Brazilian berry seeds (Eugenia uniflora) were used as an eco-friendly and low-cost biosorbent for the treatment of textile effluents containing methylene blue. Characterization techniques indicated that Brazilian berry seeds are constituted of irregular particles, mainly composed of lignin and holocellulose groups, distributed in an amorphous structure. Methylene blue biosorption was favorable at pH of 8, using a biosorbent dosage of 0.8 g L\(^{-1}\). The equilibrium was reached in the first 20 min for lower M methylene blue concentrations and 120 min for higher methylene blue concentrations. Furthermore, the general and pseudo-second-order models were suitable for describing the kinetic data. Langmuir was the most adequate model for describing the isotherm curves, predicting a biosorption capacity of 189.6 mg g\(^{-1}\) at 328 K. Biosorption was spontaneous (\(-9.54 \leq \Delta G^0 \leq -8.06\) kJ mol\(^{-1}\)) and endothermic, with standard enthalpy change of 6.11 kJ mol\(^{-1}\). Brazilian berry seeds were successfully used to remove the color of two different simulated textile effluents, achieving 92.2% and 73.5% of removal. Last, the fixed-bed experiment showed that a column packed with Brazilian berry seeds can operate during 840 min, attaining biosorption capacity of 88.7 mg g\(^{-1}\). The data here presented indicates that textile effluents containing methylene blue can be easily and successfully treated by an eco-friendly and low-cost biosorbent like Brazilian berry seeds.

**Keywords** Biosorption · Dye · Eco-friendly · Effluent · Fixed-bed · Methylene blue

**Introduction**

Nowadays, different industries, such as textile, paper, leather tanning, food processing, plastics, cosmetics, rubber, and printing, apply dyes to give color for its products (Yagub et al. 2014). An example of dye is methylene blue (MB), which presents high chemical stability, being one of the most applied dyes on the textile industries (Catanho et al. 2006). It is a cationic dye often used in the dyeing of wool and cotton fabrics. However, the incorrect treatment of textile effluents containing MB, and its release on rivers and lakes, besides affecting the visual state of the water, leads to a poor natural photosynthetic activity, thus generating harm to the ecosystem (Honorato et al. 2015). The high quantities of used dyes and its noxious effects have drawn attention of the scientific community and the governmental inspection agencies in relation to the colored effluents generated. Searching to solve the problem of colored effluents, the development of alternative, eco-friendly, and sustainable methods have increased in the last years (Bazzo et al. 2015).
Different technologies for the treatment of colored effluents can be applied; nevertheless, biosorption has gained importance because it is a simple and cost-effective operation. In addition, biosorption allows the use of a wide range of biosorbent materials (Uddin et al. 2017). In this sense, different promising biosorbent materials have been reported in the literature. Cedrela odorata seeds were applied by Babalola et al. (2016) for the removal of methylene blue, congo red, methyl orange, and crystal violet dyes from aqueous effluents. Georgin et al. (2018a) applied Araucaria angustifolia wastes to treat colored effluents containing crystal violet dye. Activated carbon from jerivá stone was tested by Carvalho to treat colored effluents containing crystal violet dye. Postai et al. (2016) used residues from Aleurites mluccana for the removal of anthraquinone and azo dyes from colored effluents. Fontana et al. (2016) used malt bagasse as an efficient and low-cost biosorbent to uptake the textile dye orange Solimax TGL from aqueous solutions. Banana peel was tested by Munagapati et al. (2018), as an effective material to remove reactive black 5 and congo red from aqueous solutions. From the above studies, it can be seen a continuous search for eco-friendly and low-cost biosorbents which are able for the treatment of textile effluents.

The Eugenia uniflora is important for the food and pharmaceutical industries. The fruits of this species are known as Brazilian berries, standing out mainly due to its astringent properties and a pleasant aroma. The fruits and leaves from Eugenia uniflora also present several interesting compounds, such as flavonoids, terpenes, tannins, anthraquinones, and essential oils. Their by-products end up being widely used by the cosmetics industry (Lima et al. 2006). However, during the processing of the fruit, 23% is residue in the form of seeds; thus, a final application is needed (Amorim et al. 2009).

In this work, Brazilian berry seeds (BBS) (Eugenia uniflora), a waste from the berries processing, was tested for the first time as an eco-friendly and low-cost biosorbent for the treatment of textile effluents containing MB. The BBS biosorbent was previously characterized by different techniques. The biosorption of MB using the BBS was evaluated in relation to the kinetics and isotherms. The BBS was tested for the treatment of simulated effluents with different compositions. Fixed-bed experiments were also performed to verify the potential of BBS to be used in continuous operations.

Materials and methods

Preparation of BBS and characterization techniques

The Brazilian berries (Eugenia uniflora) were collected around the region of the Federal University of Santa Maria (UFSM) (Rio Grande do Sul state, Brazil). First, the seeds were manually separated from the fruit pulp, washed with distilled water, sun dried during 6 h and grounded with a knife mill (Marconi, MA340). After the initial step, the powder was washed with an ethanol solution (50% v/v) at 60 °C for 40 min under stirring of 150 rpm. This process was executed four times, aiming the removal of any extractives. The solid material was then separated from the liquid phase by sedimentation and dried at 60 °C for 72 h. Last, the biosorbent was sieved using a 45 mesh, corresponding to 0.0354 cm, and named BBS powder.

