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Kinetic and Thermodynamic Studies on the Adsorption of Reactive Red 239 by Carra Sawdust Treated with Formaldehyde

Kinetic and Thermodynamic Studies on the Adsorption of Reactive Red 239 by Carra Sawdust Treated with Formaldehyde

Nedher Sanchez,[1,2] Tânia M. Benedetti,[1] Mario Vazquez,[2] Susana I. Córdoba de Torresi[1] and Roberto M. Torresi[1,*] *(1) Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo (USP), CP 26077, 05513-970, São Paulo-SP, Brazil. (2) Instituto de Química, Facultad de Ciencias Exactas y Naturales, Universidad de Antioquia, A.A.1226, Medellín, Colombia*

ABSTRACT: In this study, carra sawdust pre-treated with formaldehyde was used to adsorb reactive red 239 (RR239). The effects of several experimental conditions, including the concentration of dye, sorbent dosage, temperature, ionic strength, stirring speed and solution pH, on the kinetics of the adsorption process have been studied, and the experimental data were fitted to pseudo-second-order model. A study of the intra-particle diffusion model indicates that the mechanism of dye adsorption using carra sawdust is rather complex and is most likely a combination of external mass transfer and intra-particle diffusion. The experimental data obtained at equilibrium were analyzed using the Langmuir and Freundlich isotherm models, and the results indicated that at this concentration range, both models can be applied for obtaining the equilibrium parameters. The maximum dye uptake obtained at 298 K was found to be 15.1 mg g^{-1}. In contrast to the usual systems, the reactive dye studied in the present work is strongly attached to the sawdust even after several washes with water, allowing it to be discarded as a solid waste.

1. INTRODUCTION

Industries that produce and use dyes to colour their goods, such as the textile industry, are responsible for generating wastewater that contains approximately 10–15% of the dyes from an annual production of over 700 tonnes (Forgacs *et al*. 2004). The coloured water reduces the penetration of light, which is essential for photosynthesis. In addition, many of these dyes are toxic to some aquatic organisms and pose a serious health risk to human beings as well (Kaur and Datta 2011).

Among the dyes that are used in the textile industry, the most common ones are reactive dyes (Parson 2004). These compounds contain a reactive group that forms a chemical bond with the fibre in alkaline aqueous solutions, resulting in a high-quality product when compared with the other common dyes used for this purpose (O'Mahony *et al*. 2002). However, these types of dyes also form strong chemical bonds with water, which results in significant waste generation of up to 50% in addition to the difficulties involved in the treatment of water using conventional purification methods (Aksu and Cagatay 2006; Al-Degs *et al*. 2008).

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*Author to whom all correspondence should be addressed. E-mail: rtorresi@iq.usp.br

Among the existing methods for removing dyes from water, physical adsorption using activated carbon as an adsorbent is an attractive alternative because it has the ability to remove stable dyes that cannot be biologically degraded, which is the case with reactive dyes (Aksu and Yener 2001). However, the large-scale use of this method is restricted owing to its high cost (Meshko *et al.* 2001) and difficulties in regenerating the adsorbent (Toor and Jin 2012).

Therefore, an increasing number of studies have been focused on developing low-cost adsorbent alternatives, such as natural materials, biosorbents and waste from industries and agricultural practices (Crini 2006; Chatterjee *et al.* 2012; Dawood and Sen 2012; Nemchi *et al.* 2012; Shen *et al.* 2011) that can be applied for removal of toxic compounds after making some chemical modifications. Among the available options, sawdust, which is a waste generated from the industrial production of the wood, has emerged as a promising alternative due its biodegradability, variety and availability in large quantities (Sánchez *et al.* 2010; Ansari *et al.* 2011). In addition to the use of sawdust as an adsorbent after some chemical modifications, it can also be used as a precursor for obtaining activated carbon through pyrolysis (Gan *et al.* 2004; El-Latif and Ibrahim 2010). However, due to the large variety of both dyes and sawdust and the numerous variables that affect adsorption efficiency, such as pH and the chemical modification of the sorbent, the selection of a suitable system for the purification of a given wastewater composition still represents a challenge, which encourage more studies in this field to get a better understanding of the mechanisms that govern this process. Furthermore, the majority of the published works focus on low-cost sorbents that are not related to the uptake of reactive dyes, which are usually more difficult to be removed from water than other common dyes.

The present study is focused on the adsorption of reactive red 239 (RR 239) or Remazol Red 3BS (from DyStar - MW 1085.84 g mol^{-1} and λ_{max} = 540 - Figure 1) from water using carra sawdust that was pre-treated with formaldehyde. Carra is the common name that refers to the flowering trees of the Bombacaceae family, genus *Huberodendron*. The genus is very common in tropical countries.
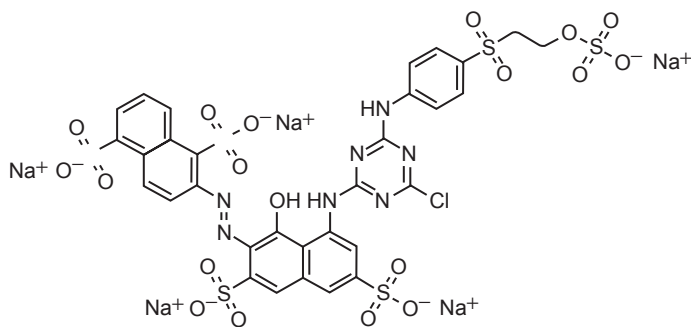

Figure 1. Representative structure of the reactive red 239 dye.

