



Application of succinylated sugarcane bagasse as adsorbent to remove methylene blue and gentian violet from aqueous solutions – Kinetic and equilibrium studies

Karla Aparecida Guimarães Gusmão^a, Leandro Vinícius Alves Gurgel^b,
Tânia Márcia Sacramento Melo^a, Laurent Frédéric Gil^{a,*}

^a Departamento de Química, ICEB, Campus Morro do Cruzeiro, Universidade Federal de Ouro Preto, 35400-000 Ouro Preto, MG, Brazil

^b Grupo de Físico-química orgânica, Departamento de Físico-química, Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trabalhador São Carlense 400, Caixa Postal 780, 13560-970 São Carlos, Brazil

ARTICLE INFO

Article history:

Received 7 March 2011

Received in revised form

31 August 2011

Accepted 9 September 2011

Available online 16 September 2011

Keywords:

Adsorption

Adsorption kinetics

Cationic dye

Methylene blue

Gentian violet

Succinylated sugarcane bagasse

ABSTRACT

In a previous work, succinylated sugarcane bagasse (SCB 2) was prepared from sugarcane bagasse (B) using succinic anhydride as modifying agent. In this work the adsorption of cationic dyes onto SCB 2 from aqueous solutions was investigated. Methylene blue, MB, and gentian violet, GV, were selected as adsorbates. The capacity of SCB 2 to adsorb MB and GV from aqueous single dye solutions was evaluated at different contact times, pH, and initial adsorbent concentration. According to the obtained results, the adsorption processes could be described by the pseudo-second-order kinetic model. Adsorption isotherms were well fitted by Langmuir model. Maximum adsorption capacities for MB and GV onto SCB 2 were found to be 478.5 and 1273.2 mg/g, respectively.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The removal of dyes from wastewater is a matter of great interest in the field of water pollution. Wastewaters from industries like dyestuffs, tannery, textiles, paper and plastics, contain various kinds of synthetic dyes [1,2]. There are more than 100,000 commercially available dyes and more than 7×10^5 metric tons of dyes are produced worldwide annually [3]. Recent studies indicate that approximately 12% of synthetic dyes are lost during manufacturing and processing operations and that 20% of the resultant color enters the environment through effluents from industrial wastewater treatment plants [4]. Wastewaters from these industries are highly colored and the release of these effluents in natural waters produces serious damage to the environment. Dyes are organic compounds with a chemical complex structure that are stable to light, heat, oxidizing agents and resistant to aerobic digestion [5,6]. Beyond the visual pollution [7], the contamination of natural waters with dyes produces modification in biological cycles affecting mainly photosynthesis process. Many dyes are also toxic and even carcinogenic

affecting aquatic living organisms [8]. Studies showed that azo dyes and their sub-products may be carcinogenic and/or mutagenic [9–11]. In this current work, the two studied dyes are the cationic dyes, methylene blue (MB) and gentian violet (GV). MB is the most commonly used substance for dyeing natural fibers as cotton or silk. It can cause eye burns by direct contact and nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia by ingestion [12]. GV is used to dye paper as a component of black inks for printing, ball-point pens and ink-jet printers and has a numerous medicinal application. It is harmful by inhalation, ingestion, through skin contact and has also been found to cause cancer and severe eye irritation in human beings [13]. Therefore, the treatment of effluent containing such dyes is of interest due to its harmful impacts on receiving waters.

Among the various chemical treatment techniques available, the most commonly used in the removal of contaminants from wastewater are reverse osmosis, ion exchange, adsorption and precipitation [14]. Due to these environmental reasons, new technologies for degradation and/or immobilization of dyes in wastewaters have been developed. Various techniques for the removal of dyes from wastewaters have also been employed [1,15]. Among these methods, adsorption is one of the most effective methods [14,16] and the main adsorbent used for this purpose is activated carbon.

* Corresponding author. Tel.: +55 31 3559 1717; fax: +55 31 3551 1707.

E-mail address: laurent@iceb.ufop.br (L.F. Gil).

However, activated carbon presents several disadvantages [17]. It is quite expensive, non-selective and ineffective against disperse and vat dyes [18]. This has led many researchers to look for more economic and effective adsorbents as potential substitutes for activated carbon. Within this goal, natural materials like wood, peat, chitin, industrial, agricultural and domestic wastes and/or by-products such as shells of almond and hazelnut, orange peel, sawdust, corncob, rice husk or sugarcane bagasse have been largely studied to adsorb synthetic dyes [2,15]. In most cases, these materials have been used as adsorbents without any chemical modification. In addition, the chemical modification can introduce functionality to these solid supports, increasing their adsorption capacity and efficiency. A few chemically modified lignocellulosic materials have also been used as dye adsorbents [19].

Sugarcane bagasse is an excellent solid support because it is inexpensive in comparison to other solid supports such as cellulose pulp, epoxy resins, chitosan, and synthetic polymers. Besides, owing to the increase of bioethanol production in countries such as Brazil, tons and tons of sugarcane bagasse have been produced. According to the last official survey from the Brazilian National Company of Supply – CONAB, an agency from the Brazilian Ministry of Agriculture, the national production of sugarcane in 2009/2010 season was 558 million tons and represents the largest recorded production since records began. On average, 250 kg of sugarcane bagasse containing 50% moisture are produced by ton of sugarcane. In the industries of sugar and ethanol, bagasse has been burned to produce steam and energy for the process; nevertheless, the leftovers are still significant. The remaining bagasse still continues to be a menace to the environment and a more suitable and economic utilization may be the production of cellulosic ethanol for automotive fuel and green polyethylene as well as resins for the treatment of wastewater effluents. The composition of sugarcane bagasse is 40–50% cellulose, 25–30% hemicelluloses, and 20–25% lignin [20].

