groups, indicating both the presence of cellulose hydroxyl groups and structural or absorbed water. The bands at 2925 cm\(^{-1}\) and 2855 cm\(^{-1}\) are due to -C-H stretching vibrations. Peaks of 1061 cm\(^{-1}\) and 794 cm\(^{-1}\) are related to the C-O-C elongation and the C-H rocking vibrations of cellulose. Some peaks at 1744 cm\(^{-1}\), 1647 cm\(^{-1}\), and 1417 cm\(^{-1}\) are associated with the -C-O vibrations of the carboxyl group. A similar molecular structure was also found by WEI et al. [12] and ALEMDAR and SAIN [13].
3.2 Adsorption kinetics and isotherms

The adsorption kinetics is a measure of control of the adsorbate diffusion in the pores under pressure, concentration, pH, and constant flow, where expressed in a curve or line, describes the retention rate of a solute in an aqueous environment for a solid interface, aiming at the equilibrium. During adsorption, two processes occur, physisorption and chemisorption. Physisorption is the result of weak attraction forces while chemisorption involves the formation of strong bonds between the solute and the adsorbate that involves the transfer of electrons [14, 15]. Adsorption kinetics are shown in Figure 3. In this test, after 120 min the equilibrium was observed, and about 88% of the 5G blue reactive dye was removed from the aqueous solution. The kinetic parameters of the proposed models (Equations 2 and 3) are presented in Table 2.

From the analysis of the parameters of the kinetic models under study (Table 2), it was noted that both can be used to describe the adsorption kinetics of the present study with R² = 0.94 and 0.99 for the pseudo-first and pseudo-second order models, respectively. However, the pseudo-second order model presented a better adjustment to the experimental data, as well as a higher value for solute adsorbed in the equilibrium, which in this case was 17.20 mg g⁻¹. A similar result was observed in MÓDENES et al. [16] using soybean hulls on the removal of BF-4B dye, which had a better adjustment with the pseudo-second order model with R² = 0.97, however, its maximum adsorption in the equilibrium remained at 8.895 mg g⁻¹. The pseudo-second order model indicates that the adsorption rate of the solute is proportional to the free sites of the adsorbent [15].

![Figure 3: Kinetic profile and mathematical modeling of adsorption of 5G blue reactive dye by soybean hulls (40°C, 90 rpm and pH 2)](image)

| MODELS                | PARAMETERS       | PARAMETERS       |
|-----------------------|------------------|------------------|
|                       | q(t) (mg g⁻¹)    | 16.56            |
|                       | k₁ (min⁻¹)       | 0.181            |
|                       | R²               | 0.9498           |
| Pseudo-first order    | q(t) (mg g⁻¹)    | 17.20            |
|                       | k₂ (g mg min⁻¹)  | 0.018            |
|                       | R²               | 0.9937           |

Another very useful tool in the compression of the process mechanisms is the isotherm, which reveal the potential for adsorption of the biosorbent by the solute in the face of the conditions of the experimental medium in which it was submitted, moreover, these isotherms are based on mathematical models, simplify-
ing the description of the adsorption and desorption data of the system, through empirical variables and simple equations [17].

It can also be said that isotherms are mechanisms of understanding adsorption and can quantitatively assess the distribution of solutes of interest in equilibrium between solid and liquid phases [18]. The adsorption isotherm of the 5G blue reactive dye using soybean hulls are shown in Figure 4. It is observed that the isotherm has a concave characteristic, indicating that the adsorption process is favorable, providing high dye removal capacity type L2 or H2, according to the classification suggested by GILES et al. [19]. This type of isotherm further suggests that the adsorbent has several finite sites, which when filled with no additional adsorption can occur, leading to the formation of a plateau. The maximum capacity \( (q_{eq}) \) obtained from the experimental data was 53.33 mg g\(^{-1}\).

![Figure 4: Equilibrium isotherm and mathematical modeling of 5G blue reactive dye adsorption by soybean hulls (40°C, 90 rpm, and pH 2).](image)

Table 3 shows the adjustment of the equilibrium data to the adsorption isothermal models represented by Equations 4 to 7. The coefficients of determination \( (R^2) \) of Langmuir, Freundlich, Redlich-Peterson, and Sips models equal or are greater than 0.90 showing that these models are suitable for representing the experimental data of adsorption of 5G blue reactive dye. However, despite presenting a good \( R^2 \), the Sips model is what is closest to the ideal, because its curve accompanies the data of the experiment, designing an \( R^2 \) of excellent value, as represented in Figure 4. Besides, the maximum adsorption capacity would be 48.13 mg g\(^{-1}\) according to the model. A similar fit was reported by HOLANDA et al. [20] which removed the Remazol turquoise textile dye using *Eichhormia crassipes* as adsorbent, where the best fit model was Sips with \( R^2 = 0.99 \).
Table 3: Equilibrium model parameters for adsorption of 5G blue reactive dye adsorption by soybean hulls (40°C, 90 rpm and pH 2)

| MODELS      | PARAMETERS | 250 MG L⁻¹ |
|-------------|------------|-------------|
|             | qmax (mg g⁻¹) | 54.97535    |
| Langmuir    | kₐ (L mg⁻¹)  | 0.0064      |
|             | R²          | 0.96229     |
|             | k (L g⁻¹)   | 12.18967    |
|             | N           | 3.72887     |
|             | R²          | 0.90663     |
| Freundlich  | b (kJ mol⁻¹) | 10.58418    |
|             | kₗ (L mg⁻¹) | 0.59718     |
|             | R²          | 0.93636     |
| Temkin      | qₗ (mg g⁻¹) | 48.13462    |
|             | kₘ (L mg⁻¹) | 0.05395     |
|             | bₗ         | 2.05158     |
|             | R²          | 0.99551     |

Sips model is characterized by being a combination of Langmuir and Freundlich models predicting the adsorption in heterogeneous systems and circumventing the limitation of the rising adsorbate concentration associated with the Freundlich isotherm. High concentrations of adsorbate presuppose Langmuir-like behavior that shows single-layer adsorption capacity, while low concentrations presume the similarity of isotherm of Freundlich, which forms more than one layer of adsorbate on the adsorbent [21]. Thus, the Sips model was chosen to represent the equilibrium data of this work.

4 CONCLUSIONS

Through the morphological characterization of the biosorbent, it was possible to evidence superficial pores in practically all their extension, a characteristic that directly influences the adsorption process. The analysis of FTIR showed, as expected, the presence of functional groups characteristic of lignocellulosic substances.

Besides, the results obtained in the kinetic and equilibrium essays in the studied conditions show that the adsorption equilibrium was obtained in about 120 min, with the removal of 88% of the dye, with the pseudo-second order model and Sips, the mathematical models that best represent the kinetic and equilibrium data, respectively. The maximum adsorption capacities calculated experimentally and predicted by the Sips model were 53.33 mg g⁻¹ and 48.13 mg g⁻¹, respectively. In general, the biosorbent studied was effective to remove the reactive dye.

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