The effects of different experimental conditions, such as contact time, pH, initial dye concentration, stirring speed, sorbent mass, temperature and ionic strength, on the adsorption efficiency were studied, and the adsorption mechanism was examined using kinetic and thermodynamic studies.

2. MATERIALS AND METHODS

2.1. Sawdust Pre-treatment

The carra tree sawdust, collected as a waste generated from furniture production at a local sawmill, was washed with hot distilled water and dried in an oven before grinding in a steel mill, the result of which yeilds 20–50 mesh particles. After this step, the ground material was treated with a 0.5% formaldehyde solution in a 1:5 (sawdust:formaldehyde w/v) ratio for 4 hours at 50 °C (Garg *et al*. 2004). Finally, after filtration and washing with water, the treated material was activated in an oven at 70 °C for 24 hours and stored in an airtight flask for subsequent use. A morphological analysis was performed by field emission scanning electron microscopy (FESEM) using a Jeol microscope, model JSM-7401F.

2.2. Dye Solutions

The effects of different variables on the adsorption kinetics were studied by systematically changing the adsorption parameters using the following conditions as a standard: dye concentration, 70 mg l^{-1}; pH, 1.6; stirring speed, 400 rpm; sorbent dosage, 83.3 mg l^{-1}; temperature, 25 °C.

The studies were conducted by changing one variable at a time while maintaining the others as the standard as follows: dye concentration, 50–300 mg l^{-1}; pH, 1.6–8.0; stirring speed, 0–1000 rpm; sorbent dosage, 16.7–100 g l^{-1}; temperature, 20–60 °C. The influence of the ionic strength was also examined by adding Na_2SO_4 to a standard solution in concentrations between 0 and 25 g l^{-1}. All of the experiments were performed in duplicates.

2.3. Adsorption Analysis

The amount of adsorbed material as a function of time was determined by UV–VIS spectroscopy using a UV–Vis spectrophotometer (HP 8453), which is set at a wavelength of 540 nm. The absorbance values were converted into concentration values using previously established calibration curves, and the obtained values were used for calculating the mass of the adsorbed material per mass of sorbent using equation (1).

$$q = (C_0 - C_t)/C_{sor} \tag{1}$$

where q is the mass of adsorbed material per mass of sorbent (mg g^{-1}), C_0 is the initial dye concentration (mg l^{-1}), C_t is the dye concentration (mg l^{-1}) at a given time t (min) and C_{sor} is the sorbent dosage (g l^{-1}).

2.4. Kinetic Studies

For kinetics analysis, linearized and non-linearized pseudo-first-order [equations (2) and (3)] (Ho 2004) and pseudo-second-order [equations (4) and (5)] (Ho and McKay 1998) models were applied for fitting the amount of adsorbed material as a function of time at different concentrations of solution:

$$\ln(q_e - q) - \ln q_e = -k_1 t \tag{2}$$

$$q = \frac{q_e}{e^{-k_1 t + 1}} \tag{3}$$

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{4}$$

$$q = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{5}$$

where k_1 (min^{-1}) is the pseudo-first-order rate constant, k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant, q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium and q (mg g^{-1}) is the amount of dye on the surface of the carra sawdust at a given time t (minutes). From the obtained parameters, the initial sorption rate, h, was calculated using equation (6):

$$h = k_2 q_e^2 \tag{6}$$

2.5. Diffusion Mechanism

The diffusion mechanism was studied using the widely accepted model developed by Weber and Morris (1963), wherein the plot of q_e as a function of $t^{1/2}$ produces a straight line if the adsorption process is controlled by intra-particle diffusion [equation (7)].

$$q = k_p t^{1/2} + Q \tag{7}$$

where k_p is the intra-particle rate constant (g mol^{-1} min$^{-1/2}$) and Q is the intercept. The plots of q_t as a function of $t^{1/2}$ at different concentrations of dye solution were used for the intra-particle diffusion studies.

2.6. Thermodynamic Analysis

The experimental data obtained as a function of temperature were used to calculate the thermodynamic parameters, $\Delta H°$, $\Delta S°$, $\Delta G°$ and E_a, using the van't Hoff, Gibbs and Arrhenius equations.

2.7. Absorption Isotherm Analysis

The adsorption mechanism was also studied at equilibrium using the Langmuir [equation (8)] and Freudlich [equation (9)] models (Freundlich 1906; Langmuir 1916; Kumar and Sivanesan 2006a), using the data obtained from the experiments that were performed with different concentrations of dye.

$$q_e = \frac{q_m K_L C_e'}{1 + K_L C_e'} \tag{8}$$

$$q_e = K_F C_e'^{1/n} \tag{9}$$

In equations (6) and (7), q_m (mg g^{-1}) is the maximum amount of adsorbed dye per mass of sorbent for the formation of one monolayer and K_L is the Langmuir constant related to the energy of adsorption. K_F and n are the Freundlich constants, and the first one is related to the amount of

adsorption and the second one with the degree of non-linearity. C'_e is the concentration of dye in the solution at equilibrium.