The following techniques were selected for the characterization of the BBS: scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffractometry (XRD). For the SEM images, the BBS samples were covered with gold through the sputtering process, using a current of 20 mA for 90 s. After this step, the SEM images were obtained using a VEGA 3 from Tescan (Czech Republic) operating at 10 kV. In the case of the FT-IR, 100 mg of KBr were mixed with 1 mg of the sample and further pressed using a Hand Press SSP-10A (Shimadzu, Japan), resulting in thin transparent inserts (less than 1 mm thick) with a diameter of 13 mm. Then, KBr/BBS mixture was scanned from 450 to 4500 cm⁻¹ using a Shimadzu FT-IR model Prestige-21 (Japan) with 45 scans and 2.0 cm⁻¹ resolution. Last, the XRD was used to determine the crystallographic structure, using a Rigaku, model MiniFlex 300 equipment (Japan).

To identify the possible nature of the sites, present on the BBC surface, as well as the pH effect on biosorption, it was realized the point of zero charge test (pH pzc) (Salleh et al. 2011). Eight NaCl solutions (0.1 mol L⁻¹) had its pH adjusted from 2 to 10. Then, a dosage of 0.8 g L⁻¹ of BBC biosorbent was added into each solution. Solutions were then agitated until reaching the equilibrium (36 h). The pH pzc was obtained from the difference between the final and initial pH (Hameed et al. 2008).

Batch biosorption tests

The biosorption essays were conducted using the cationic dye MB. MB is a synthetic dye derivate from thiazine with a molecular formula C₁₆H₁₈ClN₃S (319.87 g mol⁻¹, λmax of 664 nm). Moreover, it presents the following molecular dimensions: 14.3 Å width, 6.1 Å depth, and 4 Å thick. The molecular diameter is 8 Å, and the molecular volume is 241.9 cm³ mol⁻¹. A stock solution of MB was firstly prepared (1 g L⁻¹) using distilled water, and stocked on glass vials, being further diluted as required in each specific experiment. The equipment used to perform all the biosorption essays was the thermostatic agitator, model MA 093 from Marconi (Brazil), which was operated at 150 rpm. Batch biosorption tests were conducted as follows:

The pH tests were conducted for the following pH values: 2.0, 4.0, 6.0, 8.0, and 10.0, using 1 g L⁻¹ of BBS
biosorbent. The pH values were adjusted using sodium hydroxide or chloride acid. BBS was added to 50 mL of MB solutions with initial concentration of 60 mg L\(^{-1}\), and the solutions were agitated during 180 min at 298 K. The BBS dosage effect was analyzed for the following values: 0.50, 0.75, 1.00, 1.25, and 1.50 g L\(^{-1}\). For these assays, the pH was set at 8. The different BBS dosages were put in contact with 50 mL of MB solution with an initial concentration of 60 mg L\(^{-1}\). Solutions were stirred during 180 min at 298 K.

The biosorption kinetic experiments were conducted using the best conditions found in the pH and dosage tests. The influence of different initial MB concentrations (25, 50, 100, 200 mg L\(^{-1}\)) was evaluated. In the same form, BBS was added to 50 mL of MB solutions at 298 K. The samples were collected at predefined times: 5, 10, 15, 20, 30, 45, 60, 90, 120, and 180 min.

The equilibrium biosorption essays were made at 298, 308, 318, and 328 K, for different initial concentrations (0, 25, 50, 100, 150, and 200 mg L\(^{-1}\)). For each essay, BBS was added to 50 mL of MB solution and the solution was agitated until reaching the equilibrium.

Each sample was centrifuged (4000 rpm for 20 min) after collected, using a Centribio model 80-2B centrifuge (Brazil). The MB concentration was measured by spectrophotometry using a Shimadzu UV model mini 1240 (Japan). All tests were made in triplicates (\(n=3\)) and blanks were carried out to ensure reproducibility. The percentage of dye removal (R, %) and biosorption capacity at any time (\(q_t\), mg g\(^{-1}\)) and at equilibrium (\(q_e\), mg g\(^{-1}\)) were calculated as follows:

\[
R = \left(\frac{C_0 - C_t}{C_0}\right) \times 100. \tag{1}
\]

\[
q_t = \left(\frac{C_0 - C_t}{m}\right) \times V \tag{2}
\]

\[
q_e = \left(\frac{C_0 - C_e}{m}\right) \times V \tag{3}
\]

where \(C_0\) is the initial concentration of the MB dye in the liquid phase (mg L\(^{-1}\)), \(C_e\) is the equilibrium concentration of the MB dye in the liquid phase (mg L\(^{-1}\)), \(C_t\) is the concentration of the MB dye in the liquid phase at any time (mg L\(^{-1}\)), \(m\) is the amount of BBS biosorbent (g), and \(V\) is the volume of solution (L).

