Removal of Cibacron Brilliant Yellow 3G-P Dye from Aqueous Solutions by Brazilian Peats as Biosorbents

SUZIMARA ROVANI, ANDREIA N. FERNANDES, LIZIE D. T. PROLA, EDER C. LIMA, WMEKSON O. SANTOS, AND MATTHEW A. ADEBAYO

Institute of Chemistry, Federal University of Rio Grande do Sul (UFRGS), Porto Alegre, Brazil

Two Brazilian peat samples in different stages of decomposition, fibrous peat (FP) and decomposed peat (DP), were used as biosorbents for the removal of the textile dye Cibacron Brilliant Yellow 3G-P (CBY) from aqueous solutions. These biosorbents were characterized by Fourier transform-infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The effects of initial pH of dye solution and contact time between the dye and the biosorbents on the biosorption capacities were studied. Based on an error function ($F_{error}$) the general-order kinetic model provided the best fit to the experimental data compared with the pseudo-first-order and pseudo-second-order kinetic biosorption models. The equilibrium data were fitted to Langmuir, Freundlich, and Liu isotherm models. For both biosorbents the equilibrium data were best fitted to the Liu isotherm model. Simulated dye house effluents were used to check the applicability of the proposed biosorbents for effluent treatment.

Keywords Biosorption; General-order kinetic equation; Nonlinear isotherm fitting; Peat; Thermodynamics

Introduction

Many industries such as food, textile, leather, paper, and cosmetics use dyes to color their final products. As a consequence, large amounts of dyes are released to water effluents. The disposal of dye-contaminated effluents to the environment often leads to the following problems: coloration of natural waters, generating an aesthetic problem (Dotto et al., 2012; Shirsath et al., 2013); increase of chemical oxygen demand (COD) of the receiving water; and decrease in sunlight penetration, precluding the photosynthesis of aqueous flora (Galán et al., 2013; Hamzeh et al., 2012). Moreover, most dyes can also cause allergies (Davies and Johnston, 2011) and dermatitis (Sánchez-Gilo et al., 2010) and also lead to cancer (de Lima et al., 2007) and mutations in humans (Carneiro et al., 2010; de Lima et al., 2007). Therefore,
effluents containing dyes require treatment before being released to the environment (de Menezes et al., 2012; Gundogdu et al., 2012; Machado et al., 2011).

It is rather difficult to treat dye effluents; they are recalcitrant species because of their complex aromatic molecular structure (Eren, 2012; Prato-Garcia and Buitrón, 2011), making them more stable and nonbiodegradable (Cardoso et al., 2011; Wang and Li, 2013). One of the most employed methods for the removal of synthetic dyes from aqueous effluents is adsorption (Alencar et al., 2012a; Çelekli et al., 2012) due to its simplicity and high efficiency, as well as the availability of a wide range of adsorbents that could be applied (Alencar et al., 2012b; Young et al., 2012). This process transfers the dye from the aqueous effluent to a solid phase, markedly decreasing the dye bioavailability to live organisms (Alver, and Metin, 2012; Calvete et al., 2009; Cardoso et al., 2012). The decontaminated effluent could then be released to the environment or the water could be reutilized in the industrial process (Allen et al., 2004). Subsequently, the adsorbent can be regenerated or stored in a dry place without direct contact with the environment (Çelekli et al., 2012; Ip et al., 2009).

Activated carbon is the most employed adsorbent for dye removal from aqueous solution because of its excellent adsorption properties (Calvete et al., 2009; Li et al., 2011; Machado et al., 2011). However, the use of activated carbon for dye removal from industrial effluents is expensive due to its high initial and regeneration costs (Machado et al., 2011), limiting its widespread application for wastewater treatment. Therefore, there is growing interest in finding alternative low-cost adsorbents for dye removal from aqueous solution. Among these alternative adsorbents can be cited: modified chitosan (Piccin et al., 2009; Young, et al., 2012), microalgae (Dotto et al., 2012), modified cellulose (Wang and Li, 2013), beet pulp (Dursun and Tepe, 2011), grape bagasse (Antunes et al., 2012), aquatic plants (Gulnaz et al., 2011), de-oiled mustard (Gupta et al., 2010), de-oiled soya (Mittal et al., 2013), and peat (Allen et al., 2004; Fernandes et al., 2007, 2010; Ho and McKay, 1998; Ip et al., 2009; Ramakrishna and Viraraghavan, 1997).

Peat is a mixture of compounds formed by the decomposition of plant residues and mineral materials that have accumulated at the bottom of ponds and flooded depressions in riverine areas (Allen et al., 2004; Girardello et al., 2013; Ip et al., 2009). Peat is an organic material (<25% by weight mineral matter), whose color ranges from blond to black and is usually formed in regions where there is a lack of oxygen and where the accumulation of organic matter (OM) occurs more rapidly than its decomposition (Allen et al., 2004; Girardello et al., 2013; Ip et al., 2009). Under these conditions, a deposit of OM can reach thicknesses of several meters and occupy large areas, constituting a peatland (Girardello et al., 2013). These materials are composed mainly of lignin, cellulose, and humic substances, presenting functional groups such as carboxylic acids and phenolic or alcoholic hydroxyls, which improve the biosorption of organic molecules by peat (Fernandes et al., 2007, 2010; Girardello et al., 2013). In light of these characteristics, peat represents a powerful natural adsorbent for the removal of dyes from aqueous effluents.

There are several applications of peats as biosorbent for removal of acid and basic dyes from aqueous solutions reported in the literature (Allen et al., 2004; Ho and McKay, 1998; Ip et al., 2009; Ramakrishna and Viraraghavan, 1997; Srinivasan and Viraraghavan, 2010). In this work, a fibrous peat (FP) and a decomposed peat (DP) are proposed for the first time as potential biosorbents for removal of Cibacron Brilliant Yellow 3G-P (CBY) textile dye from aqueous solutions. This dye belongs to the reactive class, one of the most employed dye classes for dying cotton. A new
kinetic biosorption model was developed to study the biosorption of the dye on the FP and DP biosorbents.

**Experimental Section**

**Solutions and Reagents**

De-ionized water was used throughout the experiments for solution preparations. The textile dye Cibacron Brilliant Yellow 3G-P (CBY; C.I. 18972; CAS 50662-99-2; C_{25}H_{15}N_{9}Cl_{3}O_{10}S_{3}Na_{3}, 872.96 \text{ g.mol}^{-1}, \lambda_{\text{max}} = 402 \text{ nm}, \text{see Supplementary Figure 1}), at 99% purity, was furnished by Acros (Geel, Belgium). The dye was used without further purification. The CBY dye has three-sulfonate groups. These groups

![FT-IR vibrational spectra](image)

**Figure 1.** FT-IR vibrational spectra: (A) DP, (B) FP. The number indicated for the bands corresponds to wave numbers that are expressed in cm\(^{-1}\).
have negative charges even in highly acidic solutions because their $pK_a$ values are lower than zero (Roberts and Caserio, 1977). The stock solution was prepared by dissolving the dye in distilled water to the concentration of 5.00 g L$^{-1}$. Working solutions were obtained by diluting the dye stock solutions to the required concentrations. To adjust the pH solutions, 0.50 mol L$^{-1}$ sodium hydroxide solution or 0.50 mol L$^{-1}$ hydrochloric acid solution was used. The pH of the solutions was measured using a Schott Lab 850 set pH meter (Zwiesel, Germany).

**Biosorbent Preparation and Characterization**

The peat samples were collected from a peatland situated in the town of Balneário Arroio do Silva (Santa Catarina State, southern Brazil) as already described in the literature (Girardello et al., 2013). The two sampling points are situated in a region where the incidence of vegetation is dominated mainly by mosses and other bryophytes, sedges, grasses, shrubs, and small-sized trees. The classification of the samples was carried out in situ using the method proposed by von Post (1924). According to this method, the first sample (named decomposed peat, DP) was classified as H$_7$ and the second sample (named fibrous peat, FP) as H$_3$ (von Post, 1924). Prior to the experiments, the samples were washed with distilled water for 72 h, then dried at 343 K in an air supplied oven for 8 h. After that, the biosorbent was ground in a disk mill and subsequently sieved. Sample particles of diameters < 106 µm were used (Cardoso et al., 2011).

The DP and FP biosorbents were characterized by vibrational spectroscopy in the infrared region with Fourier transform-infrared (FT-IR) spectroscopy using a Varian spectrometer (Lake Forest, Calif., USA), model 640-IR, using KBr pellets, in the 4000 and 400 cm$^{-1}$ regions, with resolution of 4 cm$^{-1}$, by accumulating 100 scans (Vaghetti et al., 2003).

The scanning electron microscopy (SEM) images of DP and FP biosorbents were obtained with a Shimadzu SM4-550 (Kyoto Japan) scanning electron microscope operating at 15 keV. The peat samples were previously coated with a thin gold layer in a diode sputtering system for 10 min before analysis (Jacques et al., 2007a).