3. RESULTS AND DISCUSSION

3.1. Effect of Formaldehyde Treatment

To investigate the effect of formaldehyde on the dye adsorption capability of the sawdust, IR spectra (data not shown) and FESEM images were collected before and after treatment. FESEM images are shown in Figure 2.
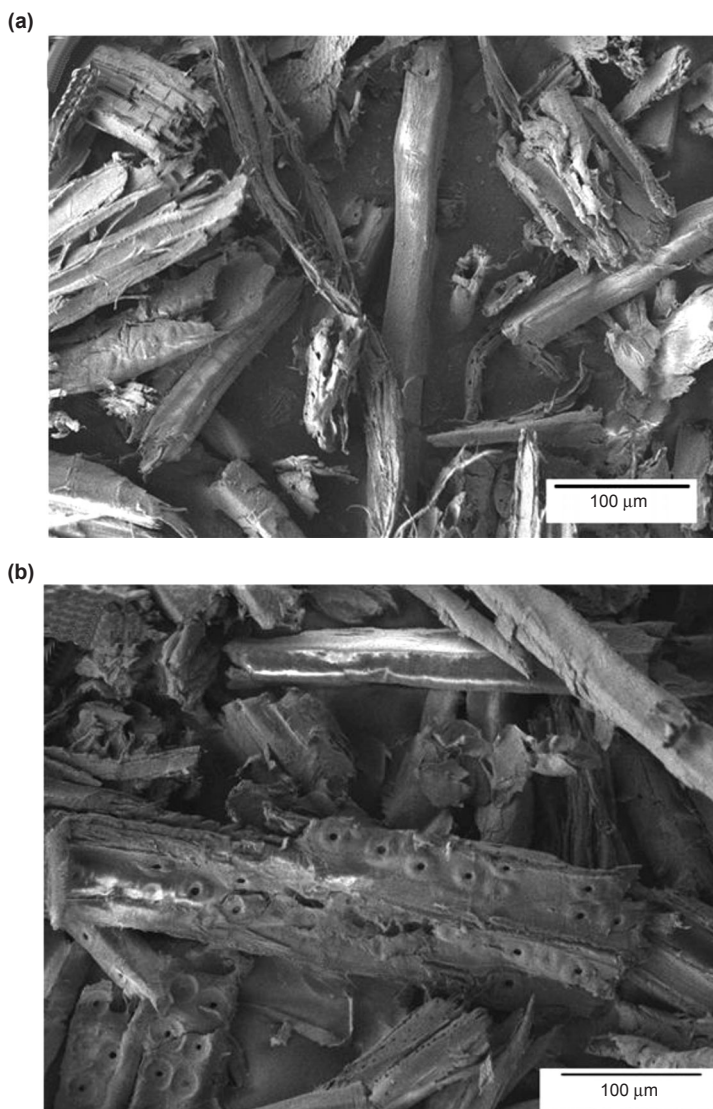
(a)

(b)

Figure 2. FESEM images of the carra sawdust before (a) and after (b) treatment with formaldehyde.

The IR spectra of both samples are very similar, which suggests that the modification of the sawdust is only morphological, which was also observed in the FESEM images. This result indicates that the sawdust maintained the same chemical characteristics after the treatment with formaldehyde. From the images, it was possible to observe that the formaldehyde physically attacks the sawdust, causing holes at the material surface. These holes increase the contact area with the dye solution, allowing it to penetrate into the holes and being adsorbed by the inner portions of the sorbent (Tumlos *et al.* 2011). In fact, the adsorption capacity of the sawdust after chemical treatment is higher when compared with the sawdust before treatment, which is observed in the amount of adsorbed dye as a function of time plots for sawdust before and after chemical treatment (Figure 3). The amount of adsorbed material was calculated from the absorbance values according to equation (1). According to the results presented in Figure 3, the adsorption capacity of sawdust is improved by approximately 21% after treatment with formaldehyde.
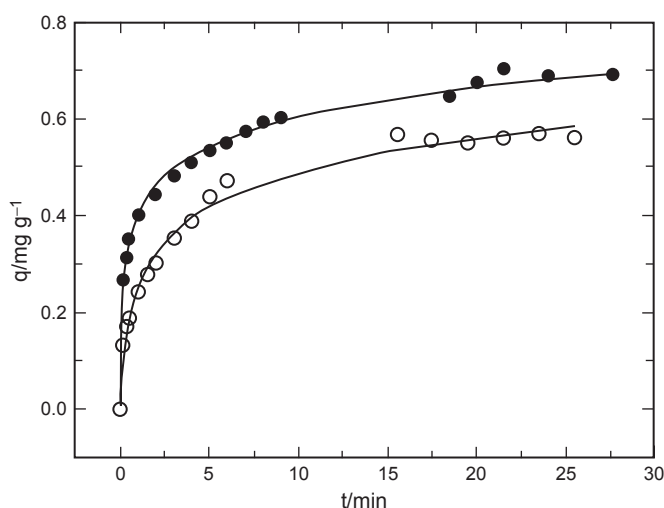

Figure 3. Amount of dye adsorbed as a function of time using sawdust before (closed circles) and after (open circles) treatment with formaldehyde. Dye concentration: 70 mg l^{-1}, dye volume: 60 ml, pH: 3.5, sorbent dosage: 83.3 g l^{-1}, stirring speed: 400 rpm, temperature: 25 °C.

3.2. Effects of Contact Time and the Initial Concentration of Dye

To establish the equilibrium time for maximum dye uptake and to study the kinetics of the sorption process, absorbance measurements of aliquots of the dye solution at different contact times ranging from 0 to 60 minutes were performed and converted into the mass of adsorbed material values using equation (1). The results are shown in Figure 4 for different concentrations of solution.