In our previous works [20,21], succinylated sugarcane bagasse, SCB 2, was prepared from sugarcane bagasse, B, using succinic anhydride as derivatizing agent. In the adsorption studies, SCB 2 exhibited maximum adsorption capacities for Cu^{2+} , Cd^{2+} , Pb^{2+} and Zn^{2+} ions of 185.2, 212.8, 416.7 and 125.0 mg/g, respectively. SCB 2 has negative charges due to the presence of carboxylate functions that are released after the modification with succinic anhydride and

treatment with sodium bicarbonate solution. These charges are able to interact with cationic dyes, removing them from aqueous solutions by adsorption process.

In the present work, the removal of the cationic dyes, methylene blue, MB, and gentian violet, GV, from aqueous single dye solutions using SCB 2 (Fig. 1), was studied. The adsorption studies were carried out using different contact times, pH, and initial dye concentration. The results were evaluated by three kinetic models and three adsorption models.

2. Materials and methods

2.1. Materials

Sugarcane bagasse was collected from an alcohol industry at Ouro Preto, Minas Gerais, Brazil. Succinic anhydride and pyridine were purchased from VETEC (Brazil). Cationic dyes, GV [C.I.: 42555, chemical formula: $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$, λ_{max} : 584 nm] and MB [C.I.: 52030, chemical formula: $\text{C}_{16}\text{H}_{18}\text{N}_3\text{OS}$, λ_{max} : 661 nm] were purchased from SYNTH (Brazil) and used without further purification.

2.2. Sugarcane bagasse preparation

Sugarcane bagasse was first dried under sunlight. The fiber and pith fractions were broken into small pieces and subsequently dried at 90 °C in an oven for 24 h. Sugarcane bagasse was reduced to powder by milling with tungsten ring mill. The powder was sieved in a four-sieve system (10, 60, 100 and 200 mesh). The fraction from 100 to 200 mesh was collected and washed with distilled water under constant stirring at 60–70 °C for elimination of residual sugars, separated by single filtration, washed with EtOH 95%, and dried at 90 °C in an oven. Finally, it was washed again in a Soxhlet apparatus with hexane-ethanol (1:1) for 4 h to eliminate extractives and lignin extracted from milling process. It was dried at 90 °C in an oven and stored in desiccator.

2.3. Synthesis of SCB 2

SCB 2 was prepared and characterized according to the methodology described by Gurgel et al. [20]. Sugarcane bagasse (5 g), succinic anhydride (15 g) and dry distilled pyridine (50 mL) were added to

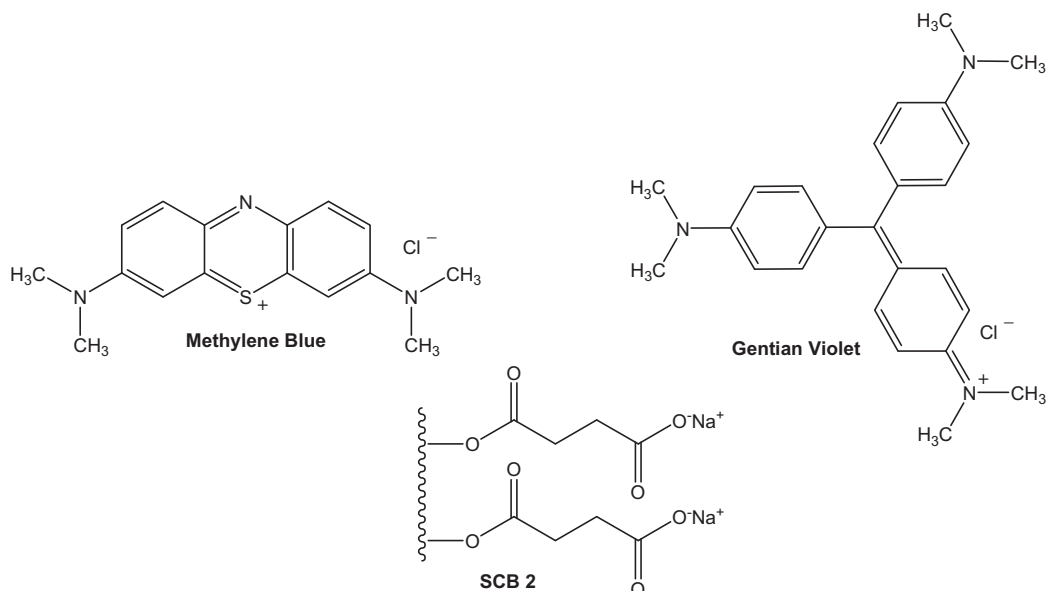


Fig. 1. Structures of methylene blue, gentian violet and SCB 2.

a round-bottom flask equipped with a reflux condenser. The mixture was heated at pyridine reflux for 24 h. At the end of the succinylation, modified bagasse was separated by filtration using a sintered glass funnel, washed with a solution of acetic acid in methylene chloride (1 mol/L), ethanol (95%), distilled water, saturated sodium bicarbonate solution, distilled water and then with acetone.

2.4. Adsorption experiments

A series of adsorption experiments of MB and GV onto SCB 2 were carried out. The parameters investigated include pH of the adsorption medium, contact time and adsorption capacity. All experiments were carried out at 25 °C. The obtained data were employed to develop equilibrium and kinetic mathematic models.