The point of zero charge ($pH_{pzc}$) of the adsorbent was determined by adding 20.00 mL of 0.100 mol L$^{-1}$ NaNO$_3$ with a previously adjusted initial pH ($pH_i$); values of the solutions were adjusted from 2.0 to 11.0 by adding 0.10 mol L$^{-1}$ HCl and/or 0.10 mol L$^{-1}$ NaOH to several 50.0 mL flat-bottom Falcon tubes containing 50.0 mg of the biosorbent, which was immediately securely capped. The suspensions were shaken in an acclimatized shaker (Oxylab, São Leopoldo, Brazil) at 298 K and allowed to equilibrate for 24 h. The suspensions were then centrifuged at 3,600 rpm for 5 min to separate the adsorbent from the aqueous solution. The initial pH values ($pH_i$) of the solutions were accurately measured using the solutions that had no contact with the solid biosorbent; and the final pH ($pH_f$) values of the supernatant after the contact with the solid were recorded. The value of $pH_{pzc}$ is the point where the curve of ΔpH ($pH_f – pH_i$) versus $pH_i$ crosses the line equal to zero (Calvete et al., 2009).

**Biosorption Studies**

The biosorption studies for evaluation of the DP and FP biosorbents for the removal of the CBY dye from aqueous solutions were carried out in triplicate using the batch contact biosorption method (Jacques et al., 2007b). For these experiments, 50.0 mg
of biosorbent was placed in different 50-mL flat-bottom Falcon tubes, each containing 20.0 mL of dye solution (20.00 to 200.0 mg L\(^{-1}\)) which were agitated for a suitable time (0.0833 to 8.00 h) in an acclimatized shaker (Oxylab, São Leopoldo, Brazil) at temperatures ranging from 298 to 323 K. The pH of the dye solutions ranged from 2.0 to 10.0. Subsequently, in order to separate the adsorbent from the aqueous solutions, the flasks were centrifuged at 14,000 rpm for 5 min using a Unicen M Herolab centrifuge (Stuttgart, Germany), and aliquots (1–10 mL) of the supernatant were properly diluted with an aqueous solution fixed at pH 2.0. The final concentrations of the dyes remaining in the solution were determined by visible spectrophotometry using a T90+ UV-VIS spectrophotometer furnished by PG Instruments (London, UK) provided with quartz optical cells. Absorbance measurements were made at the maximum wavelength (402 nm) of CBY dye.

The amount of dye uptaken and the percentage of removal of the dye by the biosorbents were calculated by applying Equations (1) and (2), respectively:

\[ q = \frac{(C_o - C_f)}{m} \times V \]  
\[ \% \text{Removal} = 100 \times \frac{(C_o - C_f)}{C_o} \]  

where \( q \) is the amount of dye adsorbed by the biosorbent (mg g\(^{-1}\)), \( C_o \) is the initial dye concentration put in contact with the biosorbent (mg L\(^{-1}\)), \( C_f \) is the dye concentration (mg L\(^{-1}\)) after the batch biosorption procedure, \( m \) is biosorbent mass (g), and \( V \) is the volume of dye solution (L).

The desorption experiments were carried out according to the following procedure: 50.0 mg L\(^{-1}\) of CBY dye was shaken with 50.0 mg of DP and FP biosorbents for 1 h; afterwards, the loaded biosorbent was filtered by 0.2 \( \mu \)m cellulose acetate and washed with water to remove the non-adsorbed dye. Then the dye adsorbed on the adsorbent was agitated with 20.0 mL of: 0.05–0.5 mol L\(^{-1}\) NaCl aqueous solutions, 0.05–0.50 mol L\(^{-1}\) NaCl + 0.05 mol L\(^{-1}\) HCl, 0.20–0.30 mol L\(^{-1}\) HCl, and ethanol + water mixtures (10–100% EtOH) for 15–60 min. The desorbed dyes were separated and estimated as described above.

**Kinetic Biosorption Models**

As reported previously (Liu and Liu, 2008; Liu and Shen, 2008), in the sense of a chemical reaction or process, a rate law’s exponents are generally unrelated to the chemical equation’s coefficients, but they sometimes are the same by coincidence. This means that there is no way to predict the reaction order without experimental data. In order to establish a general rate law equation for biosorption, the biosorption process on the surface of the adsorbent is assumed to be the rate-controlling step. In this case, attention is turned from adsorbate concentration in bulk solution to change in the effective number of biosorption sites at the surface of the biosorbent during biosorption. If the reaction rate law is applied to Equation (3), the following rate expression for biosorption can be obtained:

\[ \frac{dq}{dt} = k_N(q_e - q_t)^n \]  

where \( k_N \) is the rate constant, \( q_e \) is the equilibrium dye concentration, \( q_t \) is the adsorbed dye concentration at time \( t \).
in which $k_N$ is the rate constant, $n$ is the biosorption reaction order with regard to the effective concentration of the biosorption sites available on the surface of the adsorbent, $q_e$ is the amount adsorbed at equilibrium, and $q_t$ is the amount adsorbed at any time. Equation (3) is the result of application of the universal rate law to a biosorption process and can be used without any further assumption (Liu and Liu, 2008; Liu and Shen, 2008). Theoretically, the exponent $n$ in Equation (3) can be an integral or rational nonintegral number (Liu and Liu, 2008; Liu and Shen, 2008).

The number of biosorption sites ($h_t$) available on the surface of the adsorbent is defined by the following equation:

\[
h_t = \frac{1}{C_0} \frac{q_t}{q_e} \quad (4)
\]

The following equation describes the rate of biosorption in the function of variable ($\theta_t$):

\[
\frac{d\theta_t}{dt} = -k \cdot \theta_t^n \quad (5)
\]

where

\[
k = k_N (q_e)^{n-1}
\]

For a virgin adsorbent $\theta_t$ equals 1, and it tends to decrease during biosorption. When the biosorption process reaches its equilibrium, $\theta_t$ tends to a fixed value. If the saturation of the adsorbent occurs, $\theta_t$ would become zero (Machado et al., 2012).

Integrating Equation (5),

\[
\int_1^0 \frac{d\theta_t}{\theta_t^n} = -k \int_0^t dt
\]

This leads to:

\[
\frac{1}{1-n} \cdot [\theta_t^{1-n} - 1] = -k \cdot t \quad (7)
\]

This results in:

\[
\theta_t = [1 - k \cdot (1 - n) \cdot t]^{1/(1-n)} \quad (8)
\]

Applying the definition of parameter $k$ given by Equation (4) on Equation (8), we obtain:

\[
q_t = q_e - \frac{q_e}{[k_N (q_e)^{n-1} \cdot t \cdot (n - 1) + 1]^{1/(n-1)}} \quad (9)
\]

Equation (9) is the general kinetic biosorption equation that is valid for $n \neq 1$.

The pseudo-first-order kinetic model is a special case of Equation (5), when $n = 1$ (Liu and Liu, 2008; Liu and Shen, 2008).

\[
\frac{d\theta_t}{dt} = -k \cdot \theta_t^n \quad (10)
\]
Integrating Equation (10) gives:

\[ \theta_t = \exp(-k \cdot t) \]  

(11)

Substituting Equation (4) and the \( k = k_1 \) in Equation (11), we obtain the pseudo-first-order kinetic model:

\[ q_t = q_e[1 - \exp(-k_1 \cdot t)] \]  

(12)

Therefore, the pseudo-first-order kinetic equation (Lagernren’s equation) is a special case of general kinetic biosorption.

The pseudo-second-order kinetic model (Ho, 2006) is a special case of Equation (9) (general-order kinetic equation) when \( n = 2 \). Therefore:

\[ q_t = q_e - \frac{q_e}{k_2(q_e) \cdot t + 1} \]  

(13)

Rearranging this equation it leads to:

\[ q_t = \frac{q_e^2 k_2 t}{k_2(q_e) \cdot t + 1} \]  

(14)

The intraparticle diffusion equation was early defined (Weber and Morris, 1963) as:

\[ q_t = k_{id} \sqrt{t} + C \]  

(15)

where \( k_{id} \) is the intraparticle diffusion rate constant (\( \text{mg g}^{-1} \text{h}^{-0.5} \)) and \( C \) is a constant related to the thickness of the boundary layer (\( \text{mg g}^{-1} \)).

In this work the pseudo-first-order (Equation (12)), pseudo-second-order (Equation (14)), general-order equation (Equation (9)), and intraparticle diffusion (Equation (15)) models were utilized for evaluating the kinetics of biosorption of the dye on the biosorbents.

**Equilibrium Models**

The equilibrium of biosorption was evaluated by using the following isotherm models.

**Langmuir isotherm model** (Langmuir, 1918):

\[ q_e = \frac{Q_{max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \]  

(16)

where \( q_e \) is the amount of adsorbate adsorbed at equilibrium (\( \text{mg g}^{-1} \)), \( Q_{max} \) is the maximum biosorption capacity of the biosorbet (\( \text{mg g}^{-1} \)), \( K_L \) is the Langmuir equilibrium constant (\( \text{L mg}^{-1} \)), and \( C_e \) is the dye concentration at equilibrium (\( \text{mg L}^{-1} \)).

**Freundlich isotherm model** (Freundlich, 1906):

\[ q_e = K_F \cdot C_e^{1/n_F} \]  

(17)
where $K_F$ is the Freundlich equilibrium constant (mg g$^{-1}$ (mg L$^{-1}$)$^{-1/n_F}$) and $n_F$ is a dimensionless exponent of the Freundlich equation.

Liu isotherm model (Liu et al., 2003):

$$q_e = \frac{Q_{\text{max}} \cdot (K_g \cdot C_e)^{n_L}}{1 + (K_g \cdot C_e)^{n_L}}$$  \hspace{1cm} (18)

where $K_g$ is the Liu equilibrium constant (L mg$^{-1}$), $n_L$ is the dimensionless exponent of the Liu equation, and $Q_{\text{max}}$ is the maximum biosorption capacity of the adsorbent (mg g$^{-1}$).