Kinetic, isotherm, and thermodynamic models

The biosorption kinetics of MB on BBS biosorbent was analyzed according to the pseudo-first-order (Lagergren 1898), pseudo-second-order (Ho and McKay 1999), and general order models (Liu and Shen 2008). The Weber-Morris model was also selected for understanding the biosorption mechanism (Weber and Morris 1963; Crank 1975) (supplementary material S1). For the biosorption isotherms, the models of Langmuir (Langmuir 1918), Freundlich (Freundlich 1906), and Khan (Khan et al. 1996) were tested (supplementary material (S.2)). For the thermodynamic calculations, it was used the equilibrium constant estimated from the best isotherm model (Lima et al. 2019), and the equations presented in the supplementary material (S.3).

Textile effluent treatment using BBS

The BBS biosorbent was evaluated for the treatment of effluents containing MB and a series of other compounds found in real situations of textile industry. Two types of textile effluents were simulated, containing different compositions of dyes and salts (Table 1). For these tests, a dosage of 4.0 g L\(^{-1}\) of BBS was put in contact with the effluents A and B (Table 1), which were agitated for 240 min at 150 rpm and 298 K. Before and after the treatment with BBS, the solutions were UV-Vis scanned on the 300 to 800 nm region. The efficiency of the biosorption with BBS was evaluated in terms of total color removal (TCR, %). Total color removal was calculated from the difference between the areas under the spectral curves, before and after the treatment (Georgin et al. 2019a; Yaseen and Scholz 2019).

Fixed-bed essay and modeling

The column experiment for the BBS was performed using an acrylic column with 25 cm height and 2.5 cm diameter. The column was filled with 27.8 g of BBS. The MB solution was pumped at a volumetric flow of 20 mL min\(^{-1}\) through the system, using a peristaltic pump from Provitec (model AWV.

| Chemical compounds | Concentration (mg L\(^{-1}\)) | \(\lambda_{\text{max}}\) (nm) |
|--------------------|-------------------------------|-----------------------------|
| Effluent A         |                               |                             |
| Methylene blue     | 100                           | 664                         |
| Crystal violet     | 50                            | 586                         |
| Malachite green    | 50                            | 615                         |
| Sodium chloride (NaCl) | 100                          |                             |
| Sodium carbonate (Na\(_2\)CO\(_3\)) | 100                          |                             |
| pH                 | 9.8                           |                             |
| Effluent B         |                               |                             |
| Methylene blue     | 80                            | 664                         |
| Brilliant blue     | 50                            | 630                         |
| Basic fuchsin      | 100                           | 546                         |
| Sodium chloride (NaCl) | 100                          |                             |
| Sodium carbonate (Na\(_2\)CO\(_3\)) | 100                          |                             |
| pH                 | 8.5                           |                             |
Brazil). The samples were taken at intervals of 30 min until the concentration at the outlet of the column become constant. The MB concentrations were measured according to the section “Batch biosorption tests”. The length of mass transfer zone \( (Z_m) \), the volume of effluent \( (V_{eff,m}) \), maximum biosorption capacity \( (q_{eq,m}) \), and percentage of removal \( (R, \%) \) were estimated using the following equations (Suzuki 1990):

\[
Z_m = Z \left(1 - \frac{t_b}{t_c}\right) \tag{4}
\]

\[
V_{eff} = \frac{Q t_{total}}{m_{bio}} \tag{5}
\]

\[
q_{eq} = \frac{Q C_0}{m_{bio}} \int_0^{t_{total}} \left(1 - \frac{C_t}{C_0}\right) dt \tag{6}
\]

\[
R = \frac{100\%}{t_{total}} \int_0^{t_{total}} \left(1 - \frac{C_t}{C_0}\right) dt \tag{7}
\]

where \( Z \) is the height of the fixed bed (cm), \( Q \) is the volumetric flow (mL min\(^{-1}\)), \( t_{total} \) is total time of operation (min), \( C_0 \) is the feed concentration (mg L\(^{-1}\)), \( C_t \) is output concentration (mg L\(^{-1}\)) and \( m_{bio} \) is the biosorbed mass (g).

The breakthrough data were evaluated by the models of Bohart-Adams (Bohart and Adams 1920), Thomas (Thomas 1944) and Yoon-Nelson (Yoon and Nelson 1984). These models are presented in the supplementary material (S.4).

**Fit evaluation**

For all models used in this work, the goodness of fit was evaluated through the determination coefficient \( (R^2) \), adjusted determination coefficient \( (R^2_{adj}) \), average relative error (ARE) and minimum squared error (MSE). The equations are shown in the supplementary material (S.5). All the parameter estimations were made using script programming on Matlab 2017.