It is possible to infer that the adsorption rate decreases with increasing time until reaching equilibrium due to the continuous decrease in the driving force ($q_e - q$). The plots also demonstrate that the adsorbate uptake, q, increases with increasing C_0, which can be attributed to the mass gradient pressure that acts as a driving force to transfer the species from the bulk solution to the surface of the substrate; in fact, when the initial dye concentration increases from 50 to 300 mg l^{-1}, the equilibrium sorption capacity is increased by approximately sevenfold.
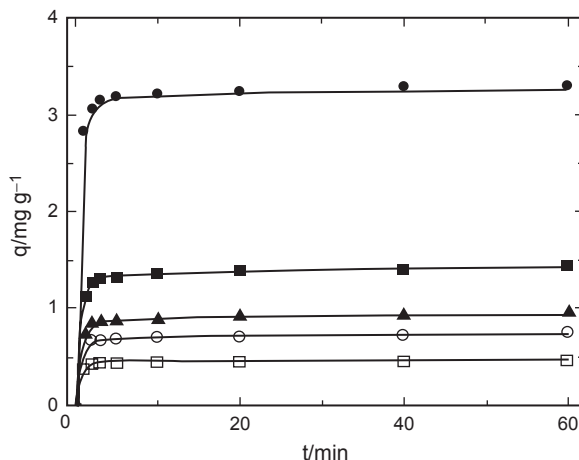
Figure 4. Mass of adsorbed dye as a function of exposure time in a solution of dye with concentrations of 50 mg l^{-1} (open squares), 70 mg l^{-1} (open circles), 100 mg l^{-1} (closed triangles), 150 mg l^{-1} (closed squares) and 300 mg l^{-1} (closed circles); Solution pH: 1.6, stirring speed: 400 rpm, sorbent dosage: 83.3 g l^{-1}, temperature: 25 °C.

3.3. Kinetic Studies

To determine the most suitable model for the kinetic studies, the obtained data were fit using both the pseudo-first and pseudo-second order linearized equations, and the obtained plots and the outputs are presented in Figure 5 and Table 1, respectively. The equations can be linearized using different methods, and the choice of the most suitable linear form is of great importance for the correct analysis. For the pseudo-first-order model, the most common linear form is the one proposed by Langergren (Lagergren 1898), whereas for the pseudo-second-order model, there are several possible options, and the one proposed by Ho and McKay (1999) is the most suitable for the present application (Kumar and Sivanesan 2006b).

From the fitted plots and obtained parameters, it is possible to observe that the experimental data were better fit with the pseudo-second-order equation, in which the correlation coefficient, R^2, was equal to unity for all concentrations, whereas for the pseudo-first-order model, this parameter is less than 0.88 in all the cases. The pseudo-second-order model assumes that the rate-limiting step is chemisorption, which involves the sharing or exchanging of electrons between the adsorbed species and the substrate (Toor and Jin 2012). In addition, the q_e values match very well with the experimental data, and by analyzing the kinetic constants k_1 and k_2, it is possible to set a tendency for k_2 with time, but this is not possible for k_1 values; in fact, the higher the concentration, the lower the kinetic constant is for the second-order model, which can be attributed to a greater competition for the surface sites at higher concentrations (Dawood and Sen 2012). However, although longer times are required to reach equilibrium at higher concentrations, it is possible to adsorb a greater amount of material with increasing concentration of the dye solution. Another observation is the h parameter: this factor indicates the initial sorption rate and the obtained values are also in agreement with the experimental data because it increases with increasing concentration of dye in the solution.

Based on these conclusions and on the fact that no difference in the kinetic parameters was observed using non-linear or linear equations (non-linear data not shown), the non-linear equation of the pseudo-second-order model was used to study the effect of the other variables on the adsorption kinetics.
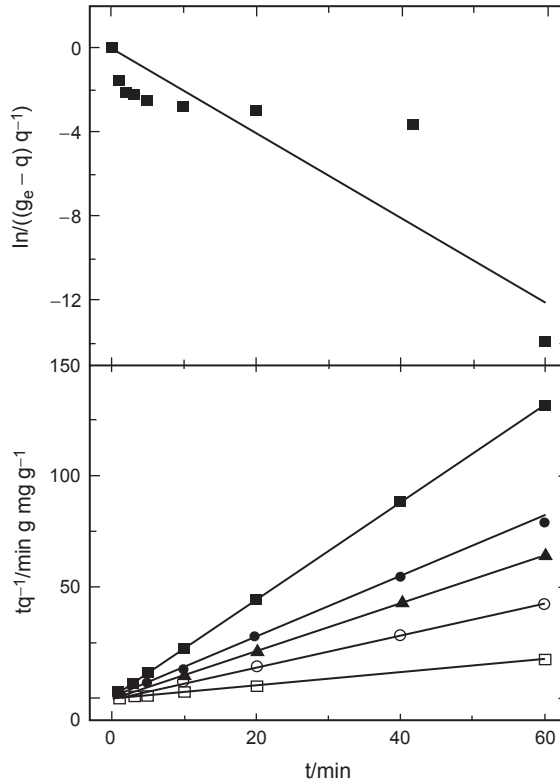
Figure 5. Plots of experimental data (dot) and fitted curves (line) following the pseudo first-order model (a) and pseudo second-order model (b); 50 mg l^{-1} (closed squares), 70 mg l^{-1} (closed circles), 100 mg l^{-1} (closed triangles), 150 mg l^{-1} (open circles) and 300 mg l^{-1} (open squares). Solution pH: 1.6, stirring speed: 400 rpm, sorbent dosage: 83.3 g l^{-1}, temperature: 25 °C.