**Quality Assurance and Statistical Evaluation of the Kinetic and Isotherm Parameters**

To establish the accuracy, reliability, and reproducibility of the collected data, all the batch biosorption measurements were performed in triplicate. Blanks were run in parallel, and they were corrected when necessary (Barbosa et al., 1999).

All dye solutions were stored in glass flasks, which were cleaned by soaking in 1.4 mol L$^{-1}$ HNO$_3$ for 24 h (Lima et al., 2003), rinsing five times with deionized water, dried, and stored in a flow hood.

For analytical calibration, standard solutions with concentrations ranging from 5.00 to 150.0 mg L$^{-1}$ of dye were employed, running against a blank solution of water adjusted to pH 2.0. The linear analytical calibration of the curve was furnished by the UVW in software of the T90+ PG Instruments spectrophotometer. The detection limit of the method, obtained with a signal/noise ratio of 3 (Lima et al., 1998), was 0.13 mg L$^{-1}$ of CBY. All the analytical measurements were performed in triplicate, and the precision of the standards was better than 3% ($n = 3$). For checking the accuracy of the CBY dye sample solutions during the spectrophotometric measurements, standards containing dyes at 50.0 mg L$^{-1}$ were employed as a quality control after every five determinations (Lima et al., 1998).

The kinetic and equilibrium models were fitted by employing a nonlinear method, with successive interactions calculated by the Levenberg-Marquardt method and also by the Simplex method, using the nonlinear fitting facilities of the software Microcal Origin 7.0. In addition, the models were also evaluated by determination coefficient ($R^2$), adjusted determination coefficient ($R_{adj}^2$), and an error function ($F_{\text{error}}$) (Calvete et al., 2010), which measures the differences in the amount of dye taken up by the biosorbent predicted by the models and the actual $q$ measured experimentally. $R^2$, $R_{adj}^2$, and $F_{\text{error}}$ are given below, in Equations (19), (20), and (21) respectively:

$$R^2 = \left( \frac{\sum_i^n (q_{i,\text{exp}} - \bar{q}_{i,\text{exp}})^2 - \sum_i^n (q_{i,\text{exp}} - q_{i,\text{model}})^2}{\sum_i^n (q_{i,\text{exp}} - \bar{q}_{i,\text{exp}})^2} \right)$$ \hspace{1cm} (19)

$$R_{adj}^2 = 1 - (1 - R^2) \cdot \left( \frac{n - 1}{n - p} \right)$$ \hspace{1cm} (20)
where $q_{i, \text{model}}$ is each value of $q$ predicted by the fitted model, $q_{i, \text{exp}}$ is each value of $q$ measured experimentally, $q_{\text{exp}}$ is the average of $q$ experimentally measured, $n$ is the number of experiments performed, and $p$ is the number of parameters of the fitted model (Royer et al., 2009).

**Simulated Dye House Effluent**

One synthetic dye house effluent containing four representative reactive dyes and one direct dye used for coloring fibers and their corresponding auxiliary chemicals was prepared at pH 2.0, using a mixture of different dyes typically used in textile industries. According to practical information obtained from a dye house, usually 20–60% of the reactive dyes and 100% of the dye bath auxiliaries remain in the spent dye bath (Hessel et al, 2007); this undergoes a 5- to 30-fold dilution during subsequent washing and rinsing stages (Calvete et al, 2009; Machado et al., 2011). The concentrations of the dyes and auxiliary chemicals selected to imitate an exhausted dye bath are given in Table I.

**Results and Discussion**

**Characterization of Biosorbents**

The FT-IR technique was used to examine the surface groups of the biosorbents (DP and FP) and to identify the groups responsible for dye biosorption. Infrared spectra of the samples were recorded in the range 4000–400 cm$^{-1}$ (Figure 1). Before the

| Dye                  | Concentration (mg L$^{-1}$) | $\lambda$ (nm) | Effluent |
|----------------------|------------------------------|----------------|----------|
| Reactive dyes        |                              |                |          |
| Cibacron Brilliant Yellow 3G-P | 20.00                        | 402            |          |
| Reactive Red 194     |                              | 505            | 5.00     |
| Reactive Orange 16   |                              | 493            | 5.00     |
| Reactive Black 5     |                              | 598            | 5.00     |
| Direct dye           |                              |                |          |
| Direct Blue 53       |                              | 607            | 5.00     |
| Auxiliary chemicals  |                              |                |          |
| Na$_2$SO$_4$         | 80.0                         |                |          |
| NaCl                 | 80.0                         |                |          |
| Na$_2$CO$_3$         | 50.0                         |                |          |
| CH$_3$COONa          | 50.0                         |                |          |
| CH$_3$COOH           | 300.0                        |                |          |
| pH                   | 2.0*                         |                |          |

*pH of the solution adjusted with 0.10 mol L$^{-1}$ HCl and NaOH.
biosorption of the CBY dye by both biosorbents, the vibrational FT-IR presented the characteristics described as follows. The intense absorption bands at 3187 and 3345 cm\(^{-1}\) are assigned to O–H and N–H stretching of various functional groups for DP and FP, respectively (Girardello et al., 2013). The absorption bands that appear in 2929 and 2851 cm\(^{-1}\) for DP and 2923 and 2850 cm\(^{-1}\) for FP are associated with asymmetric and symmetric C–H stretching of the CH\(_2\) groups of aliphatic hydrocarbons (Sathishkumar et al., 2010; Zaccone et al., 2007). These bands are more evident in biosorbent FP, confirming their lower stages of decomposition (Girardello et al., 2013). Bands at 1780 and 1715 cm\(^{-1}\) for DP and FP, respectively, are attributed to the C=O stretching of the acids, aldehydes, and ketones. Absorption bands at 1655 and 1615 cm\(^{-1}\) are assigned to C=C stretching of aromatic rings. Several bands in the range of 1632–1323 cm\(^{-1}\) are assigned to ring modes of the aromatic rings (Antunes et al., 2012; Girardello et al., 2013). In the region between 1270 and 1000 cm\(^{-1}\), where the absorption bands are attributed to C–O stretching of the aryl-esters, esters, and phenols, there are relevant differences between the two samples. These bands are more intense in the spectra of the biosorbent DP, indicating differences in the relative percentages of these groups in the peats. The FT-IR spectra of both biosorbents after biosorption of the dye presented basically the same vibrational bands of the biosorbent before biosorption (see Supplementary Figure 2). Similar behavior was reported in the literature for the adsorption of the dye Victazol Orange 3 R on mango seeds (Alencar et al., 2012a).

Scanning electron micrographs of DP and FP (Figure 2) show the differences of these materials. In this case, it can be verified that the DP aggregates are highly compact, with a globular-like structure, while the FP aggregates show a predominantly fiber-like structure. This latter structure (in the case of the FP sample) is in agreement with its classification (Girardello et al., 2013), where plant remains may be recognizable.

**Effect of Initial pH**

One of the most important factors that influences the biosorption of a dye on a solid biosorbent is pH of the adsorbate solution (Ghaedi et al., 2013; Royer et al., 2010). Different dyes will present different ranges of suitable pH depending on the type of biosorbent used. Effects of initial pH on percentage of removal of CBY dye solution (50 mg L\(^{-1}\)) using DP and FP biosorbents were evaluated within the pH range 2–10 (Figure 3). For the DP biosorbent, the percentage of dye removal was markedly decreased with increase in pH, from 43.8% dye removal at pH 2.0 to less than 4% dye removal at pH 7.0. For the FP biosorbent, the percentage of dye removal also decreased, from 72.1% at pH 2.0 to 5.7% at pH 7.0.

The point of zero charge (pH\(_{PZC}\)) of DP and FP biosorbents are 3.51 and 4.50, respectively. For pH values lower than pH\(_{PZC}\), the biosorbent presents a positive surface charge (Calvete et al., 2009). The dissolved CBY dye is negatively charged in water solutions, because it has three sulfonate groups (Roberts and Caserio, 1977). The biosorption of CBY dye takes place when the biosorbent has a positive surface charge (Calvete et al., 2009). For DP the electrostatic interaction occurs for pH < 3.51, and for FP this interaction occurs for pH < 4.50. However, when the pH value is much lower than pH\(_{PZC}\), the surface of the biosorbent becomes more positive (Mital et al., 2013). This behavior explains the high biosorption capacity of both biosorbents for CBY dye at pH 2.0. In order to continue biosorption studies,
the initial pH of dye solutions was fixed at 2.0. Under these conditions, there was no significant change in the final pH of the dye solution after the biosorption experiments (<3%).

**Kinetic Studies**

Biosorption kinetic studies are important in the treatment of dye containing aqueous effluents because they provide valuable information on the mechanism of the biosorption process (Alencar et al., 2012a, 2012b).

For evaluating the kinetics of biosorption of CBY dye using the DP and FP biosorbents, the nonlinear pseudo-first-order, pseudo-second-order, and general-order kinetic biosorption models were tested, as shown in Figures 4 and 5. The kinetic

![Figure 2. SEM images of (A) DP with magnification of 1,000×, (B) FP with magnification of 1,000×. Accelerating voltage: 15 keV.](image)
Figure 3. Effect of pH on the biosorption of CBY dye, using DP and FP biosorbents. Conditions: \( C_0 = 50.0 \text{ mg L}^{-1} \) dye solution; temperature, 298 K; mass of biosorbent, 50.0 mg.