2.4.1. Kinetic study of MB and GV adsorption onto SCB 2

Experiments with each dye and SCB 2 were performed to determine the adsorption equilibrium time. The time interval used was from 10 to 1440 min. Samples of 20 mg of SCB 2 were placed into 250-mL Erlenmeyer flasks containing 100.0 mL of dye solution at known concentrations (200 mg/L for MB and 450 mg/L for GV) under constant stirring. The experiments were made without pH correction. The pH of the solutions containing SCB 2, MB and/or GV was measured and found to be between 7.0 and 8.0. The adsorbent was separated from dye solution by centrifugation (Excelsa® II mod. 206 BL) at 3600 rpm for 20 min. The residual dye concentration was measured by collecting the supernatant and measuring the concentration of MB and GV after sorption using a UV–VIS spectrophotometer (BIOSPECTRO, SP220) at an absorbance wavelength of 661 and 584 nm, respectively. The dyes concentration was calculated from a calibration curve of absorbance versus dye concentration. The adsorption amount at time t , q_t (mg/g), was calculated by:

$$q_t = \frac{(C_i - C_t) \times V}{w} \quad (1)$$

where C_i and C_t (mg/L) are the liquid-phase concentration of dye at initial and any time, respectively, V (L) is the volume of the solution, and w (g) is the weight of adsorbent used.

2.4.2. Effect of pH on MB and GV adsorption onto SCB 2

The effect of pH on MB and GV adsorption was studied over the pH range from 2 to 10. The pH was adjusted by adding few drops of NaOH and/or HCl solutions at 0.01–1.0 mol/L. In this study, 100.0 mL of dye solution of known concentration (200 mg/L for MB and 450 mg/L for GV) at different pH values was stirred with 20 mg of SCB 2. The stirring time was 6 h and 20 h for MB and GV, respectively. The dye concentration was determined as described earlier.

2.4.3. Adsorption isotherms for MB and GV

The experiments were performed for each dye and SCB 2 to determine adsorption isotherms. Samples from 15 to 40 mg and from 25 to 60 mg of SCB 2 were employed in the adsorption experiments for MB and VC, respectively. The samples were placed into 250-mL Erlenmeyer flasks containing 100.0 mL of dye solution at known concentration (150 mg/L for MB and 400 mg/L for GV) under constant stirring. Each experiment was performed at pH of the greatest dye adsorption, 8.0 for both dyes, during the time necessary to achieve the equilibrium. The equilibrium times used in these experiments were obtained from the kinetic study and found to be 360 min for MB and 1200 min for GV, respectively. The adsorption amount at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_i - C_e \times V)}{w} \quad (2)$$

where C_i and C_e (mg/L) are the liquid-phase concentration of dye at initial and equilibrium, respectively, V (L) is the volume of the solution, and w (g) is the weight of adsorbent used.

2.5. Determination of zero charge point

The pH of zero charge point, pH_{PZC} , for SCB 2 was determined using the mass titration method described by Noh and Schwarz [22]. Solutions of 0.01 mol/L $NaNO_3$ with pH values of 3, 6, and 11 were prepared using 0.1 mol/L HNO_3 and 0.1 mol/L NaOH. In this method, 100.0 mL of the prepared solution with different initial pH was added to each 250-mL Erlenmeyer flasks containing samples of SCB 2 in order to give solid to liquid ratios of 0.05, 0.1, 0.5, 1, 5 and 10%. The equilibrium pH was measured after 24 h of shaking.

3. Results and discussion

3.1. Synthesis and characterization of SCB 2

The succinylation reaction allowed the introduction of chelating functional groups in to sugarcane bagasse by esterification. The weight gain and concentration of carboxylate functions per gram of modified bagasse were found to be 80.5% and 6.0 mmol/g. SCB 2 was also characterized by FTIR spectroscopy. The most important changes that can be noticed is the arising of a band at 2925 cm^{-1} , corresponding to asymmetric stretching of CH_2 due to introduction of the succinyl group, at 1577 cm^{-1} corresponding to asymmetric and symmetric stretching owing to the presence of carboxylate functions ($-COO^-Na^+$), and at 1743 cm^{-1} corresponding to asymmetric and symmetric stretching of ester groups ($-C-O-C=O$) owing to the introduction of succinyl group by esterification [20].

3.2. Adsorption rate

Adsorption rate was investigated by measuring the amount of adsorbed dye at different contact times and pH values.

3.2.1. Effect of contact time

The effect of contact time on the adsorption of MB and GV onto SCB 2 for a fixed initial dye concentration, 200 mg/L for MB and 450 mg/L for GV, and pH 7.0–8.0 at 25 °C is shown in Fig. 2. Noteworthy is the fact that dye uptake is rapid for the first 100 min and thereafter it proceeds at a slower rate and finally attains saturation. At this point, the amount of adsorbed dye reached

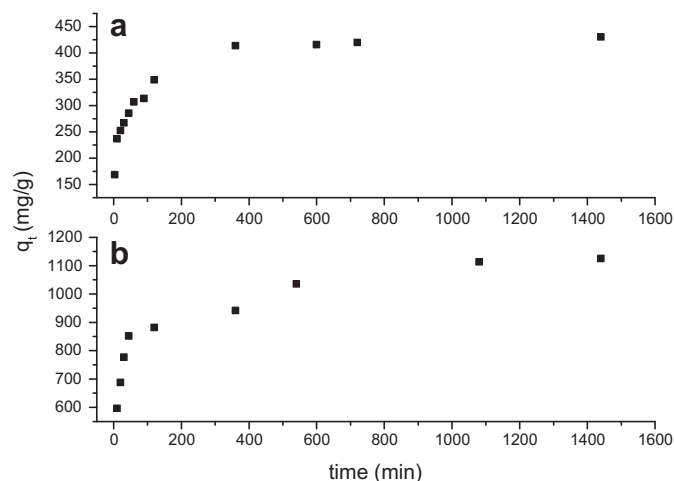


Fig. 2. Effect of contact time on the adsorption of (a) MB and (b) GV onto SCB 2.

a dynamic equilibrium state with the amount of dye in solution [23]. The time required to achieve the equilibrium state was called equilibrium time. The amount of adsorbed dye at the equilibrium time shows the maximum dye adsorption under the experimental conditions. The uptake of dye onto SCB 2 is fast at the initial stages, and thereafter, it becomes slower close to the equilibrium. It can be explained by the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a period of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases [24]. As can be seen from Fig. 2, equilibrium times of 6 h and 20 h were found for MB and GV, respectively. The result for MB adsorption is similar to those obtained by Hamdaoui [25], who found equilibrium times of 5 h for the adsorption of MB onto cedar sawdust.