TABLE 1. Obtained Parameters from Fitting the Experimental Data at Different Concentrations of Dye Solution with the Equations for the Pseudo-First-Order and Pseudo-Second-Order Models

Model	Plot	Parameters	50 mg l^{-1}	70 mg l^{-1}	100 mg l^{-1}	150 mg l^{-1}	300 mg l^{-1}
First order	$(q_e - q)/$ q_e vs. t	k_1 (min^{-1}) R_2	0.0616 0.795	0.0392 0.696	0.0593 0.880	0.0685 0.857	0.0731 0.790
Second order	t/q vs. t	q_e (g mg^{-1}) k_2 (g mg^{-1} min^{-1}) h (mg mg^{-1} min^{-1}) R^2	0.457 7.83 1.64 1.000	0.745 2.99 1.66 1.000	0.953 2.37 2.15 1.000	1.44 2.03 4.23 1.000	3.31 1.89 20.7 1.000

3.4. Sorption Mechanism

From a mechanistic point of view, identifying the rate-limiting step is an important factor to be considered in the sorption process. The intra-particle diffusion model is the most commonly used

method for studying the rate-controlling step of adsorption. If the plot of q as a function of $t^{1/2}$ yields a straight line that passes through the origin [i.e. Q in equation (7) is zero], the slowest step is the diffusion of dye molecules into the pores of the sorbent; if this case does not hold true, other steps, such as the migration of the dye molecules from the bulk solution to the surface of the sorbent, diffusion through the boundary layer to the surface of the sorbent and/or adsorption at sites, are also controlling the adsorption rate (Namasivayam and Kanchana 1992; Dulman and Cucu-Man 2009). Plots of q as a function of $t^{1/2}$ at different concentrations of solution are shown in Figure 6.

The plots exhibit two linear ranges, which indicate that the adsorption rate is controlled by two processes. The first step is related to the diffusion of dye towards the sorbent and is the fastest step where the majority of the dye adsorbs. This is followed by the second step, which consists of
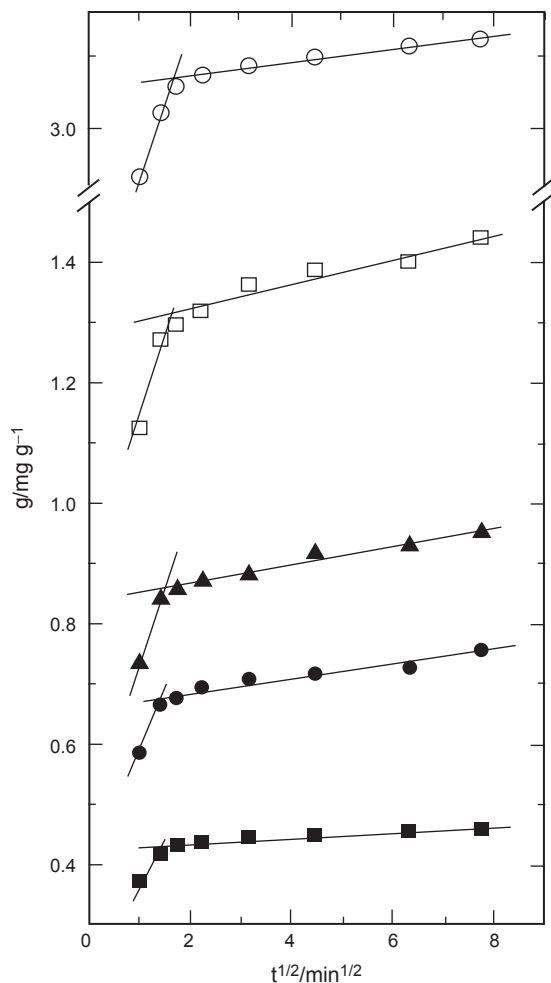

Figure 6. q as a function of $t^{1/2}$ for different concentrations of dye solution: 50 mg l^{-1} (closed squares), 70 mg l^{-1} (closed circles), 100 mg l^{-1} (closed triangles), 150 mg l^{-1} (open squares) and 300 mg l^{-1} (open circles). Solution pH: 1.6, stirring speed: 400 rpm, sorbent dosage: 83.3 g l^{-1}, temperature: 25 °C. Full lines are for indicate the two linear regions.

intra-particle diffusion (de Menezes *et al*. 2012). From the linear portion corresponding to the second step of data presented in Figure 6, the parameters k_p and Q were calculated by fitting with equation (7). The obtained k_p values (data not shown) decrease with decreasing solution concentration, which indicates that the contribution of intra-particle diffusion to the adsorption process is less significant as the amount of dye available for adsorption decreases.

3.5. Equilibrium Isotherms

To obtain information about the system at equilibrium, the q_e as a function of the concentration of solution at equilibrium (C'_e) plot was fit with the Langmuir and Freundlich isotherm equations. The results are shown in Figure 7. The C'_e values were obtained from the absorbance values of the dye solutions at the end of the adsorption process using the calibration curve. Both models fit well with the experimental data, with $R^2 > 0.999$. The calculated parameters are presented in Table 2.
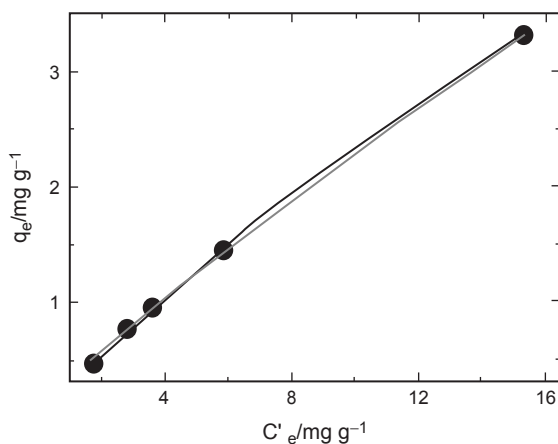

Figure 7. q_e as a function of C'_e. (closed circles) experimental data; (black full line) fitting with Freudlich model; (grey full line) fitting with Langmuir model. Solution pH: 1.6, stirring speed: 400 rpm, sorbent dosage: 83.3 g l^{-1}, temperature: 25 °C.

