Solid wastes from the enzyme production as a potential biosorbent to treat colored effluents containing crystal violet dye

Patrícia Grassi1 · Fernanda C. Drumm1 · Stéfani S. Spannemberg1 · Jordana Georgin1 · Denise Tonato1 · Marcio A. Mazutti1 · Janaína O. Gonçalves1 · Marcos L. S. Oliveira2,3 · Guilherme L. Dotto1 · Sérgio L. Jahn1

Received: 7 October 2019 / Accepted: 7 January 2020 / Published online: 15 January 2020
© Springer-Verlag GmbH Germany, part of Springer Nature 2020

Abstract
Sugarcane bagasse, a largely available waste worldwide, was submitted to solid-state fermentation (SSF) using the fungus Metarhizium anisopliae, aiming to produce enzymes. The solid waste generated from SSF was tested as an alternative biosorbent to treat colored effluents containing crystal violet (CV) dye. The biosorbent, here named BW (bagasse waste), was characterized, and experimental tests were performed to verify the influence of pH and dosage on the CV biosorption. Isotherms and biosorption kinetics were performed, and the biosorption thermodynamic parameters were determined. The potential of BW was also evaluated for the treatment of a simulated textile effluent. The maximum biosorption capacity was 131.2 mg g⁻¹ at 328 K, and the Liu was the most appropriate model to represent equilibrium data. The biosorption was spontaneous and endothermic. The use of BW in the simulated effluent showed that it is an efficient material, reaching color removal values of 85%. Therefore, the sugarcane bagasse generated from SSF can be considered a potential biosorbent to remove CV from textile effluents. This finding is relevant from the total environment viewpoint, since, at the same time, SSF generates enzymes and a solid waste, which in turn can be used as biosorbent to treat colored effluents.

Keywords
Biomass waste · Biosorption · Crystal violet · Fermentation wastes · Sugarcane bagasse

Introduction
Annually, it is estimated that more than one million ton of dyes are produced worldwide, being textile, paper, and cosmetic industries the main users of these pigments in their processes. Therefore, there is a significant amount of dyes disseminated into the environment through wastewaters. The presence of synthetic dyes in water sources directly affects the photosynthetic processes and interferes in the sunlight penetration, making it difficult. Moreover, in live organisms are highly toxic, carcinogenic and teratogenic and can also cause allergic dermatitis and mutations, even at low concentrations (Leal et al. 2018). Particularly, crystal violet is a triphenylmethane dye employed in several industries, including paper, cosmetics, textile, leather, and pharmaceutical. This dye is nonbiodegradable and remains for long time in environmental waters. It is a potential mutagenic and carcinogenic molecule (Brião et al. 2017). Thus, the removal of these pigments from effluents is extremely important for the equilibrium of the ecosystem (Naskar and Majumder 2017; Li et al. 2019a; Zhang et al. 2019).

Among the most commonly used techniques for dye removal in aqueous media, biosorption stands out due its low cost, ease of operation, and high efficiency (Abdolali et al. 2017; Kausar et al. 2018; Gonçalves et al. 2019; Li et al. 2019b). The use of biosorption together with a biosorbent obtained from residues makes the operation even more attractive, contributing to the economic and environmental viability (Li et al. 2019c, d). In this sense, several types of biomass wastes are being used as biosorbents. Some examples are pomace, peel, and by-products of industrial and agricultural...
activities, among others, which are low-cost alternatives and have great potential for removal of inorganic and organic pollutants from aqueous media (Yagub et al. 2014; Kharat 2015).

Sugarcane bagasse (SB) is an agricultural residue, an abundant by-product derived from sugarcane processing. Normally, SB is used as a source of energy in the sugar industry itself, as it serves as boiler fuel for steam generation. However, in recent years, it has been widely explored as a substrate for various biotechnological applications (Pandey et al. 2000; Martínez et al. 2017). Due to its low cost, SB has been widely studied and applied as a nutrient source or carbon source in solid-state fermentation (SSF) processes for the production of microbial enzymes, and in production of high added value biotechnological products (Mazutti et al. 2006; Aliyah et al. 2017; Marques et al. 2018; Oliveira et al. 2018; Aita et al. 2019). During the enzyme production by SSF using sugarcane bagasse, a solid waste without any application is generated (Chavan and Deshpande 2013; Bello et al. 2015; Noor et al. 2017). In this sense, the study of an alternative application for this waste, like dye biosorbent, is interesting from the environmental and economic viewpoints. From the environmental side, it is possible to reduce the solid wastes generated in SSF and, in parallel, treat a colored effluent. From the economic side, it can be considered that SSF generates not only enzymes but also an eco-friendly biosorbent.