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Fig. 1 SEM images of the BBS biosorbent at different magnifications a \( \times \) 200, b \( \times \) 500, c \( \times \) 1000, and d \( \times \) 5000
Results and discussion

BBS biosorbent characteristics

The SEM images of the BBS surface are exhibited in Fig. 1. In Fig. 1 a and b, with magnifications of × 200 and × 500, respectively, it is possible to observe that the BBS biosorbent is a particulate material, containing irregular and shapeless particles, with sizes in the order of 200 μm or less. Similar morphological aspects have already been found in other plant-based materials, such as the bark of the tree species Cedrella fissilis, Araucaria angustifolia, and Handroanthus albus (Georgin et al. 2018a; Georgin et al. 2019b; Hernandes et al. 2019). Siddiqui et al. (2018) and Kebede et al. (2018) also used caraway seed residues and Moringa stenopetala and found surfaces with similar aspects of this study. In the images depicted in Fig. 1 c and d (magnifications of × 1000 and × 5000, respectively), it can be verified that the BBS particles are formed by agglomerates of circular structures with sizes lower than 10 μm.

The FT-IR spectrum for the BBS biosorbent is presented in Fig. 2a. The wideband found at 3430 cm\(^{-1}\) is related to the bond elongation of O–H (Cao et al. 2014). The band at 2927 cm\(^{-1}\) is attributed to the C–H stretch vibrations of aliphatic molecules (Ghaedi et al. 2015). The vibrational signal at 1641 cm\(^{-1}\) is ascribed to the C=O and N–H bonds, directly
related to the amide I group (Pavan et al. 2008). The band found at 1370 cm$^{-1}$ corresponds to C–H from the methyl groups (Yang and Qiu 2010). The band around 1017 cm$^{-1}$ indicates the presence of C–O (Dahri et al. 2014). In the region of 400 cm$^{-1}$, the vibration of C–N bonds can be verified (Salem and Awwad 2014). The results indicate that the BBS contains groups that are commonly found in lignocellulosic materials. These groups in turn possess the capacity to uptake species diluted in aqueous solutions.

The XRD pattern for BBS biosorbent is presented in Fig. 2b. It is possible to observe that the material presents an amorphous characteristic, corresponding to the broad peak between the 10 and 30°. This peak is characteristic of the lignin and cellulose materials (Xu et al. 2007). Similar behavior has been also found by Siddiqui et al. (2018) for cumin seeds.

**Influence of pH and BBS dosage on biosorption**

Figure 3a shows the influence of pH on the biosorption of MB by BBS. It is possible to observe that the pH increase from 2 to 8 enhanced the biosorption capacity from 2.2 to 56.1 mg g$^{-1}$. A new increase from 8 to 10 presented no effect in the MB biosorption. This effect is a result of the BBS and MB characteristics, when submitted to solutions with different pH values. Concerning the BBS characteristics, it was found that the pH$_{pzc}$ was 6.8, as shown in Fig. 3b. So, the BBS surface is protonated at pH values lower than 6.8, and deprotonated at pH values higher than 6.8. In relation to MB, it is a cationic dye. Thus, the biosorption was more efficient at pH 8.0.

Table 2  Kinetic parameters for the MB biosorption on BBS

| MB initial concentration (mg L$^{-1}$) | 25 | 50 | 100 | 200 |
|--------------------------------------|----|----|-----|-----|
| Pseudo-first order (PFO) | | | | |
| $q_1$ (mg g$^{-1}$) | 52.4 | 76.3 | 98.8 | 130.8 |
| $k_1$ (min$^{-1}$) | 0.271 | 0.308 | 0.172 | 0.183 |
| $R^2$ | 0.983 | 0.997 | 0.949 | 0.932 |
| $R^2_{adj}$ | 0.958 | 0.992 | 0.875 | 0.836 |
| ARE (%) | 3.64 | 1.38 | 6.92 | 8.30 |
| MSE (mg g$^{-1}$)$^2$ | 4.7 | 1.9 | 53.1 | 123.2 |
| Pseudo-second order (PSO) | | | | |
| $q_2$ (mg g$^{-1}$) | 54.9 | 78.8 | 106.2 | 140.5 |
| $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.010 | 9.8 $\times$ 10$^{-3}$ | 2.6 $\times$ 10$^{-3}$ | 2.1 $\times$ 10$^{-3}$ |
| $R^2$ | 0.998 | 0.998 | 0.990 | 0.982 |
| $R^2_{adj}$ | 0.996 | 0.995 | 0.975 | 0.955 |
| ARE (%) | 1.09 | 1.07 | 2.97 | 4.22 |
| MSE (mg g$^{-1}$)$^2$ | 0.4 | 1.0 | 10.5 | 33.2 |
| General order (GO) | | | | |
| $q_n$ (mg g$^{-1}$) | 56.9 | 77.3 | 142.1 | 206.7 |
| $k_n$ (min$^{-1}$ (g mg$^{-1}$))^$-n$ | 1.3 $\times$ 10$^{-3}$ | 5.8 $\times$ 10$^{-2}$ | 3.6 $\times$ 10$^{-10}$ | 5.6 $\times$ 10$^{-14}$ |
| $n$ (–) | 2.6 | 1.5 | 5.3 | 6.7 |
| $R^2$ | 0.998 | 0.998 | 0.990 | 0.982 |
| $R^2_{adj}$ | 0.995 | 0.995 | 0.971 | 0.948 |
| ARE (%) | 0.79 | 0.37 | 0.82 | 1.56 |
| MSE (mg g$^{-1}$)$^2$ | 0.25 | 0.22 | 0.81 | 4.5 |
| $q_{exp}$ (mg g$^{-1}$) | 55.3 | 77.2 | 107.9 | 142.9 |
because the opposite charges of BBS and MB in this condition, which in turn facilitated the interaction in the surface.