TABLE 2. Parameters Obtained by Fitting the Freundlich and Langmuir Equations to the Experimental Data at Equilibrium Conditions

Freundlich		Langmuir	
K_f	N	K_L	q_m
0.305	1.14	0.0183	15.10

   The fact that both models fit well with the experimental data can be explained based on the low concentrations of dye used. By performing an analogy with the adsorption of gases, in which n is closer to unity as the pressure is diminished, the value of the n parameter obtained in the present study suggests that the dye solutions are sufficiently diluted to consider that the adsorption is directly proportional to their concentration. The calculated maximum adsorption capacity, q_m, when compared with other systems based on sawdust for dye removal presented in the literature (Table 3) indicates that this is a promising system for the removal of reactive dyes.

TABLE 3. q_m for Different Systems using Sawdust as Sorbent for the Removal of Dyes from Water

Adsorbent	Dye	q_m (mg g^{-1})	Reference
Beech wood sawdust	Direct brown	526.3	Dulman and Cucu-Man 2009
Beech wood sawdust	Direct brown 2	416.7	Dulman and Cucu-Man 2009
Pine sawdust	Acid yellow 132	398.8	Özacar and Sengil 2005
Pine sawdust	Acid blue 256	280.3	Özacar and Sengil 2005
Cedar sawdust	Methylene blue	142.36	Hamdaoui 2006
Beech wood sawdust	Basic blue 86	136.9	Dulman and Cucu-Man 2009
Meranti sawdust	Methylene blue	120.48	Ahmad *et al*. 2009
Pine Sawdust	Astrazon yellow	81.77	Ouazene and Sahmouney 2010
Treated sawdust	Basic green 4	74.5	Garg *et al*. 2003
Wood sawdust	Basic blue 69	74.4	Ho and McKay 1998
Rattan sawdust	Malachite green	62.71	Hameeda and El-Khaiary 2008
Cherry sawdust	Methylene blue	39.84	Ferrero 2007
Rubber wood sawdust	Malachite green	36.45	Kumar and Sivanesan 2007
Mansonia Sawdust	Methylene blue	33.44	Ofomaja 2009
Fir sawdust	Basic yellow 28	33.43	Laasri *et al*. 2007
Cherry sawdust	Acid blue 25	31.84	Ferrero 2007
Beech sawdust	Red basic 22	22.56	Batzias and Sidiras 2007a
Fir sawdust	Basic red 46	20.47	Laasri *et al*. 2007
Carra sawdust	**Reactive red 239**	**15.1**	**This study**
Beech sawdust	Methylene blue	13.67	Batzias and Sidiras 2007a
beech sawdust	Methylene blue	10.95	Batzias and Sidiras 2007b
Wood sawdust	Acid blue 25	5.99	Ho and McKay 1998
Neem sawdust	Basic violet 3	3.78	Khattri and Singh 2000
Neem sawdust	Basic green 4	3.42	Khattri and Singh 2000
Wood sawdust	Metanil yellow	3.49×10^{-3} [a]	Pekkuz *et al*. 2008
Wood sawdust	Methylene blue	1.17×10^{-2} [a]	Pekkuz *et al*. 2008

[a]These values are in mmol/g. M.M Metanil yellow: 319.85. M.M Methylene blue: 375.38

It is well known that reactive dyes are more complex to treat when compared with other types of dyes due to their low affinity for substrates because of their high solubility in water. Furthermore, the mechanism of colouring of reactive dyes is more complex compared with other types of dyes (Parson 2004). In some studies, the sawdust is thermally modified or is functionalized for improving the uptake capacity of reactive dyes (Lim *et al*. 2003; Chakraborty *et al*. 2006; Vijayaraghavan *et al*. 2009); however, a study that balances cost and efficiency needs to be performed to determine their economic viability.

3.5. Effect of pH

To determine how the pH value of the solution affects the adsorption of dye and to determine the most suitable pH for the effective adsorption of the RR239 dye on the sorbent, the dye adsorption as a function of time at different solution pH values was monitored, and the obtained results are shown in Figure 8.

No change in the maximum absorbance wavelength was observed for solutions at different pH values, which suggests that no modifications in the structure of the dye occurred (Dawood and Sen 2012). The experiments were performed over a pH range from 1.6 to 8.0. The highest uptake values
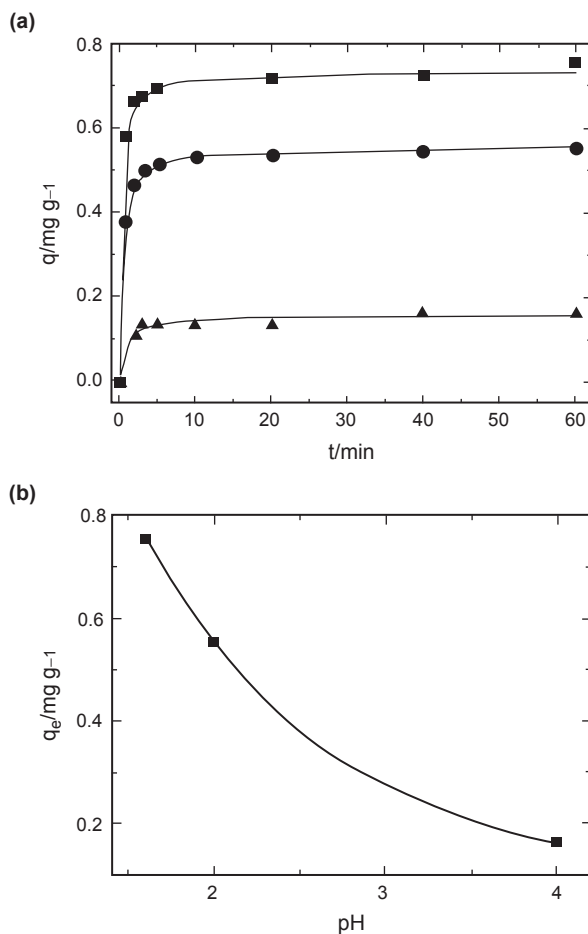
Figure 8. (a) amount of adsorbed dye per mass of sorbent as a function of time at pH 1.6 (closed squares), 2.0 (closed circles) and 4.0 (closed triangles); (b) amount of adsorbed dye per mass of sorbent at equilibrium as a function of solution pH. Dye solution concentration: 70 mg l^{-1}, stirring speed: 400 rpm, sorbent dosage: 83.3 g l^{-1}, temperature: 25 °C.