Therefore, in this work, SSF of sugarcane bagasse was carried out using the fungus *Metarhizium anisopliae*, generating enzymes and a solid waste (bagasse waste (BW)). The potential of BW as biosorbent to treat colored effluents containing CV was investigated. Firstly, the biosorbent (BW) was characterized by XRD, FTIR, SEM, BET/BJH, and pHPCz. Secondly, the effect of pH and biosorbent dosage on CV biosorption was verified. Then, equilibrium studies and kinetic assays were performed, and models were adjusted to the biosorption data. The biosorption thermodynamic behavior was evaluated. Finally, tests were carried out simulating a textile effluent, in order to verify the efficiency of BW under real conditions of a biosorption process.

**Materials and methods**

**Materials**

The solid substrate used in the fermentation was sugarcane bagasse, obtained from the micro distillery of the Federal University of Santa Maria (UFSM). The fungus *Metarhizium anisopliae* was obtained from the São Paulo Biological Institute (IBCB). The sodium chloride (NaCl) P.A and potassium carbonate (K2CO3) P.A were purchased from Contemporary Chemical Dynamics LTDA/Brazil. Deionized water was used in the preparation of the solutions.

The dyes used were purchased from Sigma-Aldrich Ltda/Brazil, with commercial quality and purity higher than 90%. The CV dye ($\lambda_{max} = 590$ nm, molar mass = $407.9$ g mol$^{-1}$, CI 548,629) was used in all biosorption assays, while the other dyes were used only in the simulated effluent, according to Table 1.

**Simultaneous production of enzymes and biosorbent by SSF**

Sugarcane bagasse was used as substrate in SSF assays to obtain cell wall–degrading enzymes (chitinase, $\beta$-1,3-glucanase, endocellulase, and exocellulase). The microorganism used in the production of enzymes in SSF from sugarcane bagasse was the fungus *Metarhizium anisopliae* IBCB 348. The conditions and parameters of fermentation are presented in Aita et al. (2019). The fermentation process was carried out, and the enzymatic production was evaluated. The best enzymatic activities obtained in the SSF were, respectively, 12.07, 11.54, 20.87, and 22.30 U g$^{-1}$ for chitinase, $\beta$-1,3-glucanase, endocellulase, and exocellulase.

After the SSF for enzyme production, a solid waste was generated. This solid waste was composed by sugarcane biomass together with the fungus *Metarhizium anisopliae* IBCB 348. This solid waste was dried at 100 °C for 1 h to reduce the moisture content and inactivate the microorganism. After that, the biomass waste was macerated and sieved, obtaining a 250-μm particle size powder. This material was named BW, and was used as biosorbent to treat colored effluents.

**Characterization of BW biosorbent**

The BW sample was characterized by X-ray diffraction (XRD) using a Rigaku Mini flex model 300 diffractometer, operating with Cu-K\(\alpha\) radiation ($\lambda = 1.5418$ Å), 30 kV, 10 mA, 0.03° step, and acquisition time 0.5 s. The functional groups present in the biosorbent sample were identified by Fourier transform infrared spectroscopy (FTIR) (Prestige, 21210045, Japan) in the range 800–4500 cm$^{-1}$. Surface area, pore volume, and pore size distribution were determined by N$_2$ adsorption/desorption isotherms (ASAP 2020 Micromeritics), where the surface area was determined based on the Brunauer–Emmett–Teller (BET) method. The total pore volume was determined using the nitrogen desorption branch.
on the Brunauer–Emmett–Teller (BET) method and the pore volume and pore size distribution by the BJH method. The morphology of the biosorbent was verified with the aid of scanning electron microscopy (SEM) (Tescan-Vegan 3 equipment). The point of zero charge (pH_{pcz}) of the biosorbent was determined by the method described by Postai et al. (2016).