Figure 4. Kinetic biosorption curves of CBY dye using DP biosorbent: (A) \( C_0, 50.0 \text{ mg L}^{-1} \); (B) \( C_0, 100.0 \text{ g L}^{-1} \); (C) \( C_0, 50.0 \text{ mg L}^{-1} \); (D) \( C_0, 100.0 \text{ mg L}^{-1} \). Conditions: pH 2.0; DP biosorbent mass, 50.0 mg; temperature, 298 K.
parameters for the three kinetic models are listed in Table II. Taking into account that the experimental data were fitted to nonlinear kinetic models, an error function ($F_{error}$) was used to evaluate the fitting of the experimental data. The lower the $F_{error}$, the lower the difference of the $q$ calculated by the model from the experimentally measured $q$ (see Equation (21)). It should be pointed out that the $F_{error}$ utilized in this work takes into account the number of fitted parameters ($p$ term in Equation (21)); it has been reported in the literature (El-Khaiary and Malash, 2011; El-Khaiary, et al., 2010) that depending on the number of parameters present in a nonlinear equation, it has the best fitting of the results. For this reason, the number of fitting parameter should be considered in the calculation of $F_{error}$.

In order to compare the different kinetic models, the $F_{error}$ of each individual model was divided by the $F_{error}$ of minimum value ($F_{error}$ ratio). It was observed that the minimum $F_{error}$ values were obtained by the general-order kinetic model. The pseudo-first-order kinetic model has $F_{error}$ ratio values ranging from 1.96 to 2.02 (DP) and 2.02 to 2.48 (FP). Also, for the pseudo-second-order model, the $F_{error}$ ratio values ranged from 2.02 to 2.24 (DP) and 2.36 to 3.29 (FP). These results indicate that the general-order kinetic model should best explain the biosorption process of CBY dye using DP and FP biosorbents.

Figure 5. Kinetic biosorption curves of CBY dye using FP biosorbent: (A) $C_o$, 50 mg L$^{-1}$; (B) $C_o$, 100.0 mg L$^{-1}$; (C) $C_o$, 50.0 mg L$^{-1}$; (D) $C_o$, 100.0 mg L$^{-1}$. Conditions: pH 2.0; FP biosorbent mass, 50.0 mg; temperature, 298 K.
Taking into account that the general-order kinetic equation presents different orders ($n$) when the concentration of the adsorbate is changed (see Table II), it is difficult to compare the kinetic parameters of the model. Therefore, it is useful to use the initial sorption rate $h_0$ (Ho and McKay, 1998) to evaluate the kinetics of a given model using the following equation:

$$h_0 = \frac{k_n}{q_e}$$ (22)

In which $h_0$ is the initial sorption rate (mg g$^{-1}$ h$^{-1}$), $k_n$ is the rate constant (h$^{-1}$ (g mg$^{-1}$)$n^{-1}$), $q_e$ is the amount biosorbed at equilibrium (mg g$^{-1}$), and $n$ is the order of the kinetic model. It should be stressed that when $n = 2$, this equation is the same as initial the sorption rate first introduced by Ho and McKay (1998). It was observed that increasing the initial dye concentration led to an increase in the initial sorption rate for all kinetic models, as expected, indicating that there is coherence with the experimental data. Taking into account that the kinetic data were better fitted by the general-order kinetic model, since the order of a biosorption process should follow the same logic as a chemical reaction, where the order is experimentally measured (Alencar et al., 2012b), instead of being subjected to a previously

### Table II. Kinetic parameters for CBY biosorption using DP and FP biosorbent; conditions: temperature, 298 K; pH 2.0; mass of biosorbent, 50.0 mg

| Kinetic Model          | DP (50.00 mg L$^{-1}$) | FP (50.00 mg L$^{-1}$) | 100.00 mg L$^{-1}$ | 50.00 mg L$^{-1}$ | 100.00 mg L$^{-1}$ |
|------------------------|------------------------|------------------------|-------------------|-------------------|-------------------|
| **Pseudo-first order** |                        |                        |                   |                   |                   |
| $k_1$ (h$^{-1}$)       | 0.918                  | 0.968                  | 1.45              | 1.42              |
| $q_e$ (mg g$^{-1}$)    | 8.23                   | 12.8                   | 14.28             | 19.9              |
| $h_0$ (mg g$^{-1}$ h$^{-1}$) | 7.56                  | 12.4                   | 20.67             | 28.3              |
| $R_{adj}^2$            | 0.9972                 | 0.9975                 | 0.9964            | 0.9972            |
| $F_{error}$            | 0.1549                 | 0.2296                 | 0.2928            | 0.3590            |
| **Pseudo-second order** |                        |                        |                   |                   |                   |
| $k_2$ (g mg$^{-1}$ h$^{-1}$) | 0.103                 | 0.0709                 | 0.1088            | 0.0768            |
| $q_e$ (mg g$^{-1}$)    | 9.79                   | 15.2                   | 16.2              | 22.5              |
| $h_0$ (mg g$^{-1}$ h$^{-1}$) | 9.90                  | 16.3                   | 28.5              | 39.0              |
| $R_{adj}^2$            | 0.9973                 | 0.9967                 | 0.9951            | 0.9951            |
| $F_{error}$            | 0.1545                 | 0.2632                 | 0.3420            | 0.4769            |
| **General order**      |                        |                        |                   |                   |                   |
| $k_N$ (h$^{-1}$ (g mg$^{-1}$)$n^{-1}$) | 0.471                 | 0.468                  | 0.666             | 0.638             |
| $q_e$ (mg g$^{-1}$)    | 8.65                   | 13.4                   | 14.7              | 20.4              |
| $N$                    | 1.34                   | 1.31                   | 1.33              | 1.30              |
| $h_0$ (mg g$^{-1}$ h$^{-1}$) | 8.56                  | 13.9                   | 23.5              | 31.9              |
| $R_{adj}^2$            | 0.9993                 | 0.9993                 | 0.9991            | 0.9995            |
| $F_{error}$            | 0.0767                 | 0.1173                 | 0.1447            | 0.1449            |
| **Intraparticle**      |                        |                        |                   |                   |                   |
| $k_{id,2}$ (mg g$^{-1}$ h$^{-0.5}$) | 1.95                  | 3.15                   | 2.95              | 3.94              |
| $R^2$                  | 0.9816                 | 0.9978                 | 0.9867            | 0.9859            |

*Second stage.*
stipulated model, more confident initial sorption rates \((h_0)\) were obtained by the general-order kinetic model.

The intraparticle diffusion model (Weber and Morris, 1963) was also used to verify the influence of mass transfer resistance on the binding of CBY dye to the biosorbents (Table II and Figures 4C, 4D, 5C, and 5D). The intraparticle diffusion constant, \(k_{id} (\text{mg g}^{-1} \text{h}^{-0.5})\), can be obtained from the slope of the plot of \(q_t\) versus the square root of time. These figures show the plots of \(q_t\) versus \(t^{1/2}\), with three linear sections for CBY dye using the DP and FP biosorbents. These results imply that the biosorption processes involve more than one sorption rate. For both biosorbents, the biosorption process exhibits three stages, which can be attributed to each linear section of Figures 4C, 4D, 5C, and 5D. The first linear section was attributed to the diffusional process of the dye to the biosorbent surface; hence, it was the fastest sorption stage. The second section, ascribed to intraparticle diffusion, was a delayed process. The third stage may be regarded as diffusion through smaller pores, which is followed by the establishment of equilibrium (Cardoso et al., 2011). The \(k_{id}\) values for biosorption of CBY on FP biosorbent are 51.3\% (50.00 mg L\(^{-1}\)) and 25.1\% (100.00 mg L\(^{-1}\)) higher than the value for \(k_{id}\) obtained for the biosorption of CBY dye on DP biosorbent, for the same initial dye concentration. This difference in the \(k_{id}\) values is related to differences in the textural properties of the samples as already reported in the literature (Cardoso et al., 2011) and is also in agreement with the results discussed above in the characterization of the biosorbents. The increase in the macropore structure of the FP biosorbent should facilitate the diffusion of CBY dye molecules through the macropores (Ip et al., 2009). As the adsorbate diffuses through the pores of the biosorbent, the dye could be biosorbed at the internal sites of the FP biomaterial, therefore, a fast kinetics of biosorption (increasing the intraparticle diffusion) and higher sorption capacity of FP biosorbent than DP biosorbent is expected. On the other hand, for DP biosorbent, with a lower number of macropore structures, biosorption is limited to the external surface of the biosorbent, decreasing the total amount biosorbed (Ip et al., 2009), and also leading to a slower kinetics of biosorption of CBY dye.

It was observed in Figures 4 and 5 that the minimum contact time of CBY dye with the DP and FP biosorbents to reach equilibrium was about 4.5 h for both biosorbents. To continue this work, the contact time between the DP and FP biosorbents with CBY dye was fixed at 6.0 h. An increase in the contact time utilized in this work was a guarantee that for CBY dye equilibrium would be attained even at higher adsorbate concentrations (Machado et al., 2011).