The BBS dosage effect on the removal percentage and biosorption capacity of MB is shown in Fig. 3c. The different dosages (0.5 to 1.5 g L\(^{-1}\)) were tested with 50 mL of MB solutions at an initial concentration of 60 mg L\(^{-1}\) and pH 8. The percentage of MB removal ranged from 83 to 91% with BBS dosage increase. In contrast, the biosorption capacity values decreased from 106.0 to 38.6 mg g\(^{-1}\). This expected behavior can be related to several aspects. The first one, from a mathematical viewpoint, is that the biosorption capacity is inversely proportional to the adsorbent dosage; thus, its increase causes a direct decrease of the adsorbent capacity (Ghosh and Bhattacharyya 2002). Second, from a molecular viewpoint, the removal increase and adsorption decrease in related to the increase of total biosorption sites (Franco et al. 2019). The decrease in biosorption capacity \( (q) \) occurs due to the superposition and aggregation of biosorption sites. In Fig. 3c, the intersection between the curves of biosorption capacity and removal percentage indicates the appropriate dosage, which in this case was 0.8 g L\(^{-1}\).

### Biosorption kinetics and modeling

The kinetic profiles of the MB biosorption onto BBS, obtained at different initial concentrations, are shown in Fig. 4. The curves were obtained at pH of 8 and BBS dosage of 0.8 g L\(^{-1}\). Evidently, all curves started from \( q_t = 0 \) and the biosorption equilibrium was attained along the time until reach the equilibrium. However, it was observed that the curves at lower initial MB concentrations (25 and 50 mg L\(^{-1}\)) were faster. At lower initial MB concentrations, the biosorption equilibrium was attained.

### Table 3 Estimated Weber-Morris parameters for the biosorption of MB onto BBS

| Parameters | MB initial concentration (mg L\(^{-1}\)) |
|------------|---------------------------------------|
|            | 25                                    |
|            | 50                                    |
|            | 100                                   |
|            | 200                                   |
|            | S1                                    |
|            | S2                                    |
| \( k_{WB} \) (mg g\(^{-1}\) min\(^{-1/2}\)) | 18.24                                |
|            | 0.78                                  |
| \( C \) (mg g\(^{-1}\)) | 27.46                                |
|            | 0.48                                  |
| \( D_e \) (cm\(^2\) s\(^{-1}\)) | 9.28 \times 10\(^{-11}\)              |
|            | 1.82 \times 10\(^{-11}\)              |
| \( R^2 \) | 0.999                                 |
|            | 0.85668                               |

### Table 4 Isotherm parameters for the MB biosorption on BBS

| Model   | 298 | 308 | 318 | 328 |
|---------|-----|-----|-----|-----|
| Langmuir |     |
| \( q_L \) (mg g\(^{-1}\)) | 179.7 |
| \( K_L \) (L mg\(^{-1}\)) | 0.081 |
| \( R^2 \) | 0.990 |
| \( R^2_{adj} \) | 0.983 |
| ARE (%) | 11.91 |
| MSE (mg g\(^{-1}\)^2) | 49.1 |
| Freundlich |     |
| \( K_F \) (mg g\(^{-1}\)(mg L\(^{-1}\)y\(^{-1/2}\))) | 29.2 |
| \( 1/n_F \) (dimensionless) | 2.51 |
| \( R^2 \) | 0.956 |
| \( R^2_{adj} \) | 0.983 |
| ARE (%) | 21.5 |
| MSE (mg g\(^{-1}\)^2) | 209.3 |
| Khan     |     |
| \( q_mK \) (mg g\(^{-1}\)) | 152.7 |
| \( a \) (L mg\(^{-1}\)) | 0.101 |
| \( b \) (dimensionless) | 0.935 |
| \( R^2 \) | 0.989 |
| \( R^2_{adj} \) | 0.972 |
| ARE (%) | 12.76 |
| MSE (mg g\(^{-1}\)^2) | 72.7 |

**Fig. 5** Equilibrium curves for the MB/BBS system (BBS dosage = 0.8 g L\(^{-1}\), pH = 8, 150 rpm, \( V = 50 \) mL)
at around 20 min, while at higher MB concentrations (100 and 200 mg L$^{-1}$), the equilibrium was reached at around 120 min. This suggests that the diffusive effects inside the BBS particle were most pronounced at higher concentrations. Similar behavior has been reported by Neupane et al. (2014) in the adsorption of crystal violet onto pineapple leaves.