**Biosorption experiments**

Initially, the effect of the initial pH on CV dye biosorption by BW was evaluated. The experiments were performed using 1.0 g L\(^{-1}\) biosorbent in 50 mL of dye solution (100 mg L\(^{-1}\)). The pH was adjusted (4, 5, 6, 7, 9, and 10) with the aid of phosphate disodium buffer. The vials were kept under stirring (150 rpm for 120 min) at room temperature (298 K). After, aliquots were removed and centrifuged (Centribio, 80-2B, Brazil). Remaining concentration in the solutions was determined using a Biospectro SP-22 (Brazil) type spectrometer.

From the best pH condition, the effect of biosorbent dosage was evaluated. The experiments were performed under the same conditions employed in the previous tests, but varying the biosorbent dosage in the solution (0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 g L\(^{-1}\)). The biosorption capacity and removal percentage of CV were calculated according to Eqs. (1) and (2), respectively:

\[ \%R = \left( \frac{C_0 - C_f}{C_0} \right) 100\% \]  
\[ q = \left( \frac{C_0 - C_f}{m} \right) V \]  

where \(C_0\) and \(C_f\) are the initial and final CV concentrations in liquid phase (mg L\(^{-1}\)), \(m\) is the mass of BW, and \(V\) is the solution volume.

**Equilibrium studies and thermodynamic parameters**

To construct the equilibrium biosorption isotherms, the biosorption experiments were performed under the best conditions of pH and dosage previously obtained. The initial concentration was varied in 25, 50, 75, 100, 200, and 300 mg L\(^{-1}\), and different temperatures were tested (298–328 K). The solutions containing CV dye and BW were stirred until equilibrium. The equilibrium was considered after three consecutive equal measurements of CV concentration in liquid phase. The biosorption capacity was calculated according to Eq. (2), where the final concentration is the equilibrium concentration value. The equilibrium biosorption data were adjusted using the Langmuir (1918), Freundlich (1906), and Liu et al. (2003) isotherm equations (Supplementary Material, Table S1).

In the thermodynamic study, the changes in Gibb’s free energy (\(\Delta G^0\)), enthalpy (\(\Delta H^0\)), and entropy (\(\Delta S^0\)) were calculated. The thermodynamic parameters were calculated from Eqs. (3) to (5) (Lima et al. 2019).

\[ \Delta G^0 = -RT\ln(K_c) \]  
\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \]  
\[ \ln(K_c) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \]

where \(K_c\) is the thermodynamic equilibrium constant, \(T\) is the absolute temperature (K), and \(R\) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)).

**Biosorption kinetic studies**

In the best condition determined in previous tests, the kinetic analysis was performed to determine the time required for the system reach equilibrium. Assays were performed using different dye concentrations of 50, 75, and 100 mg L\(^{-1}\) under stirring of 150 rpm. Samples were collected at different pre-established time intervals until the equilibrium. Previous studies indicated that the amount of sample taken during the experiment does not significantly affect the final condition. The biosorption capacity was determined according to Eq. (2), where final concentration is the dye concentration at time \(t\) (mg L\(^{-1}\)). Afterward, the experimental data were adjusted to the pseudo-first-order (PFO) (Lagergren 1898), pseudo-second-order (PSO) (Ho and Mckay 1998), and Elovich (Zeldowitsch 1934) models (Supplementary Material, Table S2).

**Fitting and evaluation of the biosorption models**

The parameters of the kinetic and equilibrium models were determined by nonlinear regression by minimizing the least-squares function using the Quasi-Newton method. Calculations were performed using Statistic7.0 software (Statsoft, USA). The quality of the adjustments was assessed by the determination coefficient (\(R^2\)), adjusted coefficient of determination (\(R^2_{adj}\)), and average relative error (\(ARE\)) (Grassi et al. 2019).

**Biosorption of textile effluent using BW**

To analyze the efficiency of BW in the biosorption of simulated effluent, a solution containing dyes and salts present in industrial textile effluents was prepared. The composition and characteristics of the simulated effluent are presented in Table 1. The biosorption tests were performed in the best conditions determined in previous experiments. A determined dosage of BW was put in contact with 50 mL of simulated effluent solution under stirring of 150 rpm at 298 K for 120 min. Curves of absorbance versus wavelength were
acquired before and after the treatment. Color removal was determined by the ratio between these spectrophotometric curves using Origin 2015 software (Georgin et al. 2016).