**Equilibrium Studies**

A biosorption isotherm describes the relationship between the amount of adsorbate adsorbed by the biosorbent \((q_e)\) and the adsorbate concentration remaining in the solution after the system attains equilibrium \((C_e)\), keeping constant the temperature of the process. The biosorption parameters of the equilibrium models often provide some insight into the biosorption mechanism, surface properties, and affinity of the biosorbent to the adsorbate. In this work, the Langmuir (Langmuir, 1918), the Freundlich (Freundlich, 1906), and the Liu (Liu et al., 2003) isotherm models were tested.

The isotherms of biosorption were carried out from 298 to 323 K with CBY dye on the DP and FP biosorbents and were performed using the best experimental conditions previously described above (see Table III, and Figure 6). Figure 6 shows
| Temperature (K) | DP        | FP        | DP        | FP        |
|----------------|-----------|-----------|-----------|-----------|
|                | 298       | 303       | 308       | 313       | 318       | 323       | 298       | 303       | 308       | 313       | 318       | 323       |
| Langmuir       |           |           |           |           |
| $Q_{\text{max}}$ (mg g$^{-1}$) | 22.8      | 24.5      | 35.7      | 30.8      | 40.2      | 29.5      | 24.4      | 26.8      | 33.1      | 34.7      | 33.5      | 35.5      |
| $K_L$ (L mg$^{-1}$) | 0.0213    | 0.0174    | 0.0116    | 0.0100    | 6.24 x 10$^{-3}$ | 9.89 x 10$^{-3}$ | 0.133     | 0.120     | 0.0713    | 0.0590    | 0.0696    | 0.0585    |
| $R^2_{\text{adj}}$ | 0.9988    | 0.9989    | 0.9973    | 0.9974    | 0.9947    | 0.9998    | 0.9769    | 0.9792    | 0.9933    | 0.9840    | 0.9873    | 0.9910    |
| $F_{\text{error}}$ | 0.1816    | 0.1710    | 0.3649    | 0.2890    | 0.4160    | 0.0864    | 1.070     | 1.120     | 0.7658    | 0.7121    | 1.085     | 0.9203    |
| Freudlich      |           |           |           |           |
| $K_F$ (mg g$^{-1}$ (mg L$^{-1}$)$^{-n_F}$) | 2.03      | 1.48      | 1.19      | 0.922     | 0.615     | 0.870     | 7.74      | 7.80      | 6.46      | 6.21      | 6.37      | 6.42      |
| $n_F$          | 2.29      | 1.96      | 1.66      | 1.65      | 1.43      | 1.64      | 4.15      | 3.85      | 2.96      | 2.86      | 2.91      | 2.91      |
| $R^2_{\text{adj}}$ | 0.9719    | 0.9798    | 0.9807    | 0.9811    | 0.9825    | 0.9901    | 0.9855    | 0.9868    | 0.9840    | 0.9998    | 0.9873    | 0.9909    |
| $F_{\text{error}}$ | 0.8640    | 0.7266    | 0.9813    | 0.7797    | 0.7575    | 0.5472    | 0.8458    | 0.8939    | 1.188     | 1.129     | 1.086     | 0.9250    |
| Liu            |           |           |           |           |
| $Q_{\text{max}}$ (mg g$^{-1}$) | 20.9      | 22.0      | 28.1      | 24.4      | 25.6      | 26.9      | 31.9      | 35.7      | 40.2      | 42.3      | 45.1      | 47.3      |
| $K_g$ (L mg$^{-1}$) | 0.0255    | 0.0216    | 0.0185    | 0.0158    | 0.0139    | 0.0119    | 0.0584    | 0.0492    | 0.0415    | 0.0349    | 0.0294    | 0.0258    |
| $n_L$          | 1.145     | 1.13      | 1.26      | 1.24      | 1.40      | 1.07      | 0.5568    | 0.568     | 0.726     | 0.734     | 0.653     | 0.660     |
| $R^2_{\text{adj}}$ | 0.9998    | 0.9997    | 0.9999    | 0.9998    | 0.9998    | 1.000     | 0.9998    | 0.9999    | 0.9999    | 0.9998    | 0.9999    | 0.9999    |
| $F_{\text{error}}$ | 0.0728    | 0.0917    | 0.0802    | 0.0691    | 0.0866    | 0.0300    | 0.1017    | 0.1028    | 0.1211    | 0.1285    | 0.1347    | 0.0746    |

Table III. Isotherm parameters for CBY biosorption using DP and FP biosorbents; conditions: biosorbent mass, 50.0 mg; pH 2.0, contact time, 6h.
the isotherms of biosorption of CBY dye using DP and FP biosorbents at 298 K. Based on the $F_{error}$ (see Table III), the Liu (Liu et al., 2003) model was the best isotherm model for both biosorbents at all six temperatures studied. In order to compare the different equilibrium models, the $F_{error}$ of each model was divided by the $F_{error}$ of minimum value ($F_{error}$ ratio). It was observed that the minimum $F_{error}$ values were obtained by the Liu equilibrium model at all six temperatures studied (Table III), which means that the $q$ fit by the isotherm model was close to the $q$ measured experimentally. The Langmuir and Freundlich isotherm models could not suitably fit our experimental data, presenting $F_{error}$ ratios ranging from 1.86 to 4.80 (DP) and from 5.54 to 12.33 (FP). Also, the Freundlich isotherm presented $F_{error}$ ratios ranging from 7.93 to 18.24 (DP) and from 8.32 to 12.40 (FP).

Figure 6. Isotherms of adsorption of CBY dye at 298 K: (A) DP, (B) FP. Conditions: pH 2.0; FP biosorbent mass, 50.0 mg; time of contact, 6.0 h.
The Langmuir isotherm model is based on the following principles (Langmuir, 1918): adsorbates are chemically adsorbed at a fixed number of well-defined sites, each site can only hold one adsorbate species, all sites are energetically equivalent, and there are no interactions between the adsorbate species. The Freundlich isotherm model assumes that the concentration of the adsorbate on the adsorbent surface increases with adsorbate concentration. Theoretically, using this expression, an infinite amount of adsorption can occur (Freundlich, 1906). The Liu isotherm model (Liu et al., 2003) is a combination of the Langmuir and Freundlich isotherm models; therefore, the monolayer assumption of the Langmuir model is ruled out and the infinite adsorption assumption that originates from the Freundlich model is also discarded. The Liu model predicts that the active sites of the adsorbent cannot present the same energy. Therefore, the adsorbent may present active sites preferred by the adsorbate molecules for occupation (Liu et al., 2003); however, saturation of the active sites should occur, unlike in the Freundlich isotherm model. Taking into account that the biosorbents used in this study have different functional groups, it is expected that the activate sites of the biosorbents will not have the same energy.

Based on the Liu isotherm model the maximum amounts of CBY biosorbed were 26.9 and 47.3 mg g\(^{-1}\), using DP and FB biosorbents, respectively. Considering that is very difficult to compare the sorption capacities of different adsorbents for a specific dye, since the number of dyes available for industrial use is too high, Table IV presents a list of adsorbents used to adsorb different dyes. These values indicate that DP and FP are fairly good biosorbents for the removal of dyes from aqueous solutions (see Table IV and the references cited). The early results of use of peat as biosorbent show that this biomaterial is good for biosorption of basic dyes, however, for acid dyes, it is not as good. Taking into account that the CBY reactive dye presents sulfonic groups as acid dyes, it can be inferred that our results are better than the earlier reported values of maximum sorption capacity of peat for acid dyes (Ip et al., 2009; Ramakrishna and Viraraghavan, 1997; Srinivasan and Viraraghavan, 2010).

It should be stressed that the maximum amounts biosorbed (\(Q_{\text{max}}\)) of the CBY dye by the FP biosorbent were 43.1–76.2% higher than that with the DP biosorbent. The kinetics of biosorption of CBY dye on the FP biosorbent was faster than that of the DP biosorbent. Considering the initial sorption rate (\(h_0\)) of CBY dye taken up by DP and FP biosorbents (see Table II), obtained by the general-order kinetic model, it was observed that \(h_0\) of the FP biosorbent increased from 129% to 175% when compared with \(h_0\) obtained for the DP biosorbent. It can be concluded that the better textural properties of the FP biosorbent (fibrous form, with higher number of macropores) than that of the DP biosorbent (compact form), as already reported for other biosorbents (Alencar et al., 2012a; Cardoso et al., 2011), contributed to a faster diffusion of CBY dye through the pores of the biosorbent, also allowing higher amounts of CBY dye to be biosorbed by the FP biosorbent.

**Thermodynamics of Biosorption**

Thermodynamic parameters related to the biosorption process, i.e., Gibbs free energy change (\(\Delta G^\circ\), kJ mol\(^{-1}\)), enthalpy change (\(\Delta H^\circ\), kJ mol\(^{-1}\)), and entropy change (\(\Delta S^\circ\), J mol\(^{-1}\) K\(^{-1}\)), are determined by the following equations:

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{23}
\]

\[
\Delta G^\circ = -RT\ln(K) \tag{24}
\]
The combination of Equations (23) and (24) gives:

\[
\ln(K) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \times \frac{1}{T}
\]

(25)
where $R$ is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), $T$ is the absolute temperature (Kelvin), and $K$ represents the equilibrium biosorption constants of the isotherm fits. It has been reported in the literature that different biosorption equilibrium constants ($K$) were obtained from different isotherm models (Alencar et al., 2012a, 2012b; Gupta et al., 2010; Leechart et al., 2009; Machado et al., 2011, 2012). Thermodynamic parameters of biosorption can be estimated from the $K_R$ (Liu equilibrium constant), as already reported (Machado et al., 2011, 2012). The $\Delta H^\circ$ and $\Delta S^\circ$ values can be calculated from the slope and intercept of the linear plot of $\ln(K)$ versus $1/T$.