In comparison to most of the published reports in the literature, equilibrium times are lower than those presented in this work. On the other hand, the concentrations of dyes employed in those papers are lower than those employed in this work. At low dye concentrations, the vacant surface sites adsorb the dye more rapidly. One explanation for this observation may be the fact that at low concentration almost all dye molecules are adsorbed very quickly on the outer surface. Further increases in the initial dye concentration led to fast saturation of adsorbent surface, and thus, most of the dye adsorption took place slowly inside the pores by intra-particle diffusion. Steric repulsion between molecules of the solute can also minimize adsorption process [23,26].

3.2.2. Effect of pH

The pH is one of most important parameters for adsorption control. Adsorption of MB and GV onto SCB 2 as function of pH is shown in Fig. 3. The adsorption of both dyes increases when the pH was increased and reached a maximum at approximately pH values

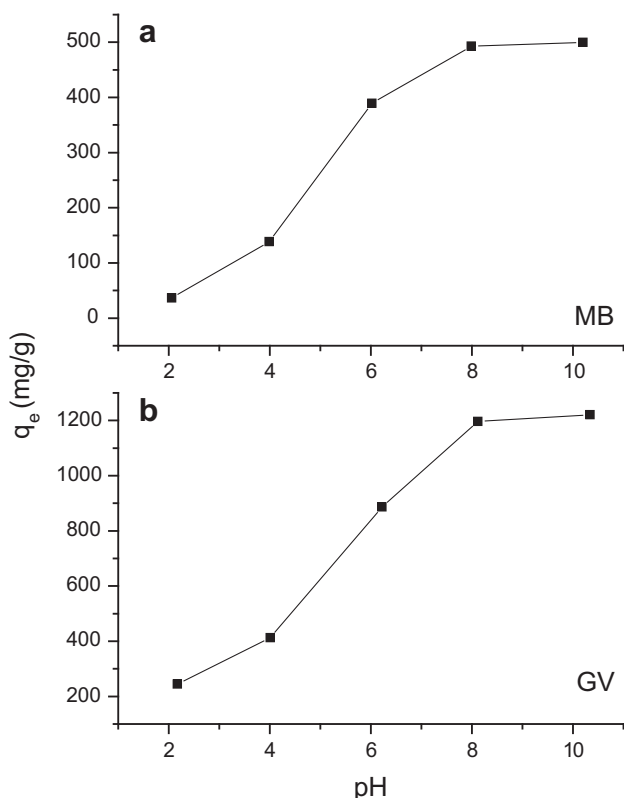


Fig. 3. Effect of initial pH on the adsorption of (a) MB and (b) GV onto SCB 2.

of 8.0 for the MB and GV. This result can be explained by considering the cationic nature of the dyes. Low pH values between 2 and 5 were unfavorable for MB and GV adsorption by SCB 2 because of the presence of an excess of hydronium (H_3O^+) ions that competes with dye cations for the adsorption sites. At acidic pH values, the number of negatively charged adsorbent sites ($-COO^-$) decreased and apparently did not favor the adsorption of positively charged dye cations [27]. For pH values higher than pH_{PZC} for SCB 2 ($pH_{PZC} = 5.26$) the number of negatively charged adsorbent sites increases [28], and consequently higher amounts of MB and GV are adsorbed by SCB 2. This observation makes it possible to conclude that the adsorption mechanism is based on electrostatic interactions between the negatively surface charged adsorbent and positively charged MB and GV dyes [26,29].

A similar tendency was noticed by Uddin et al. [30] for the adsorption of MB onto tea waste at optimum pH of 8.0, and Royer et al. [28] for the adsorption of MB onto Brazilian pine-fruit shell and carbonized forms at an optimum pH of 8.5.

Based on the obtained results for the adsorption of MB and GV onto SCB 2 as a function of contact time and pH, a contact time of 6 h and 20 h, and a pH of 8.0 for MB and GV were chosen to perform the studies as a function of initial dye concentration and build adsorption isotherms.

3.2.3. Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and are important in optimizing the use of an adsorbent in a real adsorption processes. Various isotherm models are available in the literature. Three of the most widely used isotherms were chosen to evaluate the equilibrium results: Langmuir, Freundlich and Temkin isotherms.

Langmuir adsorption isotherm theory [31,32] is based on five assumptions: (1) adsorption is limited to the formation of a monolayer, or the number of adsorbed species does not exceed the total surface sites; (2) the energy of adsorption is independent, on the other hands, all surface sites have the same energy or equal affinity for the adsorbate; (3) both solute and solvent have equal molar surface areas; (4) both surface and bulk phases exhibit ideal behavior, e.g. no solute–solute or solute–solvent interaction in either phase; and (5) it assumes that all sites are initially free and does not consider any reverse reaction of a displaced ion, such as protons with the site. Eq. (3) is a linearized and rearranged form of the general form of Langmuir equation [29,33].

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} \times b} + \frac{C_e}{Q_{max}} \quad (3)$$

where q_e (mg/g) is the equilibrium adsorption capacity, Q_{max} (mg/g) is the maximum amount of the dye per unit weight of the SCB 2 to form a complete monolayer coverage on the surface bound at high equilibrium dye concentration C_e (mg/L) and b (L/mg) is the Langmuir constant related to the affinity of binding sites. Q_{max} represents the practical limiting adsorption capacity when the surface is fully covered with dye, assisting in the comparison of adsorption performance, and b indicates the bond energy of the adsorption reaction between dye and material.