were observed at a pH of 1.6, and these values exponentially decreased with increasing basicity until pH = 4. At pH = 6 and 8, no measurable values were obtained. At equilibrium, the amount of adsorbed material increases by approximately 4.6 times by decreasing the pH from 4.0 to 1.6.

The explanation for this behaviour is based on the fact that the pH of the solution can affect the surface charge of the sorbent. The point of zero charge (pH_{PZC}) is the pH value where the surface charge of the sorbent is zero. The surface charge is positive at pH values less than the pH_{PZC} and negative above this point. Because the reactive dye studied in the present work possess a negative charge due the presence of highly dissociated SO_4^{-2} groups (Leechart *et al*. 2009), if the predominant mechanism for adsorption is the electrostatic attraction (Mahmoodi *et al*. 2011) (which indeed is, once it follows pseudo-second-order kinetic model), a positively charged sorbent surface is favourable for adsorption due to electrostatic attraction, whereas adsorption does not occur when the surface of the sorbent is negatively charged. Based on these assumptions, the pH_{PZC} value of the sawdust used in the present work must be between 4 and 6, which is in agreement with the majority of the sawdusts studied for this purpose (Shukla *et al*. 2002).

Regarding the kinetic parameters (data not shown) obtained from fitting the experimental data with the pseudo-second-order model, no significant effect of pH on the kinetic constant was observed; however, the calculated values of q_e decreased with increasing pH, which indicates that the adsorption capacity decreases with increasing pH.

3.6. Effect of Sorbent Dose

To study the effect of the dosage of sorbent on the adsorption of the dye, the amount of adsorbed material per mass of sorbent as a function of time was monitored at different dosages of sorbent, and the obtained plots and the absolute mass of the adsorbed dye at equilibrium as a function of the dosage of sorbent are shown in Figure 9.
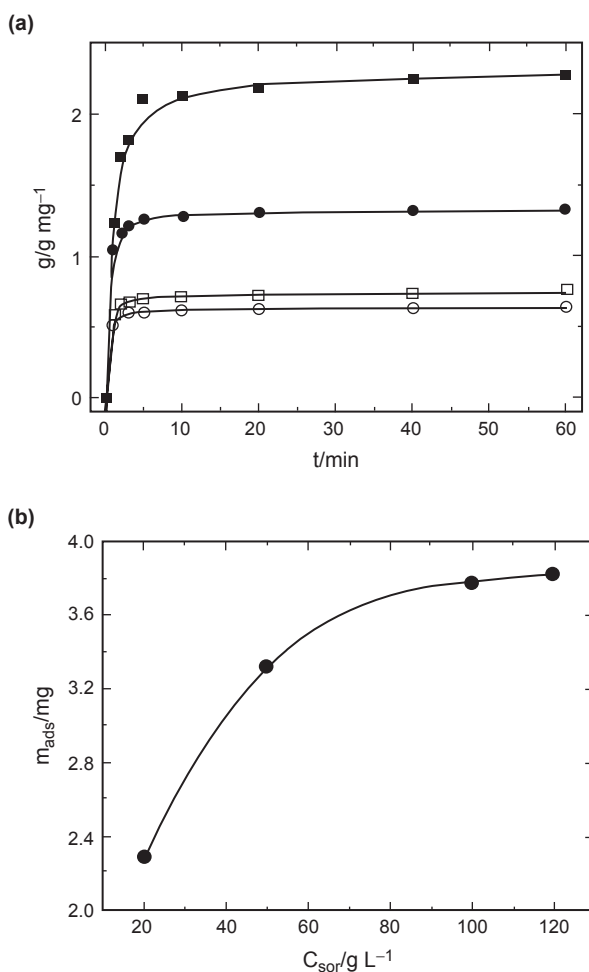

Figure 9. (a) amount of adsorbed dye per mass of sorbent as a function of time for different sorbent dosages: 16.7 g l^{-1} (closed squares), 41.7 g l^{-1} (closed circles), 83.3 g l^{-1} (open squares) and 100 g l^{-1} (open circles); (b) mass of adsorbed material as a function of sorbent dosage. Dye solution concentration: 70 mg l^{-1}, stirring speed: 400 rpm, pH: 1.6, temperature: 25 °C.

According to the results presented in Figure 9(b), the amount of adsorbed dye increased from 60% to 98% when the dosage of sorbent was increased from 16.7 to 100 g l^{-1} due to the increase of adsorption sites; however, the increment is not linear, which indicates that a lower portion of sawdust is participating in the adsorption process with increasing dosage. In fact, by observing the results shown in Figure 9(a), the amount of adsorbed dye per mass of sorbent decreased from 2.3 to 0.64 mg g^{-1} when the dosage of the sorbent is increased. This behaviour can be attributed to aggregation of the sorbent, which results in a decrease of the number of adsorption sites due to the overlapping of sorbent particles and an increase in the dye diffusion path (Garg *et al.* 2004). The effect of sorbent dosage on the kinetic parameters, which were calculated by fitting the experimental data at different sorbent dosage plots with the pseudo-second-order model, can be observed in Table 4.