The thermodynamic results are depicted in Table V. The $R^2$ values of the linear fit were at least 0.999, indicating that the values of enthalpy and entropy calculated for both biosorbents were confident. In addition, the magnitude of enthalpy was consistent with a physical sorption for both biosorbents (Sun and Wang, 2010). The kind of interaction can be classified, to a certain extent, by the magnitude of enthalpy change. Physical sorption such as hydrogen bonding, is usually lower than 25 kJ mol$^{-1}$ (Sun and Wang, 2010). Enthalpy changes ($\Delta H^\circ$) indicate that the biosorption followed an endothermic process. Negative values of $\Delta G^\circ$ indicate that CBY dye biosorption by DP and FP biosorbents was a spontaneous and favorable process for all the temperatures studied. The positive values of $\Delta S^\circ$ confirmed a high preference of CBY molecules on the surface of DP and FP and also suggested the possibility of some structural changes or readjustments in the dye-carbon biosorption complex (Asouhidou et al., 2009). Furthermore, the physical interactions of CBY dye with DP and FP biosorbents are coherent with the FT-IR spectra of the biosorbents after biosorption (see Figure 1). The vibrational bands did not present significant changes in their wave numbers after biosorption, indicating that the interaction of the dye with the biosorbent presents very low energy, which is compatible with a physical biosorption, as previously reported (Alencar et al., 2012a).

**Desorption Experiments**

In order to check the reuse of the DP and FP biosorbents for the biosorption of CBY dye, desorption experiments were carried out. The eluents, 0.05–0.5 mol L$^{-1}$ NaCl aqueous solutions, 0.05–0.50 mol L$^{-1}$ NaCl + 0.05 mol L$^{-1}$ HCl, 0.20–0.30 mol L$^{-1}$ HCl, and ethanol + water mixtures (10–100% EtOH), were tested for regeneration of the loaded biosorbent (see Table VI). For both biosorbents 50% EtOH + 50% H$_2$O solution and 80% EtOH + 20% H$_2$O desorbed the CBY dye uptaken by the DP and FP biosorbents immediately (at least 95.56%). On the other hand, the recoveries of the biosorbent using aqueous NaCl, NaCl + HCl solutions, and HCl solutions of different concentrations as regenerating solutions occurred with lower efficiency even after 1 h of agitation (recoveries < 26%). The time of desorption was set only at 1 h to verify the economic viability of regenerating the biosorbent materials. Cycles of biosorption/desorption were carried out, and after four cycles, the efficiency for CBY dye removal was decreased by about 8.5%. Therefore, the use of DP and FP biosorbents for CBY dye biosorption could be economically viable since it allows regeneration.

**Treatment of a Simulated Dye House Effluent**

In order to verify the efficiency of the DP and FP biosorbents for removal of dyes from textile effluents, a simulated dye house effluent was prepared, based on the
Table V. Thermodynamic parameters of the biosorption of CBY dye on DP and FP biosorbents; conditions: Mass of biosorbent, 50.0 mg; pH 2.0; contact time, 6h

|          | Temperature (K) |          |          |          |          |          |
|----------|----------------|----------|----------|----------|----------|----------|
|          | 298            | 303      | 308      | 313      | 318      | 323      |
| DP       |                |          |          |          |          |          |
| $K_g$ (L mol$^{-1}$) | $2.22 \times 10^4$ | $1.89 \times 10^4$ | $1.62 \times 10^4$ | $1.38 \times 10^4$ | $1.21 \times 10^4$ | $1.04 \times 10^4$ |
| $\Delta G^\circ$ (kJ mol$^{-1}$) | $-24.80$ | $-24.80$ | $-24.81$ | $-24.80$ | $-24.86$ | $-24.84$ |
| $\Delta H^\circ$ (kJ mol$^{-1}$) | $-24.12$ | —       | —       | —       | —       | —       |
| $\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$) | $2.24$ | —       | —       | —       | —       | —       |
| $R^2$    | 0.9997         | —       | —       | —       | —       | —       |
| FP       |                |          |          |          |          |          |
| $K_g$ (L mol$^{-1}$) | $5.10 \times 10^4$ | $4.30 \times 10^4$ | $3.63 \times 10^4$ | $3.04 \times 10^4$ | $2.56 \times 10^4$ | $2.25 \times 10^4$ |
| $\Delta G^\circ$ (kJ mol$^{-1}$) | $-26.86$ | $-26.88$ | $-26.88$ | $-26.87$ | $-26.84$ | $-26.91$ |
| $\Delta H^\circ$ (kJ mol$^{-1}$) | $-26.62$ | —       | —       | —       | —       | —       |
| $\Delta S^\circ$ (JK$^{-1}$ mol$^{-1}$) | $0.80$ | —       | —       | —       | —       | —       |
| $R^2$    | 0.9992         | —       | —       | —       | —       | —       |


Table VI. Desorption of CBY dye loaded on DP and FP biosorbents; conditions for adsorption: initial dye concentration, 50 mg L\(^{-1}\); mass of biosorbent, 50.0 mg; pH 2.0; time of contact, 1h

| Eluent (mol L\(^{-1}\)) | TD % Desorption | TF % Desorption |
|-------------------------|----------------|----------------|
| 0.05 NaCl               | 25.10          | 22.84          |
| 0.10 NaCl               | 19.07          | 21.71          |
| 0.20 NaCl               | 23.78          | 16.44          |
| 0.30 NaCl               | 22.65          | 17.57          |
| 0.40 NaCl               | 20.58          | 15.50          |
| 0.50 NaCl               | 17.38          | 15.31          |
| 0.05 NaCl + 0.05 HCl    | 6.45           | 6.68           |
| 0.10 NaCl + 0.05 HCl    | 6.64           | 5.38           |
| 0.20 NaCl + 0.05 HCl    | 7.77           | 8.06           |
| 0.30 NaCl + 0.05 HCl    | 7.96           | 8.25           |
| 0.40 NaCl + 0.05 HCl    | 6.64           | 6.00           |
| 0.50 NaCl + 0.05 HCl    | 7.20           | 7.25           |
| 0.20 HCl                | 7.58           | 7.74           |
| 0.30 HCl                | 9.09           | 10.31          |
| EtOH (%)                |                |                |
| 10 EtOH + 90 H\(_2\)O   | 62.00          | 64.50          |
| 20 EtOH + 80 H\(_2\)O   | 61.58          | 61.46          |
| 50 EtOH + 50 H\(_2\)O   | 95.56          | 97.36          |
| 80 EtOH + 20 H\(_2\)O   | 95.65          | 98.52          |
| 100 EtOH + 0 H\(_2\)O   | 83.21          | 85.21          |

Figure 7. UV-vis spectra of simulated dye effluent before and after adsorption treatment with DP and FP biosorbents. For composition of effluents, see Table I.
amount of dyes and inorganic compounds that could be observed in a dye house effluent (see Table I; Hessel et al., 2007). The UV-visible spectra of untreated effluent and that treated with DP and FP were recorded from 350 to 800 nm (Figure 7). The area under the absorption bands from 350 to 800 nm was utilized to monitor the percentage of dye mixture removed from the simulated dye effluents. The FP biosorbent removed 94.7% (Figure 7), and the DP adsorbent removed only 57.8% (Figure 7) of the dye mixture. The efficiency of FP biosorbent for treating a simulated dye house effluent presented good performance for treating dye-contaminated industrial effluents. On the other hand, the DP biosorbent is not suitable for treating industrial effluents because of its low sorption capacity. The better textural properties of FP biosorbent than those of DP biosorbent contribute to faster diffusion of a mixture of dyes through the pores of the biosorbent and also allow higher amounts of these species to be removed from the aqueous effluent.

Conclusions

Decomposed peat (DP) and fibrous peat (FP) are alternative biosorbents to remove the textile dye Cibacron Brilliant Yellow 3G-P (CBY) from aqueous solutions. DP and FP were characterized by FT-IR spectroscopy, SEM, and \( p_{H_{pc}} \). CBY dye interacts with the biosorbents at the solid/liquid interface when suspended in water. The best conditions were established for pH and contact time to saturate the available sites located on the biosorbent surface. Four kinetic models were used to test the experimental data, and the general-order kinetic model gave the best fit. The fact that the kinetic data were better fitted by the general-order kinetic model is an indication that the order of a biosorption process should follow the same logic as a chemical reaction, where the order is experimentally measured instead of being subjected to a previously given model, as is traditionally reported in the literature. In addition, the intraparticle diffusion model gave multiple linear regions, which suggested that biosorption may also be followed by multiple sorption rates. The minimum equilibration time of the dye was obtained after 4.5 h of contact between CBY dye and the DP and FP biosorbents. The equilibrium isotherm of these dyes was obtained, and the data were best fitted to the Liu isotherm model. The maximum amounts of CBY adsorbed were 26.9 (323 K) and 47.3 (298 K) mg g\(^{-1}\), using DP and FP as biosorbents, respectively. The thermodynamic parameters of biosorption (\( \Delta H^o; \Delta S^o, \) and \( \Delta G^o \)) were calculated. The magnitude of enthalpy of biosorption is compatible with a physical interaction of CBY dye with both DP and FP biosorbents, and it is also in good agreement with the FT-IR vibrational bands obtained after the biosorption batch procedure. For treatment of simulated industrial textile effluents, the FP biosorbent exhibited good performance, removing 94.7% of a dye mixture in a medium containing high saline concentrations. The reusability of the DP and FP biosorbents was evaluated by experiments of biosorption and desorption, and it was verified that mixtures of ethanol + water (50 + 50 or 80 + 20) were able to regenerate the biosorbents by at least 95.56%.