A linearized plot of C_e/q_e versus C_e was obtained from the model and is shown in Fig. 4. Q_{max} and b were computed from the slopes and intercepts of the straight lines. Table 1 lists the calculated results.

One of the essential characteristics of the Langmuir isotherm can be expressed by a separation factor, R_L ; which is defined as

$$R_L = \frac{1}{1 + (bC_i)} \quad (4)$$

where C_i is the initial concentration of dye (mg/L). The value of R_L indicates whether an isotherm is irreversible ($R_L = 0$), favorable

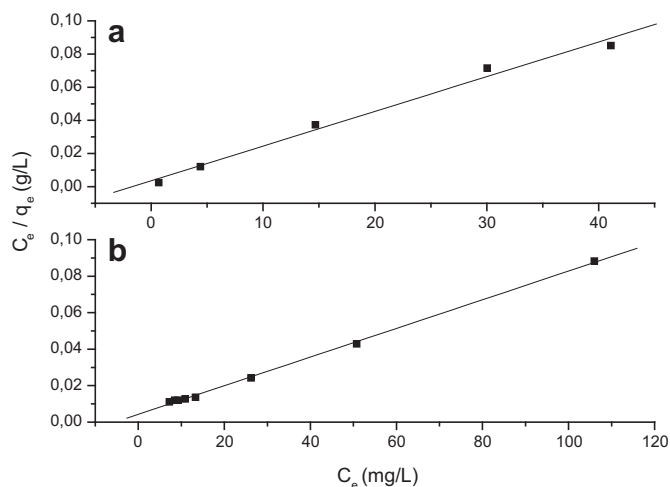


Fig. 4. Langmuir plots for the adsorption of (a) MB and (b) GV onto SCB 2.

($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). The obtained values of R_L were found to be 0.0112 and 0.0122 for MB and GV, respectively. These R_L values showed that the adsorption of both dyes on SCB 2 is favorable.

Freundlich isotherm [34] is an adsorption model for a single solute system. Freundlich model is based on an empirical equation of the distribution of solute between the solid phase and aqueous phase at equilibrium. It is not restricted to the formation of a monolayer in comparison with Langmuir theory. It also assumes that the adsorbate concentration increases so too does the concentration of adsorbate on the adsorbent surface. Theoretically, using this expression, an infinite adsorption amount can occur. Freundlich isotherm can be expressed in its linear form as shown below:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (5)$$

where K ($\text{mg/g (L/mg)}^{1/n}$) and n are the Freundlich constants. The term $1/n$ indicates the intensity of adsorption, in other words, the effectiveness of adsorption. Thus, when $1/n$ is less than unity, the adsorption is favorable. Values of K and n are calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ and are listed in Table 1.

Tempkin and Pyzhev [35] considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. Tempkin isotherm has generally been used in the linearized and rearranged form as shown by Eq. (6):

$$q_e = B \ln A + B \ln C_e \quad (6)$$

where A is an equilibrium constant of binding corresponding to the maximum energy of binding (mg/L) and the constant B is related to the heat of adsorption. A plot of q_e versus $\ln C_e$ enables the

Table 2
Comparison of maximum adsorption capacities for MB and GV taken-up.

Adsorbent	Dye	Q_{max} (mg/g)	Source
Succinylated sugarcane bagasse SCB 2	MB	478.47	This work
Brazilian pine-fruit shell	MB	252	[28]
Carbonaceous Brazilian pine-fruit shell	MB	529	[28]
Tea waste	MB	85.16	[30]
Activated carbon	MB	588	[37]
Citric acid esterifying wheat straw	MB	312.50	[19]
Succinylated sugarcane bagasse SCB 2	GV	1273.16	This work
Citric acid esterifying wheat straw	GV	227.27	[19]
Hardwood sawdust	GV	341	[36]
Sunflower seed hulls	GV	92.59	[23]
Activated carbon prepared from rice husk	GV	64.875	[29]

determination of the isotherm constants A and B . Values of A and B as obtained are shown in Table 1.

The obtained results for MB and GV adsorption onto SCB 2 for each model are presented in Table 1. The correlation coefficients, R^2 , were used to compare the three isotherm models. As can be seen from Table 1, Langmuir model showed a higher correlation coefficient than Freundlich and Tempkin models. Similar results were reported for the adsorption of MB onto cedar sawdust [25] and tea waste [30] and for the adsorption of VC onto hardwood sawdust [36]. The Q_{max} of the SCB 2 for MB and GV using Langmuir model were found to be 478.5 and 1273.2 mg/g, respectively (Table 1).

Removal of cationic dyes from aqueous solutions by various modified adsorbents has been performed by a number of research groups in the world. Some recently reported results for adsorbents prepared from agricultural wastes are shown in Table 2 and compared with SCB 2. The most important parameter to compare the adsorption performance is the Langmuir Q_{max} value, since it is a measure of maximum adsorption capacity of an adsorbent. The value of Q_{max} for MB adsorption obtained from the present study is larger than those from most of previous works. It has been found that only two adsorbents presented better adsorption efficiency than MB in the literature. For GV adsorption onto SCB 2, the obtained value was 1273.2 mg/g, and it is very higher in comparison with other adsorbents as can be seen from Table 2. These outstanding sorption capacities for GV and MB adsorption place SCB 2 as one of the best adsorbents for basic dyes removal from aqueous solutions.

3.3. Adsorption kinetics

Kinetic models are used to determine the rate of the adsorption process and how this rate controls the equilibrium time. The adsorption of a solute as a dye by a solid support in aqueous solution is a phenomenon whose kinetics is often complex. The mechanism of adsorption depends on the physical and/or chemical characteristics of the adsorbent, as well as on the mass-transport process. In order to investigate the mechanism of dye adsorption onto SCB 2, three kinetic models were studied: pseudo-first-order, pseudo-second-order and Elovich. These models are the most used to describe dye and other pollutants adsorption such as heavy metals onto solid adsorbents [38].