Results and discussion

Characteristics of waste biomass biosorbent

The XRD pattern of BW (Fig. 1) showed a pronounced peak in the range of 20° to 35° indicating an amorphous structure. This can be attributed to the biomass composition (sugarcane bagasse), which have high content of hemicellulose and lignin (Xu et al. 2007). Similar results were found by Buthiyappan et al. (2019) in the synthesis of green adsorbent from sugarcane bagasse, where the XRD analysis also indicated the amorphous nature.

Figure 2 shows FT-IR of BW biosorbent, where it can be observed the band at 3442 cm$^{-1}$, which is attributed to the axial deformation of the O–H group, resulting from the presence of cellulose and hemicellulose (Angelova et al. 2016). The bands around 2921 and 2857 cm$^{-1}$ can be attributed to the vibrational elongation of carbon–hydrogen (C–H) bonds present in polysaccharides (Sriharsha et al. 2017); the band at 2303 cm$^{-1}$ is relative to the (C–O) bonds of primary alcohols, and the band 1693 cm$^{-1}$ is characteristic of carbonyl (C=O), both present in cellulose. At 1730, 1640, and 1520 cm$^{-1}$, the bands can be attributed to the amide group bonds C=O and N–H, respectively (Pavan et al. 2008). The band at 1328 cm$^{-1}$ is associated with CH$_2$ deformations present in polysaccharides (Siddiqui et al. 2018). The vibrations of the C–O bond are attributed for the range 1250–1046 cm$^{-1}$. Bonds (C–O–C) appear in both the cellulose and lignin strands, 1520 cm$^{-1}$ and 1046 cm$^{-1}$, which are the vibration bands of the pyranose (cellulose) ring. FT-IR spectrum showed the presence of characteristic polysaccharide compounds present in sugarcane bagasse, complex sugars such as cellulose and hemicellulose, as well as lignin. These groups can be able to uptake CV from aqueous media.

Figure 3 shows the nitrogen adsorption–desorption isotherms of the BW biosorbent. According to the IUPAC classification, this is a type IV isotherm and indicates that BW is a mesoporous biosorbent (Thommes et al. 2015). The BET analysis showed that BW has surface area of 1.89 m$^2$ g$^{-1}$; the pores have an average size of 8.81 nm, and the pore volume was 0.00196 cm$^3$ g$^{-1}$. Comparing with commercial materials, these are low values. However, comparing with biosorbents, these values are adequate. It should be highlighted that the potential of the biosorbents is mainly based in the surface chemistry, being that the textural characteristics are less important (Yagub et al. 2014).

Figure 4 shows the SEM images of BW, where it can be verified that the biosorbent has a heterogeneous surface, with...
fibrous structure and presence of irregular cavities. The characteristics presented in Fig. 4 corroborate with the BET analysis (Fig. 3) and also with the peculiar properties of lignin and cellulose present in BW. Comparing BW (Fig. 4a–d) with raw sugarcane bagasse (Fig. 4e), it can be seen that the raw material (Fig. 4e) possesses a fibrous structure without cavities, which is typical of this type of biomass. The fibrous structure was maintained for BW, but several cavities appeared. Evidently, this is a result of the fermentative process where the sugarcane bagasse was used as substrate. The
The presence of cavities is particularly important, since it allows the transference of CV molecules inside the BW particles, increasing the biosorption capacity of the material.

**Effect of pH and biosorbent dosage on the CV biosorption**

To evaluate the pH effect on the biosorption, the determination of the point of zero charge (pH\textsubscript{PCZ}) of BW is fundamental. The point of zero charge (pH\textsubscript{PCZ}) of BW is shown in Fig. 5a, where the value obtained was 6.5. The pH\textsubscript{PCZ} of a material is the pH value where the amount of acidic and basic functional groups is equal on the surface (Postai et al. 2016). Therefore, when the pH of the solution is below the pH\textsubscript{PCZ}, BW has a positively charged surface due to protonation, and when the values exceed 6.5, BW has a negatively charged surface.

The effect of pH on the CV biosorption by BW was verified by varying the values from 4 to 10, and the results are shown in Fig. 5b. It is possible to observe that the biosorption capacity of CV on BW ranged from 63 to 87 mg g\textsuperscript{-1} and that the pH increase has favored the process. This may have occurred because at acidic pHs occurs the protonation of functional groups present on the surface of BW, causing electrostatic repulsion with the positively charged CV dye. However at basic pHs, there is deprotonation of these groups, thus favoring the electrostatic attraction between the CV dye and BW biosorbent and consequently increasing the biosorption capacity (Chakraborty et al. 2011). Similar results were found by Ahmad (2009) in the adsorption of crystal violet dye by pinus bark. The best pH was selected as 7.5. This is the normal pH of the CV solution, and is within the range of textile effluents.