Acknowledgments

The authors are grateful to the Materials Characterization Laboratory of Caxias do Sul University (LCMat-UCS) for the use of the SEM microscope.
Funding

We are also grateful to the National Council for Scientific and Technological Development (CNPq, Brazil), to the Coordination of Improvement of Higher Education Personnel (CAPES, Brazil), to the Academy of Sciences for Developing World (TWAS), and to the Foundation for Research Support in the State of Rio Grande do Sul (FAPERGS, Brazil) for financial support and fellowships.

Supplemental Material

Supplemental data for this article can be accessed on the publisher’s website.

References

Alencar, W. S., Acayanka, E., Lima, E. C., Royer, B., de Souza, F. E., Lameira, J., and Alves, C. N. (2012a). Application of Mangifera indica (mango) seeds as a biosorbent for removal of Victazol Orange 3R dye from aqueous solution and study of the biosorption mechanism, Chem. Eng. J., 209, 577–588.

Alencar, W. S., Lima, E. C., Royer, B., dos Santos, B. D., Calvete, T., da Silva, E. A., and Alves, C. N. (2012b). Application of aqai stalks as biosorbents for the removal of the dye Procion Blue MX-R from aqueous solution, Sep. Sci. Technol., 47, 513–526.

Allen, S. J., Mckay, G., and Porter, J. F. (2004). Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems, J. Colloid Interface Sci., 280, 322–333.

Alver, E., and Metin, A. U. (2012). Anionic dye removal from aqueous solutions using modified zeolite: Adsorption kinetics and isotherm studies, Chem. Eng. J., 200–202, 59–67.

Antunes, M., Esteves, V. I., Guégan, R., Crespo, J. S., Fernandes, A. N., and Giovanela, M. (2012). Removal of diclofenac sodium from aqueous solution by Isabel grape bagasse, Chem. Eng. J., 192, 114–121.

Asouhidou, D. D., Triantafyllidis, K. S., Lazaridis, N. K., Matis, K. A., Kim, S. S., and Pinnavaia, T. J. (2009). Sorption of reactive dyes from aqueous solutions by ordered hexagonal and disordered mesoporous carbons, Microporous Mesoporous Mater., 117, 257–267.

Barbosa, Jr., F., Krug, F. J., and Lima, E. C. (1999). On-line coupling of electrochemical preconcentration in tungsten coil electrothermal atomic absorption spectrometry for determination of lead in natural waters, Spectrochim. Acta Part B, 54, 1155–1166.

Calvete, T., Lima, E. C., Cardoso, N. F., Dias, S. L. P., and Pavan, F. A. (2009). Application of carbon adsorbents prepared from the Brazilian pine-fruit-shell for removal of Procion Red MX 3B from aqueous solution—Kinetic, equilibrium, and thermodynamic studies, Chem. Eng. J., 155, 627–636.

Calvete, T., Lima, E. C., Cardoso, N. F., Vaghetto, J. C. P., Dias, S. L. P., and Pavan, F. A. (2010). Application of carbon adsorbents prepared from Brazilian-pine fruit shell for the removal of reactive orange 16 from aqueous solution: Kinetic, equilibrium, and thermodynamic studies, J. Environ. Manage., 91, 1695–1706.

Cardoso, N. F., Lima, E. C., Pinto, I. S., Amavisca, C. V., Royer, B., Pinto, R. B., Alencar, W. S., and Pereira, S. F. P. (2011). Application of cupuassu shell as biosorbent for the removal of textile dyes from aqueous solution, J. Environ. Manage., 92, 1237–1247.

Cardoso, N. F., Lima, E. C., Royer, B., Bach, M. V., Dotto, G. L., Pinto, L. A. A., and Calvete, T. (2012). Comparison of Spirulina platensis microalgae and commercial activated carbon as adsorbents for the removal of Reactive Red 120 dye from aqueous effluents, J. Hazard. Mater., 241–242, 146–153.
Carneiro, P. A., Umbuzeiro, G. A., Oliveira, D. P., and Zanoni, M. V. B. (2010). Assessment of water contamination caused by a mutagenic textile effluent/dyehouse effluent bearing disperse dyes, *J. Hazard. Mater.*, **174**, 694–699.

Çelekli, A., Ilgın, G., and Bozkurt, H. (2012). Sorption equilibrium, kinetic, thermodynamic, and desorption studies of Reactive Red 120 on *Chara contraria*, *Chem. Eng. J.*, **191**, 228–235.

Davies, R. F., and Johnston, G. A. (2011). New and emerging cosmetic allergens, *Clin. Dermatol.*, **29**, 311–315.

de Lima, R. O. A., Bazo, A. P., Salvadori, D. M. F., Rech, C. M., Oliveira, D. P., and Umbuzeiro, G. A. (2007). Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source, *Mutat. Res., Genet. Toxicol. Environ. Mutagen.*, **626**, 53–60.

de Menezes, E. W., Lima, E. C., Royer, B., de Souza, F. E., dos Santos, B. D., Gregório, J. R., Costa, T. M. H., Gushikem, Y., and Benvenuti, E. V. (2012). Ionic silica based hybrid material containing the pyridinium group used as adsorbent for textile dye, *J. Colloid Interface Sci.*, **378**, 10–20.

Dotto, G. L., Lima, E. C., and Pinto, L. A. A. (2012). Biosorption of food dyes onto *Spirulina platensis* nanoparticles: Equilibrium isotherm and thermodynamic analysis, *Bioresour. Technol.*, **103**, 123–130.

Dursun, A. Y., and Tepe, O. (2011). Removal of Chemazol Reactive Red 195 from aqueous solution by dehydrated beet pulp carbon, *J. Hazard. Mater.*, **194**, 303–311.

El-Khaiary, M. I., and Malash, G. F. (2011). Common data analysis errors in batch adsorption studies, *Hydrometallurgy*, **105**, 314–320.

El-Khaiary, M. I., Malash, G. F., and Ho, Y. S. (2010). On the use of linearized pseudo-second-order kinetic equations for modeling adsorption systems, *Desalination*, **257**, 93–101.

Eren, Z. (2012). Ultrasound as a basic and auxiliary process for dye remediation: A review, *J. Environ. Manage.*, **104**, 127–141.

Errais, E., Duplay, J., Darragi, F., Rabet, I. M., Aubert, A., Huber, F., and Morvan, G. (2011). Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters, *Desalination*, **275**, 74–81.

Fernandes, A. N., Almeida, C. A. P., Menezes, C. T. B., Debacher, N. A., and Sierra, M. M. D. (2007). Removal of methylene blue from aqueous solution by peat, *J. Hazard. Mater.*, **144**, 412–419.

Fernandes, A. N., Almeida, C. A. P., Debacher, N. A., and Sierra, M. M. D. (2010). Isotherm and thermodynamic data of adsorption of methylene blue from aqueous solution onto peat, *J. Mol. Struct.*, **982**, 62–65.

Freundlich, H. (1906). Über die Adsorption in Lösungen, *Z. Phys. Chem.*, **57**, 385–470.

Galan, J., Rodriguez, A., Gomez, J. M., Allen, S. J., and Walker, G. M. (2013). Reactive dye adsorption onto a novel mesoporous carbon, *Chem. Eng. J.*, **219**, 62–68.

Ghaedi, M., Karimi, F., Barazesh, B., Sahraei, R., and Daneshfar, A. (2013). Removal of Reactive Orange 12 from aqueous solutions by adsorption on tin sulfide nanoparticle loaded on activated carbon, *J. Ind. Eng. Chem.*, **19**, 756–763.

Girardello, F., Guégan, R., Esteves, V. I., Baumvol, I. J. R., Sierra, M. M. D., Crespo, J. S., Fernandes, A. N., and Giovanella, M. (2013). Characterization of Brazilian peat samples by applying a multi-method approach, *Spectrosc. Lett.*, **46**, 201–210.

Gulnaz, O., Sahmurova, A., and Kama, S. (2011). Removal of Reactive Red 198 from aqueous solution by *Potamogeton crispus*, *Chem. Eng. J.*, **174**, 579–585.

Gundogdu, A., Duran, C., Senturk, H. B., Soylak, M., Ozdes, D., Serencam, H., and Imamoglu, M. (2012). Adsorption of phenol from aqueous solution on a low-cost activated carbon produced from tea industry waste: Equilibrium, kinetic, and thermodynamic study, *J. Chem. Eng. Data*, **57**, 2733–2743.
Gupta, V. K., Jain, R., Malathi, S., and Nayak, A. (2010). Adsorption-desorption studies of indigocarmine from industrial effluents by using deoiled mustard and its comparison with charcoal, *J. Colloid Interface Sci.*, **348**, 628–633.