Table 1
Isotherm parameters for the adsorption of MB and GV onto SCB 2.

Langmuir	Freundlich		Tempkin					
	MB	GV	MB	GV				
Q_{max} (mg/g)	478.5	1273.2	K (mg/g)	301.1	483.3	A (mg/L)	1115.18	5.22
b (L/mg)	0.587	0.184	n	9.708	4.578	B	42.36	204.76
R^2	0.9996	0.9998	R^2	0.9842	0.9036	R^2	0.9622	0.8630

The pseudo-first-order kinetic model of Lagergren [39] is more suitable for lower concentrations of solute and its linear form is

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where q_t (mg/g) is the amount of adsorbate adsorbed at time t (min); q_e (mg/g) is the adsorption capacity in the equilibrium; k_1 (min^{-1}) is the rate constant of pseudo-first-order model.

The values of k_1 and q_e for the adsorption of MB and GV onto SCB 2 were determined from the plot of $\log(q_e - q_t)$ versus t . The obtained straight line yields k_1 as the slope and $\ln q_e$ as the intercept.

The pseudo-second-order model of Ho and McKay [40] based on adsorption capacity can be represented in the linear form as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where q_e (mg/g) and q_t (mg/g) are the solute amounts adsorbed per unit mass of adsorbent at equilibrium time and at time t (min) and k_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$). The equilibrium constants of pseudo-second-order model, k_2 and q_e can be obtained from the slope and intercept of the plot of t/q_t versus t (Fig. 5).

Elovich model suggests that the chemisorption, i.e. a chemical reaction, is probably the mechanism that controls the rate of adsorption [41]. This model can be applied with success in liquid solution and the linear form of the Elovich equation is:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (9)$$

where α (mg/g h) is the initial sorption rate and β (g/mg) is the desorption constant.

The values α and β can be calculated from the slope and intercept of the plot of q_t versus $\ln t$ that yields a straight line.

As can be seen from Table 3, the values of R^2 are closer to unit for pseudo-second-order model than pseudo-first-order model and Elovich model. Thus, the pseudo-second-order model can describe the both dyes adsorption by SCB 2. Furthermore, values of $q_{e,cal}$ calculated from pseudo-second-order model were in good agreement with experimental values, $q_{e,exp}$, than those calculated from pseudo-first-order model. Adsorption phenomenon followed the pseudo-second-order model during all period of adsorption and thus supports the model presupposition that the adsorption is

Table 3

Kinetic parameters for the adsorption of MB and GV onto SCB 2.

	MB	GV
$q_{e,exp}$ (mg/g)	430.1	1125.0
<i>Pseudo-first-order</i>		
k_1 (min^{-1})	0.00127	0.00098
$q_{e,cal}$ (mg/g)	191.98	506.22
R^2	0.8581	0.9474
<i>Pseudo-second-order</i>		
k_2 (g/mg min)	0.0001	0.000033
$q_{e,cal}$ (mg/g)	434.34	1133.66
R^2	0.9998	0.9992
<i>Elovich equation</i>		
α (mg/g min)	660.28	5861.43
β (g/mg)	0.0221	0.0101
R^2	0.9895	0.9818

controlled by a chemical process, i.e. chemisorption [41]. Values of R^2 for Elovich model were lower than pseudo-second-order model and thus indicate that Elovich model cannot be adequate to describe the kinetic of adsorption of MB and GV onto SCB 2. Similar results were found for the adsorption of MB and GV onto sepiolite [38] and for the adsorption of MB onto hazelnut Shell [42].

3.4. Adsorption mechanism

The adsorption mechanism for dyes removal by adsorption using an adsorbent material can be assumed as involving three steps in which bulk diffusion is considered to be instantaneous, i.e. migration of the dye from the bulk of the solution to the surface of the adsorbent, is ignored:

- (1) Diffusion of dye through the boundary layer to the surface of the adsorbent;
- (2) Intra-particle diffusion: Dye transfer from the exterior surface of the adsorbent to the interior pores of the particle through a pore diffusion or intra-particle diffusion mechanism;
- (3) Adsorption of dye in an active site on the surface of material via ion exchange, complexation and/or chelation.

In many cases, there is a possibility that intra-particle diffusion will be the rate-limiting step, which is normally determined using the equation proposed by Weber and Morris [43]:

$$q_t = k_{id} t^{0.5} + C_i \quad (10)$$

where q_t (mg/g) is the adsorbed amount at time t and k_{id} ($\text{mg/g h}^{0.5}$) is the intra-particle rate constant. According to Eq. (10), a plot of q_t versus $t^{0.5}$ should be a straight line with a slope k_{id} and intercept C_i when adsorption mechanism follows the intra-particle diffusion process. Values of C_i give an idea of the thickness of the boundary layer. The larger the intercept, the greater will be the boundary layer effect. Values of k_{id} and intercept C_i are presented in Table 4.

If the line passes through the origin, the rate-limiting process is then due only to the intra-particle diffusion. Fig. 6 shows the straight lines of the plot of q_t versus $t^{0.5}$ with multi-linearity for both dyes using SCB 2 as adsorbent. This behavior indicates

Table 4

Adsorption mechanism by intra-particle diffusion model.