The effect of biosorbent dosage on CV biosorption is shown in Fig. 6. It can be observed that the increase in BW dosage causes an increase in the percentage of removal due to the higher quantity of active sites (Mall et al. 2006). However, the increase in BW dosage causes a reduction in biosorption capacity, which can be attributed to the particle aggregation (Kulkarni et al. 2017). Due to these results, the best BW dosage was 1.0 g L\textsuperscript{-1}. This value is the intersection of both curves in Fig. 6, and was selected because it provides a good correlation between the percentage of removal (87.7%) and biosorption capacity (87.7 mg g\textsuperscript{-1}).

**Biosorption equilibrium isotherms**

Biosorption isotherms were performed by varying the temperature and the initial concentration of CV. The defined pH was 7.5, and the BW dosage was 1.0 g L\textsuperscript{-1}. The curves are shown in Fig. 7. The curves presented a convex shape being characterized as L type. This type of isotherm is characterized by an inclined portion at lower equilibrium concentrations, and by a plateau at higher concentrations. In this work, the inclined portion could be ascribed to the high availability and affinity of biosorption sites. It is important to highlight that a strong inclination was verified, indicating high biosorption capacities coupled with high removal
percentages. The plateau was observed at higher equilibrium concentrations. This shows that the biosorption sites on the BW surface were fully occupied by the CV molecules. Concerning now the temperature effect, it was observed that the biosorption capacity of BW presented a directly proportional behavior, indicating that higher temperatures favored the biosorption of CV. This behavior occurs because, at higher temperatures, the dye molecules are more excited and with higher mobility. Consequently, the interactions with the adsorbent are facilitated. In parallel, a swelling effect can be occurred in the BW structure at higher temperatures. This effect opens the biosorbent structure, facilitating the dye penetration and generating new biosorption sites. Similar results were found by Streit et al. (2019) in the removal of dyes using biological sludge from a wastewater treatment plant.

The equilibrium data were adjusted to the Freundlich, Langmuir, and Liu models, where the parameters are presented in Table 2. The model that best represented the experimental data was Liu due to the high values of $R^2$ and $R^2_{\text{adj}}$ and the low value $\text{ARE}$ values. Moreover, it can be observed in Table 2 that $q_{\text{ml}}$ of Liu model presented higher values at 328 K, thus indicating that the temperature increase favors the interaction dye/biosorbent making higher the biosorption capacity of BW. Similar results were obtained by Machado et al. (2014) in adsorption of a textile dye from aqueous solutions by carbon nanotubes. Furthermore, the higher CV/BW affinity at higher temperatures was confirmed by the increase in $k_g$ with the temperature (Table 2).

Table 3 presents the comparison of BW with various types of materials used for CV removal, in terms of biosorption capacity. From Table 3, it is possible to verify that the BW presented high biosorption capacity (131.24 mg g$^{-1}$) when compared with other materials showed in the literature. This indicates that the use of BW is promising in the removal of contaminants present in liquid effluents. In addition to the interesting biosorption capacity, other advantages should be considered. The use of BW as biosorbent can solve the problem of waste generation in SSF for enzyme production. BW has low cost since is a waste and, also, is biodegradable. It should be highlighted that an identical biosorption isotherm of CV dye was obtained using only the sugarcane bagasse (before fermentation) (41.45% cellulose, 36.14% hemicellulose, 22.01% lignin). The maximum adsorption capacity was 98.45 mg g$^{-1}$. This result is in agreement with the study of Chakraborty et al. (2012). For the system CV/sugarcane bagasse, these authors obtained adsorption capacity of 82.96 mg g$^{-1}$, using 2.0 g L$^{-1}$ of sugarcane bagasse, 200 mg L$^{-1}$ of CV initial concentration, pH of 8.0, and stirring rate of 165 rpm. This result indicates that the wastes of the fungus Metarhizium anisopliae that remained on the sugarcane bagasse after the fermentation presented an important role to improve the biosorption capacity of the raw sugarcane bagasse.