Hamzeh, Y., Ashori, A., Azadeh, E., and Abdulkhani, A. (2012). Removal of acid orange 7 and remazol black 5 reactive dyes from aqueous solutions using a novel biosorbent, *Mater. Sci. Eng. C.*, **32**, 1394–1400.

Hessel, C., Allegre, C., Maisseu, M., Charbit, F., and Moulin, P. (2007). Guidelines and legislation for dye house effluents, *J. Environ. Manage.*, **83**, 171–180.

Ho, Y. S. (2006). Review of second-order models for adsorption systems, *J. Hazard. Mater.*, **136**, 681–689.

Ho, Y. S., and McKay, G. (1998). Sorption of dye from aqueous solution by peat, *Chem. Eng. J.*, **70**, 115–124.

Ip, A. W. M., Barford, J. P., and McKay, G. (2009). Reactive Black dye adsorption/desorption onto different adsorbents: Effect of salt, surface chemistry, pore size and surface area, *J. Colloid Interface Sci.*, **337**, 32–38.

Jacques, R. A., Bernardi, R., Caovila, M., Lima, E. C., Pavan, F. A., Vaghetto, J. C. P., and Airoldi, C. (2007a). Removal of Cu(II), Fe(III) and Cr(III) from aqueous solution by aniline grafted silica gel, *Sep. Sci. Technol.*, **42**, 591–609.

Jacques, R. C., Lima, E. C., Dias, S. L. P., Mazzocato, A. C., and Pavan, F. A. (2007b). Yellow passion-fruit shell as biosorbent to remove Cr(III) and Pb(II) from aqueous solution, *Sep. Purif. Technol.*, **57**, 193–198.

Jesus, A. M. D., Romão, L. P. C., Araújo, B. R., Costa, A. S., and Marques, J. J. (2011). Use of humin as an alternative material for adsorption/desorption of reactive dyes, *Desalination*, **274**, 13–21.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.*, **40**, 1361–1403.

Leechart, P., Nakbanpote, W., and Thiravetyan, P. (2009). Application of ‘waste’ wood-shaving bottom ash for adsorption of azo reactive dye, *J. Environ. Manage.*, **90**, 912–920.

Li, W. H., Yue, Q. Y., Gao, B. Y., Ma, Z. H., Li, Y. J., and Zhao, H. X. (2011). Preparation and utilization of sludge-based activated carbon for the adsorption of dyes from aqueous solutions, *Chem. Eng. J.*, **171**, 320–327.

Lima, E. C., Brasil, J. L., and Santos, A. H. D. P. (2003). Evaluation of Rh, Ir, Ru, W-Rh, W-Ir, and W-Ru as permanent modifiers for the determination of lead in ashes, coals, sediments, sludges, soils, and freshwaters by electrothermal atomic absorption spectrometry, *Anal. Chim. Acta.*, **484**, 233–242.

Lima, E. C., Krug, F. J., Nobrega, J. A., and Nogueira, A. R. A. (1998). Determination of ytterbium in animal faeces by tungsten coil electrothermal atomic absorption spectrometry, *Talanta*, **47**, 613–623.

Liu, Y., and Liu, Y. J. (2008). Review—Biosorption isotherms, kinetics and thermodynamics, *Sep. Purif. Technol.*, **61**, 229–242.

Liu, Y., and Shen, L. A. (2008). General rate law equation for biosorption, *Biochem. Eng. J.*, **38**, 390–394.

Liu, Y., Xu, H., Yang, S. F., and Tay, J. H. (2003). A general model for biosorption of Cd\(^{2+}\), Cu\(^{2+}\) and Zn\(^{2+}\) by aerobic granules, *J. Biotechnol.*, **102**, 233–239.

Machado, F. M., Bergmann, C. P., Fernandes, T. H. M., Lima, E. C., Royer, B., Calvete, T., and Fagan, S. B. (2011). Adsorption of Reactive Red M-2BE dye from water solutions by multi-walled carbon nanotubes and activated carbon, *J. Hazard. Mater.*, **192**, 1122–1131.

Machado, F. M., Bergmann, C. P., Lima, E. C., Royer, B., de Souza, F. E., Jauris, I. M., Calvete, T., and Fagan, S. B. (2012). Adsorption of Reactive Blue 4 dye from water solutions by carbon nanotubes: Experiment and theory, *Phys. Chem. Chem. Phys.*, **14**, 11139–11153.
Madrakian, T., Afkhami, A., and Ahmadi, M. (2012). Adsorption and kinetic studies of seven different organic dyes onto magnetite nanoparticles loaded tea waste and removal of them from wastewater samples, Spectrochim. Acta A, 99, 102–109.

Mittal, A., Jhare, D., and Mittal, J. (2013). Adsorption of hazardous dye Eosin Yellow from aqueous solution onto waste material de-oiled soya: Isotherm, kinetics and bulk removal, J. Mol. Liq., 179, 133–140.

Piccin, J. S., Vieira, M. L. G., Gonçalves, J. O., Dotto, G. L., and Pinto, L. A. A. (2009). Adsorption of FD&C Red N° 40 by chitosan: Isotherms analysis, J. Food Eng., 95, 16–20.

Prato-Garcia, D., and Buitrón, G. (2011). Degradation of azo dye mixtures through sequential hybrid systems: Evaluation of three advanced oxidation processes for the pre-treatment stage, J. Photochem. Photobiol. A., 223, 103–110.

Ramakrishna, K. R., and Viraraghavan, T. (1997). Dyes removal using low-cost adsorbents, Water Sci. Technol., 36, 189–196.

Roberts, J. D., and Caserio, M. C. (1977). Basic Principles of Organic Chemistry, 2nd ed., W.A. Benjamin, London.

Royer, B., Cardoso, N. F., Lima, E. C., Macedo, T. R., and Airoldi, C. (2010). A useful organofunctionalized layered silicate for textile dye removal, J. Hazard. Mater., 181, 366–374.

Royer, B., Cardoso, N. F., Lima, E. C., Ruiz, V. S. O., Macedo, T. R., and Airoldi, C. (2009). Organofunctionalized kenyaite for dye removal from aqueous solution, J. Colloid Interface Sci., 336, 398–405.

Sánchez-Gilo, A., Gómez-De La Fuente, E., Calzado, L., and López-Estebananz, J. L. (2010). Textile contact dermatitis in a patient sensitized to Reactive Orange 107 dye, Actas Dermosifiliogr., 101, 278–279.

Sathishkumar, M., Pavagadhi, S., Vijayaraghavan, K., Balasubramanian, R., and Ong, S. L. (2010). Experimental studies on removal of Microcystin-LR by peat, J. Hazard. Mater., 184, 417–424.

Shirsath, S. R., Patil, A. P., Patil, R., Naik, J. B., Gogate, P. R., and Sonawane, S. H. (2013). Removal of Brilliant Green from wastewater using conventional and ultrasonically prepared poly(acrylic acid) hydrogel loaded with kaolin clay: A comparative study, Ultrason. Sonochem., 20, 914–923.

Silva, L. S., Lima, L. C. B., Silva, F. C., Matos, J. M. E., Santos, M. R. M. C., Santos, Jr., L. S., Sousa, K. S., and da Silva F, E. C. (2013). Dye anionic sorption in aqueous solution onto a cellulose surface chemically modified with aminoethanethiol, Chem. Eng. J., 218, 89–98.

Srinivasan, A., and Viraraghavan, T. (2010). Decolorization of dye wastewaters by biosorbents: A review, J. Environ. Manage., 91, 1915–1929.

Sun, C. L., and Wang, C. S. (2010). Estimation on the intramolecular hydrogen-bonding energies in proteins and peptides by the analytic potential energy function, J. Mol. Struct., 956, 38-43.

Vaghi, B. C. P., Zat, M., Bentes, K. R. S., Ferreira, L. S., Benvenutti, E. V., and Lima, E. C. (2003). 4-Phenylenediampropylsilica xerogel as a sorbent for copper determination in waters by slurry-sampling ETAAS, J. Anal. At. Spectrom., 18, 376–380.

von Post, L. (1924). Das genetische System der Organogenen Bildungen Schwedens, Int. Commun. Soil Sci., 22, 287–304.

Wang, L., and Li, J. (2013). Adsorption of C.I. Reactive Red 228 dye from aqueous solution by modified cellulose from flax shive: Kinetics, equilibrium, and thermodynamics, Ind. Crops Prod., 42, 153–158.

Weber, Jr., W. J., and Morris, J. C. (1963). Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div., 89, 31–59.

Xing, G., Liu, S., Xu, Q., and Liu, Q. (2012). Preparation and adsorption behavior for brilliant blue X-BR of the cost-effective cationic starch intercalated clay composite matrix, Carbohydr. Polym., 87, 1447–1452.
Yazdanbakhsh, M., Tavakkoli, H., and Hosseini, S. M. (2011). Characterization and evaluation catalytic efficiency of La$_{0.5}$Ca$_{0.5}$NiO$_3$ nanopowders in removal of reactive blue 5 from aqueous solution, *Desalination*, 281, 388–395.

Young, K. T., Shik, P. S., and Sung-Yong, C. (2012). Adsorption characteristics of Reactive Black 5 onto chitosan beads cross-linked with epichlorohydrin, *J. Ind. Eng. Chem.*, 18, 1458–1464.

Zaccone, C., Miano, T. M., and Shotyk, W. (2007). Qualitative comparison between raw peat and related humic acids in an ombrotrophic bog profile, *Org. Geochem.*, 38, 151–160.