	MB			GV		
	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
k_{id} (mg/g h ^{0.5})	47.53	11.36	0.90	73.19	10.41	6.381
C_i (mg/g)	86.25	207.92	395.52	365.57	771.66	890.96
R^2	1	0.9868	0.9853	0.9977	0.9658	0.9748

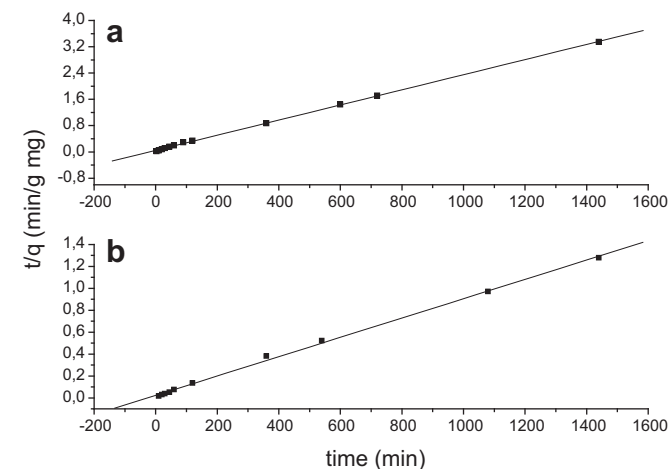


Fig. 5. Pseudo-second-order kinetic plot for adsorption of (a) MB and (b) GV onto SCB 2.

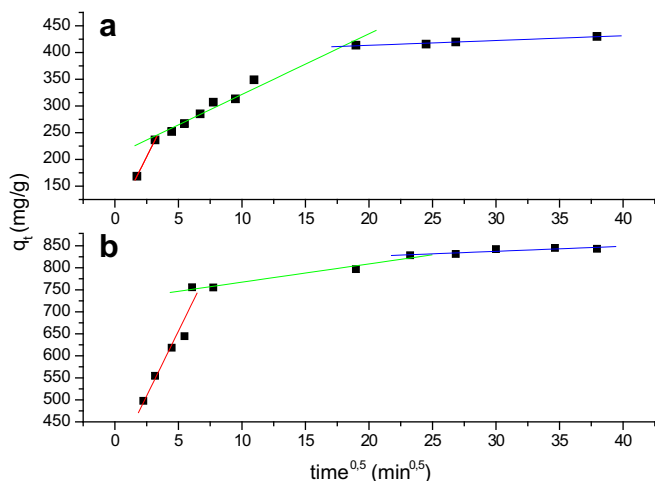


Fig. 6. Intra-particle diffusion model, (a) MB and (b) GV.

that adsorption processes involve more than one single kinetic stage [28].

The first linear portion (sharpest portion) was attributed to film diffusion, i.e. transport of dye particles from limit layer to adsorbent surfaces and corresponds to the faster stage of adsorption. The second linear portion corresponds to the gradual adsorption stage where the intra-particle diffusion is the rate-limiting. The third linear portion can be considered as the final equilibrium stage where intra-particle diffusion begins to slow down because of the extremely low dye concentration in the solution and the dye particles occupied all the active sites of SCB 2 adsorbent.

The different adsorption rates noticed showed that the adsorption of both dyes onto SCB 2 was initially fast and decreases with time.

4. Conclusions

Succinylated sugarcane bagasse (SCB 2) prepared from sugarcane bagasse, an important agricultural waste, after only one chemical modification step showed to be very efficient for removing MB and GV from aqueous solutions by adsorption. Equilibrium adsorption times were found to be 6 h and 20 h for MB and GV, respectively and optimum pH for both dyes removal was found to be equal to 8.0. The results of equilibrium adsorption were evaluated by three adsorption models and experimental data fitted very well to the Langmuir model. Maximum adsorption capacities for removal of MB and GV were found to be 478.5 and 1273.2 mg/g, respectively. This value of Q_{max} for MB adsorption is larger than those in most of the reports published in the literature. For GV, maximum adsorption capacity was found to be 1273.2 mg/g and it is higher than other adsorbents capacities reported at present moment in the literature. Three kinetic models were used to model the kinetics of adsorption. The adsorption process was well described by pseudo-second-order model, however the intra-particle diffusion model yielded three linear regions, which suggested that the adsorption can be also described by multiple sorption rates. SCB 2 exhibited remarkable adsorption capacities for removal of GV and MB from aqueous single solutions.

Acknowledgments

The authors are grateful to Universidade Federal de Ouro Preto, FAPEMIG, CNPq and CAPES. Authors would also like to thank

Dr. Jason G. Taylor (UFOP) for insightful discussion and for reviewing the manuscript for its English usage.