Aiming to better understand and describe the biosorption of MB on BBS, the abovementioned kinetic models (supplementary material (S.1)) were used. The estimated parameters of each model are presented in Table 2. The choice of the best model was based on the statistical indicators and physical meaning of the parameters. Considering the statistical indicators, it can be seen that PSO and GO models were more accurate than PFO to describe the biosorption kinetic profiles. PSO and GO presented $R^2$ and $R^2_{adj}$ higher than 0.945, and also, lower values of ARE and MSE. At lower concentrations (25 and 50 mg L$^{-1}$), the GO model was better than PSO, predicting more accurately the experimental equilibrium biosorption capacity ($q_{exp}$ near to $q_n$). On the other hand, at MB concentrations of 100 and 200 mg L$^{-1}$, the GO model (in spite of the good statistical indicators) was not able to predict the $q_{exp}$ values, and also, provided $k_p$ values without physical meaning. In conclusion, for lower MB concentrations, the PSO model is preferred.

The Weber-Morris model showed that the biosorption of MB onto the BBS was separated in two stages (Fig. S1). The first initial stage is related to the external mass transfer of the MB. The external mass transfer can be related to different aspects such as initial concentration, agitation speed and favorable interactions on the system (Tran et al. 2017). The second stage can be classified as the intraparticle diffusion step. In this case, the diffusion of the adsorbate molecules inside the particle (Weber and Smith 1987) occurs. This indicates that the biosorption of the MB onto the BBS has depended of both mechanisms. Furthermore, from the estimated parameters (Table 3), it was possible to conclude that the increase of the initial concentration of MB increased the effective diffusion from $9.28 \times 10^{-11}$ to $3.65 \times 10^{-10}$ cm$^2$ s$^{-1}$.

### Biosorption equilibrium and thermodynamics

The equilibrium curves for the MB biosorption onto BBS at different temperatures are exhibited in Fig. 5. The obtained isotherm curves were favorable of the “L” type. It can be observed an inclined portion at lower equilibrium concentrations, demonstrating the affinity between MB and BBS. With the increase in the equilibrium concentration ($C_{eq}$), the biosorption capacity ($q_{eq}$) tended to a constant value, but the plateau was not observed. The temperature effect on the equilibrium curves was little pronounced. The temperature increase provided a little increase in the biosorption capacity, from 152.7 (298 K) to 164.1 mg g$^{-1}$ (318 K). This trend can be attributed to the reduction in the solution viscosity and consequent increase in the mobility of MB molecules in solution. Bulut and Aydin (2006) reported a similar trend in the adsorption of MB onto wheat straw, raising the adsorption capacity from 16.6 to 21.5 mg g$^{-1}$, for the temperature variation of 303 to 323 K. For the same temperature variation, Hameed and Ahmad (2009) reported the increase of MB adsorption, from 82.6 to 142.9 mg g$^{-1}$.

The parameters of Langmuir, Freundlich and Khan models are listed in Table 4. Analyzing the statistical indicators ($R^2 \geq 0.989$, $R^2_{adj} \geq 0.982$, ARE $\leq 12.84\%$, MSE $\leq 58.3$ (mg g$^{-1}$)), it is possible to conclude that the Langmuir model was the most suitable when compared with the Khan and Freundlich. Furthermore, the $K_L$ and $q_L$ parameters presented conformity with the experimental data, i.e., both increases as the temperature raises. The maximum biosorption capacity of BBS for MB was 189.6 mg g$^{-1}$ at 328 K.

Taking into consideration the Langmuir isotherm, it was estimated the equilibrium constant, which is further used for the determination of thermodynamic parameters (Table 5). The biosorption of MB onto BBS was favorable and spontaneous ($-9.54 \leq \Delta G^0 \leq -8.06$ kJ mol$^{-1}$). The endothermic nature of the MB biosorption onto BBS was confirmed by the $\Delta H^0$ value of 6.11 kJ mol$^{-1}$. From the magnitude of $\Delta H^0$, it indicates that the biosorption of the MB onto the BBS has depended of both mechanisms. Furthermore, from the estimated parameters (Table 3), it was possible to conclude that the increase of the initial concentration of MB increased the effective diffusion from $9.28 \times 10^{-11}$ to $3.65 \times 10^{-10}$ cm$^2$ s$^{-1}$.

### Tables

| Table 5 | Thermodynamic parameters for the MB biosorption on BBS |
|---------|------------------------------------------------------|
| T(K)    | $k_c$ (L·mol$^{-1}$) | $\Delta G^0$ (kJ·mol$^{-1}$) | $\Delta H^0$ (kJ·mol$^{-1}$) | $\Delta S^0$ (kJ·mol$^{-1}$·K$^{-1}$) |
| 298     | 25.87 | -8.06 | 6.11 | 0.047 |
| 308     | 28.39 | -8.57 |         |        |
| 318     | 29.03 | -8.91 |         |        |
| 328     | 33.02 | -9.54 |         |        |

| Table 6 | Estimated partition values for the adsorption kinetics of MB onto BBS for different initial concentrations |
|---------|--------------------------------------------------------------------------------------|
| Sorbent | $C_0$ (mg L$^{-1}$) | $C_e$ (mg L$^{-1}$) | $q$ (mg g$^{-1}$) | $K_D$ (mg g$^{-1}$ (mg L$^{-1}$)) |
| BBS     | 25              | 3.37            | 57.25           | 16.96 |
| Dosage 0.8 g L$^{-1}$ | 50              | 11.80           | 77.25           | 6.54 |
| Time 180 min | 100             | 12.21           | 107.94          | 8.84 |
| pH 8.0   | 200             | 75.05           | 150.77          | 2.00 |
| Temperature 298 K |                    |                 |                 |     |
can be assumed that a physical biosorption occurred in the MB biosorption onto BBS. Finally, minor rearrangements of MB molecules on the BBS surface were indicated by the positive value of the entropy change. The entropy was more important than the enthalpy in the MB biosorption by BBS, since the term $T \Delta S_0$ was the unique in Eq. 9 (supplementary material (S.3)) that have contributed to obtain negative $\Delta G_0$ values.