### Biosorption thermodynamic parameters

Thermodynamic parameters were estimated using Eqs. (3)–(5). The $K_C$ values were estimated considering the molecular weight of CV and the activity coefficients.
(Streit et al. 2019). The $R^2$ value of the Vant’ Hoff plot was 0.9543. The thermodynamic parameters of CV biosorption by BW are depicted in Table 4. $\Delta G^\circ$ values that presented negative sign confirm the biosorption spontaneity. Furthermore, $\Delta G^\circ$ values were more negative at 328 K, confirming that the biosorption was favored by the temperature increase. The positive sign of $\Delta H^\circ$ indicates that the biosorption process was endothermic, corroborating the behavior shown in Fig. 7. The magnitude of $\Delta H^\circ$ suggests physical biosorption, mainly due electrostatic interactions (Machado et al. 2014), which is in accordance with the pH effect. The positive value of $\Delta S^\circ$ showed an increase in randomness at the solid–solution interface during the biosorption process. Considering Eq. (4), the term $T \Delta S^\circ$ contributed more than the term $\Delta H^\circ$ to find negative sign for $\Delta G^\circ$. This indicates that the biosorption process BW/CV was entropy controlled.

### Biosorption kinetics

The contact time is an important response in wastewater treatment plants. When biosorption occurs in a shorter time, the biosorbent is preferred for use in wastewater treatment. Here, the kinetics of CV biosorption was performed by varying the contact time from 0 to 150 min, pH 7.5, BW dosage of 1.0 g L$^{-1}$, and at different initial dye concentrations. Figure 8 shows the biosorption capacity as a function of time. In Fig. 8, it can be observed that the increase in CV initial concentration causes an increase in the biosorption capacity. This is due to the high concentration gradient. The curves presented two steps until they reach the equilibrium. A fast initial step occurred until 5 min, with high biosorption rate. From 5 to 105 min, the biosorption capacity increased, but, at a lower biosorption rate. The equilibrium time was reached at 105 min.

The pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich models were used to verify the best fit of kinetic biosorption data. CV biosorption kinetic parameters are shown in Table 5. The high values of $R^2 (R^2 > 0.976)$ and $R^2_{\text{adj}} (R^2_{\text{adj}} > 0.974)$ and the low ARE values ($\text{ARE} < 6.57\%$) shown in Table 5 indicated that the Elovich model was the most suitable to represent the experimental data of CV biosorption on BW. The Elovich model is often used for systems where the biosorbent surface is heterogeneous (Aljeboree et al. 2017). This is in agreement with the BW surface, which has

| Table 3 | Comparison of different materials used for the removal of CV from aqueous solutions in terms of capacity |
| Material | pH | $T$ (K) | $C_0$ (mg L$^{-1}$) | $q_m$ (mg g$^{-1}$) | Reference |
| BW | 7.5 | 328 | 50–200 | 131.24 | This work |
| Chitin nano whiskers | 8.0 | 298 | 250 | 39.56 | Gopi et al. (2016) |
| Coniferous pinus bark | 8.0 | 303 | 10–50 | 32.78 | Ahmad (2009) |
| Orange peel | 7.0 | 298 | 10–120 | 14.30 | Annadurai et al. (2002) |
| Functionalized carbon nanotubes | 8.0 | 298 | 50–150 | 90.52 | Sabna et al. (2016) |
| Biopolymers with peanut hull waste biomass | 7.0 | 323 | 50–150 | 100.60 | Tahir et al. (2017) |
| Date palm leaves | 10.0 | 328 | 15–50 | 37.74 | Ghazali et al. (2018) |
| Terminalia arjuna sawdust waste | 7.0 | 298 | 50 | 45.99 | Shakoor and Nasar (2018) |
| Biomass of Sapindus mukorossi | 4.0 | 318 | 100 | 28.00 | Samal et al. (2019) |
| Eggshells | 8.0 | 293 | 50 | 70.93 | Chowdhury et al. (2013) |

| Table 4 | Thermodynamic parameters for the biosorption of CV on BW |
| Temperature (K) | $\Delta G^\circ$ (kJ mol$^{-1}$) | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$) |
| 298 | $-28.42$ | 25.18 | 0.180 |
| 308 | $-30.04$ | 25.18 | 0.180 |
| 318 | $-32.02$ | 25.18 | 0.180 |
| 328 | $-33.75$ | 25.18 | 0.180 |

Fig. 8 Kinetic curves of the CV biosorption by BW
energetically different sites on the surface. Similar results were found by Grassi et al. (2019) in the kinetic assays of crystal violet cationic dye adsorption by the inactive biomass of the fungus Diaporthe Schini.