References

- [1] Forgacs E, Cserhati T, Oros G. Removal of synthetic dyes from wastewaters: a review. *Environment International* 2004;30:953–71.
- [2] Gupta VK, Carrott PJM, Carrott Ribeiro, Suhas MML. Low-cost adsorbents: growing approach to wastewater treatment – a review. *Critical Reviews in Environmental Science and Technology* 2009;39:783–842.
- [3] Pearce CI, Lloyd JR, Guthrie JT. The removal of colour from textile wastewater using whole bacterial cells: a review. *Dyes and Pigments* 2003;58:179–96.
- [4] Essawy AA, Ali AEH, Abdel-Mottaleb MSA. Application of novel copolymer-TiO₂ membranes for some textile dyes adsorptive removal from aqueous solution and photocatalytic decolorization. *Journal of Hazardous Materials* 2008;157:547–52.
- [5] Sun QY, Yang LZ. The adsorption of basic dyes from aqueous solution on modified peat-resin particle. *Water Research* 2003;37:1535–44.
- [6] Gupta VK, Mittal A, Krishnan L, Gajbe V. Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash. *Separation and Purification Technology* 2004;40:87–96.
- [7] Gupta VK, Mittal A, Jain R, Mathur M, Sikarwar S. Adsorption of Safranin-T from aqueous solution using waste materials – activated carbon and activated rice husks. *Journal of Colloid and Interface Science* 2006;303:80–6.
- [8] O'Neill C, Hawkes FR, Hawkes DL, Lourenco ND, Pinheiro HM, Delee W. Colour in textile effluents – sources, measurement, discharge consents and simulation: a review. *Journal of Chemical Technology and Biotechnology* 1999;74: 1009–18.
- [9] Kunz A, Peralta-Zamora P, Moraes SG, Durán N. Novas tendências no tratamento de efluentes têxteis. *Química Nova* 2002;25:78–82.
- [10] Gupta VK, Jain R, Varshney S. Removal of reactive golden yellow 3 RFN from aqueous solution using wheat husk – an agricultural waste. *Journal of Hazardous Materials* 2007;142:443–8.
- [11] Mittal A, Mittal J, Malviya A, Gupta VK. Removal and recovery of chrysoidine Y from aqueous solutions by waste materials. *Journal of Colloid and Interface Science* 2010;344:497–507.
- [12] Rafatullah M, Sulaiman O, Hashim R, Ahmad A. Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of Hazardous Materials* 2010;177: 70–80.
- [13] Ahmad R. Studies on adsorption of crystal violet dye from aqueous solution onto coniferous pinus bark powder (CPBP). *Journal of Hazardous Materials* 2009;171:767–73.
- [14] Gupta VK, Suhas, Ali I, Saini VK. Removal of rhodamine B, fast green, and methylene blue from wastewater using red mud, an aluminum industry waste. *Industrial and Engineering Chemistry Research* 2004;43:1740–7.
- [15] Gupta VK, Suhas. Application of low-cost adsorbents for dye removal – a review. *Journal of Environmental Management* 2009;90:2313–42.
- [16] Dabrowski A. Adsorption – from theory to practice. *Advances in Colloid and Interface Science* 2001;93:135–224.
- [17] Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials* 2003;97: 219–43.
- [18] Crini G. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource Technology* 2006;97:1061–85.
- [19] Gong RM, Zhu SX, Zhang DM, Chen J, Ni SJ, Guan R. Adsorption behavior of cationic dyes on citric acid esterifying wheat straw: kinetic and thermodynamic profile. *Desalination* 2008;230:220–8.
- [20] Gurgel LVA, Freitas RP, Gil LF. Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. *Carbohydrate Polymers* 2008;74:922–9.
- [21] Pereira FV, Gurgel LVA, Aquino SF, Gil LF. Removal of Zn²⁺ from electroplating wastewater using modified wood sawdust and sugarcane bagasse. *Journal of Environmental Engineering* 2009;135:341–50.
- [22] Noh JS, Schwarz JA. Effect of HNO₃ treatment on the surface-acidity of activated carbons. *Carbon* 1990;28:675–82.
- [23] Hameed BH. Equilibrium and kinetic studies of methyl violet sorption by agricultural waste. *Journal of Hazardous Materials* 2008;154:204–12.
- [24] Mall ID, Srivastava VC, Kumar GVA, Mishra JM. Characterization and utilization of mesoporous fertilizer plant waste carbon for adsorptive removal of dyes from aqueous solution. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2006;278:175–87.
- [25] Hamdaoui O. Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *Journal of Hazardous Materials* 2006;135: 264–73.
- [26] Hameed BH, El-Khaiary MI. Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull. *Journal of Hazardous Materials* 2008;155:601–9.
- [27] Garg VK, Kumar R, Gupta R. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*. *Dyes and Pigments* 2004;62(1):1–10.
- [28] Royer B, Cardoso NF, Lima EC, Vaghetti JCP, Simon NM, Calvete T, et al. Applications of Brazilian pine-fruit shell in natural and carbonized forms as

- adsorbents to removal of methylene blue from aqueous solutions – kinetic and equilibrium study. *Journal of Hazardous Materials* 2009;164:1213–22.
- [29] Mohanty K, Naidu JT, Meikap BC, Biswas MN. Removal of crystal violet from wastewater by activated carbons prepared from rice husk. *Industrial and Engineering Chemistry Research* 2006;45:5165–71.
- [30] Uddin MT, Islam MA, Mahmud S, Rukanuzzaman M. Adsorptive removal of methylene blue by tea waste. *Journal of Hazardous Materials* 2009;164: 53–60.
- [31] Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of Colloid and Interface Science* 1918;57:1361–403.
- [32] Rosen MJ. *Surfactants and interfacial phenomena*. 2nd ed. New York: John Wiley and Sons; 1989.
- [33] Ho YS, Chiu WT, Wang CC. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. *Bioresource Technology* 2005;96:1285–91.
- [34] Freundlich H. Adsorption in solution. *Zeitschrift für Physikalische Chemie* 1906;57:385–470.
- [35] Tempkin MJ, Pyzhev V. *Acta Physicochimica URSS* 1940;12:217–22.
- [36] Chakraborty S, De S, DasGupta S, Basu JK. Adsorption study for the removal of a basic dye: experimental and modeling. *Chemosphere* 2005; 58:1079–86.
- [37] El Qada EN, Allen SJ, Walker GA. Adsorption of basic dyes from aqueous solution onto activated carbons. *Chemical Engineering Journal* 2008;135: 174–84.
- [38] Dogan M, Ozdemir Y, Alkan M. Adsorption kinetics and mechanism of cationic methyl violet and methylene blue dyes onto sepiolite. *Dyes and Pigments* 2007;75:701–13.
- [39] Lagergren S. Zur Theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar* 1898;24(4):1–39.
- [40] Ho YS, McKay G. Kinetic models for the sorption of dye from aqueous solution by wood. *Process Safety and Environmental Protection* 1998;76:183–91.
- [41] Crini G, Badot PM. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: a review of recent literature. *Progress in Polymer Science* 2008;33: 399–447.
- [42] Sanchez-Martin J, Gonzalez-Velasco M, Beltran-Heredia J, Gragera-Carvajal J, Salguero-Fernandez J. Novel tannin-based adsorbent in removing cationic dye (methylene blue) from aqueous solution. Kinetics and equilibrium studies. *Journal of Hazardous Materials* 2010;174:9–16.
- [43] Weber WJ, Morris JC. Kinetics of adsorption on carbon from solution. *Journal of the Sanitary Engineering Division* 1963;89(SA2):31–59.