### Partition factor and sorbent comparison

Usually, maximum biosorption capacity is used to compare the performance of a determined sorbent material. However, biosorption capacity is a very sensitive variable, since it depends on different operational conditions (pH, dosage, initial concentration, temperature) (Siddiqui et al. 2019). One way to evaluate the sorbent is using the partition coefficient ($K_D$, mg g$^{-1}$ (mg L$^{-1}$)$^{-1}$) (Vikrant and Kim 2019), which is estimated according to the following Equation:

$$K_D = \frac{q_e}{C_e} = \frac{q_e}{C_0R}$$  \hspace{1cm} (8)

The first step is the self-evaluation of the sorbent in relation to its kinetics, here presented in Table 6. It was found that the coefficient of partition ($K_D$) tends to decrease with the increase in initial concentration ($C_0$), which is expected since the final equilibrium concentration ($C_e$) increases. This similar behavior has been also found by Siddiqui and collaborators (2019). Second, the BBS was evaluated using the maximum biosorption capacity and the partition coefficient in relation to other works present in the literature (Table 7). At first glance, using the $q_m$ as a comparison, the BBS is stated as

### Table 7  Comparison of maximum biosorption capacities and partition coefficient for different materials used to treat MB containing solutions

| Adsorbent                      | pH  | $T$ (K) | $C_0$ (mg L$^{-1}$) | $q_m$ (mg g$^{-1}$) | $C_e$ (mg L$^{-1}$) | $K_d$ (mg g$^{-1}$)(mg L$^{-1}$)$^{-1}$ | References                        |
|-------------------------------|-----|---------|---------------------|---------------------|---------------------|---------------------------------------|-----------------------------------|
| BBS                           | 8   | 328     | 25–200              | 189.6               | 65                  | 2.9169                                | This work                         |
| Spent coffee                  | 5   | 298     | 50–500              | 18.71               | 240                 | 0.0780                                | Franca et al. (2009)               |
| Glass hollow fiber            | 7   | 318     | 20–200              | 44.38               | 100                 | 0.4438                                | Zhang et al. (2019)               |
| Pará chestnut husk            | 4   | 328     | 100–400             | 83.8                | 450                 | 0.1862                                | Georgin et al. (2018b)            |
| Activated corn                | 5   | 298     | 20–160              | 254                 | 160                 | 1.5875                                | Fan et al. (2014)                 |
| AC/cellulose films            | 7   | 328     | 20–100              | 110.35              | 45                  | 2.4522                                | Somsesta et al. (2020)            |
| AC from A. donax              | 10  | 318     | 100–400             | 480.77              | 160                 | 3.0048                                | Üner (2019)                       |
| Soursop and sugarcane wastes  | 5.5 | 298     | 50–200              | 55.39/17.43         | 55/80               | 1.007/4.589                          | Meili et al. (2019)               |
| Modified celery               | 6.8 | 323     | 100–700             | 526.32              | 225                 | 2.3392                                | Mohebali et al. (2018)            |
| Ouricuri fibers               | 5.5 | 298     | 20–450              | 31.7                | 160                 | 0.1981                                | Meili et al. (2016)               |
| P. granatum husk              | 5   | 298     | 5–500               | 68.4                | 215                 | 0.3181                                | Bretanha et al. (2014)            |
| Pine cone biomass             | 7.28| 303     | 20–60               | 109.89              | 40                  | 2.7473                                | Sen et al. (2010)                 |
| Modified pine cone            | 9.2 | 303     | 20–90               | 142.25              | 55                  | 2.5864                                | Yagub et al. (2013)               |

![Fig. 6](image_url)  
**Fig. 6** UV-Vis spectra for the simulated effluents before and after the biosorption: a effluent A and b effluent B.
the third better from the selected works. Nevertheless, when using the K_D, it was found that the BBS reaches the second position in relation to performance, being the first the activated carbon from Arundo donax reported by Üner (2019). This biosorption performance coupled with its eco-friendly character and low-cost, becomes BBS a promising material for MB removal from textile effluent.

**MB/BBS system interaction**

Figure 7 shows the proposed interaction between the MB and the BBS. In general, it is known that agro waste materials are mainly composed of lignin, cellulose, and hemicellulose (Chen, 2014, Siddiqui and Chaudhry 2019). These molecules often present OH groups that are able to perform hydrogen and electrostatic bonds with the MB (Abdulla et al. 2019; Fatima et al. 2019).