### Potential of BW for textile effluent treatment

Removal of the dyes present in the simulated textile effluent using BW was performed under the conditions described in Table 1, and using 1 g L\(^{-1}\) of biosorbent at pH of 7.5. This type of evaluation is important to verify the biosorbent behavior in situations where there are several dyes and salts in solution, which is common in textile effluents. In Fig. 9, it can be seen the visible spectra of the textile effluent before and after biosorption using BW. In the spectrum before treatment, there are two strong bands with higher values of absorbance. These bands are relative to the presence of the dyes crystal violet, red procion, basic fuchsin, and methylene blue. After the biosorption using BW, the spectrum was strongly amortized, showing that biosorption using BW was efficient to treat the simulated textile effluent. In quantitative terms, the color removal was 85%, demonstrating that BW is an efficient and promising material for the treatment of effluents containing dyes and salts, presenting a high potential in multiple component systems. For comparison, Georgin et al. (2018) showed a removal percentage of around 80% using Araucaria angustifolia bark to treat a simulated dye house effluent containing various dyes and inorganic salts.

### Conclusions

Sugarcane BW, a residue generated in the solid state fermentation, was evaluated as a potential biosorbent to treat textile effluents containing crystal violet dye. This is important from the total environment viewpoint, since it is a possibility to add value for a SSF waste. The biosorption equilibrium and kinetics were represented, respectively, by the Liu and Elovich models. The biosorption of CV on BW was a physical and endothermic process. The best operation conditions for the biosorption process were 328 K, pH of 7.5, and BW dosage of 1.0 g L\(^{-1}\). In such conditions, the biosorption capacity was 131.2 mg g\(^{-1}\), which is a competitive value comparing with other used materials. The application of the biosorbent in the simulated effluent showed that BW is an efficient material to treat textile effluents containing dyes and salts, removing up to 85% of its color. In summary, SSF of sugarcane bagasse using the fungus Metarhizium anisopliae generates, at the same time, enzymes as main product, and a biosorbent (BW) as co-product. The BW co-product, in turn, is a promising material to treat textile effluents by biosorption.

### References

Abdolali A, Ngo HH, Guo W, Zhou JL, Zhang J, Liang S, Chang SW, Nguyen DD, Liu Y (2017) Application of a breakthrough biosorbent for removing heavy metals from synthetic and real wastewaters in a lab-scale continuous fixed-bed column. Bioresour Technol 229:78–87

Ahmad R (2009) Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP). J Hazard Mater 171:767–773

Aita BC, Spannemberg SS, Schmaltz S, Zabot GL, Tres MV, Kuhn RC, Mazutti MA (2019) Production of cell–wall degrading enzymes by solid–state fermentation using agroindustrial residues as substrates. J Environ Chem Eng 7:103–113
from biological sludge and its application for dyes removal from aqueous solutions. Sci Total Environ 660:277–287
Tahir N, Bhatti HN, Iqbal M, Noreen S (2017) Biopolymers composites with peanut hull waste biomass and application for crystal violet adsorption. Int J Biol Macromol 94:210–220
Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, Sing KSW (2015) Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). Pure Appl Chem 87:1051–1069
Xu Z, Wang Q, Jiang Z, Yang XX, Ji Y (2007) Enzymatic hydrolysis of pretreated soybean straw. Biomass Bioenergy 31:162–167
Yagub MT, Sen TK, Afroze S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: a review. Adv Colloid Interf Sci 209:172–184
Zeldowitsch J (1934) Über den mechanismus der katalytischen oxydation von CO an MnO2. Acta Physicochim URSS 1:364–449
Zhang L, Sellaoui L, Franco DSP, Dotto GL, Bajahzar A, Belmabrouk H, Bonilla-Petriciolet A, Oliveira MLS, Li Z (2019) Adsorption of dyes brilliant blue, sunset yellow and tartrazine from aqueous solution on chitosan: analytical interpretation via multilayer statistical physics model. Chem Eng J In press:122952

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.