**Treatment of textile effluents by biosorption with BBS**

When a biosorption study is performed for dyes removal, normally, synthetic solutions containing only one dye and water are used to test the biosorbent (this evaluation is here presented in sections “Influence of pH and BBS dosage on biosorption”, “Biosorption kinetics and modeling”, and “Biosorption equilibrium and thermodynamics”). However, textile effluents contain a series of compounds and more than one dye. So, the potential of a biosorbent need to be evaluated

| Model          | Parameter value          |
|----------------|--------------------------|
| Bohart-Adams   |                          |
| \(k_{BA} \) (L mg\(^{-1}\) min\(^{-1}\)) | \(7.3 \times 10^{-5}\) |
| \(N_{BA} \) (mg L\(^{-1}\)) | 504.13 |
| \(R^2\)       | 0.998                    |
| MSE            | \(2.092 \times 10^{-3}\) |
| Thomas         |                          |
| \(k_{th} \) (L mg\(^{-1}\) min\(^{-1}\)) | \(7.3 \times 10^{-5}\) |
| \(q_{th} \) (mg g\(^{-1}\)) | 89.02 |
| \(q_{eq} \) (mg g\(^{-1}\)) | 88.9 |
| \(R^2\)       | 0.998                    |
| MSE            | \(2.092 \times 10^{-3}\) |
| Yoon-Nelson    |                          |
| \(k_{YN} \) (min\(^{-1}\)) | 0.0073 |
| \(\tau\) (min\(^{-1}\)) | 1237 |
| \(\tau_{exp}\) (min\(^{-1}\)) | 1095 |
| \(R^2\)       | 0.998                    |
| MSE            | \(2.092 \times 10^{-3}\) |

Fig. 7 Proposed interaction for the MB/BBS system

Fig. 8 Breakthrough curve for the MB biosorption onto BBS
in real conditions. In this work, two different simulated effluents (Table 1) were prepared and treated using the BBS biosorbent. The spectra of these effluents before and after biosorption with BBS are presented in Fig. 6. Before biosorption, the areas under the curves were 726.684 and 406.054 for the effluents A and B, respectively. After the biosorption process using BBS, these values decreased to 56.448 and 107.64. It was possible to estimate a color removal of 92.2% for the effluent A and 73.5% for the effluent B. Furthermore, in both cases, it is possible to observe a band at 320 nm, which indicates the possible formation of a new compound due to breakage of covalent bonds present in the dyes. Nevertheless, the BBS was able to uptake the unknown compound. Thus, the BBS biosorbent presented potential to be applied in the treatment of textile effluents, which are composed by different dyes and inorganic salts.

**Fixed-bed results**

In biosorption studies, it is also fundamental to verify the possibility of the biosorbent to be used in fixed bed columns. Here, the fixed bed test was performed according to the section “Fixed-bed essay and modeling”, and the resulting breakthrough curve is presented in Fig. 7. It was found and inclined breakthrough curve, which is excellent for scale up purposes. The fixed bed packed with BBS was efficient to treat the MB solution until 840 min (breakthrough time, \( t_b \)). Until this point, the removal percentage was higher than 99%. After this point, the outlet MB concentration started to increase, until reach the exhaustion time at 1630 min. As consequence, the length of mass transfer zone (\( Z_m \)) was 12.1 cm, and the stoichiometric biosorption capacity was 88.92 mg g\(^{-1}\).

Thomas, Yoon-Nelson and Bohart-Adams, namely the dynamic models, were able to describe the breakthrough curve with \( R^2 \) of 0.998 and MSE of 2.092 \( \times 10^{-3} \) (Table 8). In addition, from the Thomas model, it was possible to estimate the biosorption capacity of 89.02 mg g\(^{-1}\), which was close with the experimental value (\( q_{eq} \)). The parameter \( \tau \) of the Yoon-Nelson model was 1237 min and was near with the experimental value (1095 min). These evaluations showed that the dynamic models can be applied to describe and predict the behavior of the breakthrough curve in the biosorption of MB onto the BBS biosorbent (Fig. 8).

**Conclusion**

In this work, it was prepared a biosorbent from the Brazilian berry seeds (BBS). The biosorbent was characterized and further applied in biosorption experiments. The major conclusions are as follows:

BBS biosorbent is mainly composed of irregular and shapeless particles, with sizes in the order of 200 \( \mu \)m, being nitrogen, oxygen, hydrogen, and carbon arranged its amorphous structure. Biosorption of MB on BBS was more favorable at pH 8. The better BBS dosage was 0.8 g L\(^{-1}\). At lower MB concentrations, biosorption was faster, reaching the equilibrium in 20 min, being the general order model the most adequate to represent the curves. However, for higher MB concentrations, the equilibrium was reached in 120 min and the pseudo-second order was the best model.

The Langmuir model is the proper one to represent the equilibrium curves. The maximum biosorption capacity was 189.6 mg g\(^{-1}\). The process was spontaneous, favorable and endothermic.

BBS material was able to remove 92.2% and 73.5% of the color for two types of textile effluents.

The fixed-bed experiment indicated that the biosorbent can be further applied on the continuous MB removal.

All these aspects indicated that BBS is a promising biosorbent to be used in the treatment of textile effluents.

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