TABLE 4. Kinetic Parameters Calculated by Fitting Experimental Data at Different Sorbent Dosages

Sorbent dosage/g l^{-1}	k_2/g mg^{-1} min^{-1}	q_e/mg g^{-1}
16.7	0.55	2.32
41.7	2.79	1.32
83.3	5.35	0.73
100	7.51	0.63

According to the calculated parameters, longer times are required to reach equilibrium when the sorbent dosage is higher. Furthermore, the amount of adsorbed dye per mass of sorbent at equilibrium is lower with increasing amounts of sawdust. These outcomes are in agreement with the experimental observations.

3.7. Effect of Stirring Speed

Solution stirring can be employed to decrease the effect of mass gradient of dye from the bulk solution to the sorbent interface on the kinetics of the adsorption process (Kumar and Sivanesan 2006b). Figure 10 presents the plots of mass of adsorbed dye per mass of sorbent as a function of time at different stirring speeds.
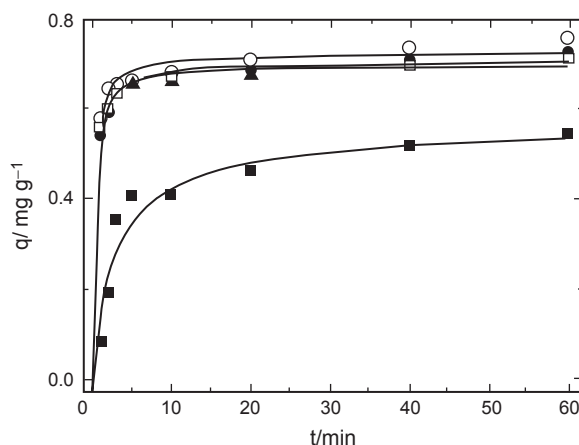

Figure 10. Amount of adsorbed dye per mass of sorbent as a function of time for different stirring speeds: 20 g l^{-1} (closed squares), 50 g l^{-1} (closed circles), 100 g l^{-1} (open squares) and 120 g l^{-1} (open circles). Dye solution concentration: 70 mg l^{-1}, Sorbent dosage: 83.3 g l^{-1}, pH: 1.6, temperature: 25 °C.

According to the obtained plots, a significant increase in the amount of adsorbed material is observed when the solution is agitated; however, the increase of stirring speeds does not affect the adsorption capacity because from 130 to 1000 rpm, no significant improvement in the amount of adsorbed material is observed. The kinetic parameters (data not shown), which were calculated by fitting the experimental data with the pseudo-second-order model, indicate that the kinetic constant increases by approximately eightfold from 0 to 130 rpm, and it is essentially constant with further increases in the stirring speed. Regarding the effect on q_e, a 1.45-time increase was observed.

These results indicate that stirring influences how fast a system achieves equilibrium, which is slower when agitation is employed; however, the improvement in the amount of adsorbed material at this point is not significant because it is changed by other parameters. In fact, there is no creation of new adsorption sites by employing agitation, whereas by changing other parameters, such as the sorbent dosage or pH, it is possible to increase the amount of sites available for the adsorption of dye.

3.8. Effect of Ionic Strength

Wastewater contains salts in a wide range of concentrations depending on its source and quality, which makes it necessary to understand how these ionic compounds affect the adsorption of dye. Figure 11 presents the plot of the amount of adsorbed dye at equilibrium as a function of the Na_2SO_4 concentration in the dye solution.

From the obtained results, it can be seen that an increase in the salt concentration results in an increase in the amount of dye adsorbed at equilibrium. The effect of adding salt is more significant until 10 g l^{-1} and it is essentially unchanged with further increases in concentration. Usually, when the forces between the adsorbent and sorbent are attractive, as it is in this case, the increase in ionic strength should decrease the adsorption capacity (Newcombe and Drikas 1997), which is the opposite of what was observed. Nevertheless, the higher adsorption capacity of reactive dyes can be attributed to the aggregation of dye molecules, which is induced by the addition of salt into the solution (Alberghina *et al*. 2000; Al-Degs *et al*. 2008).
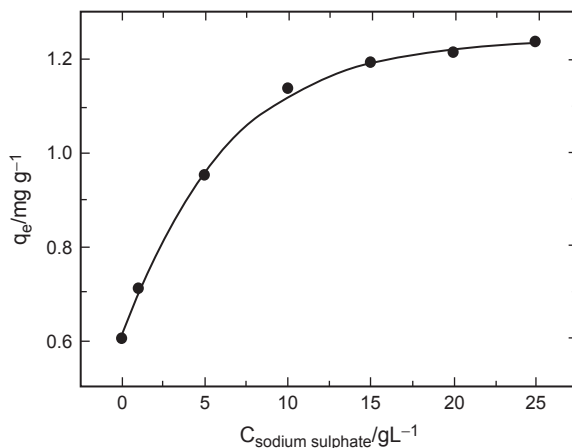

Figure 11. Amount of adsorbed dye per mass of sorbent as a function of the concentration of Na_2SO_4. Dye solution concentration: 70 mg l^{-1}, Sorbent dosage: 83.3 g l^{-1}, pH: 1.6, temperature: 25 °C, stirring speed: 400 rpm.

3.9. Effect of Temperature

Calculating the effect of temperature on the adsorption of dyes provides information about the spontaneity of the process and whether it is an endothermic or exothermic process. The activation energy, E_a, was obtained by fitting the plot of lnK as a function of 1/T with the Arrhenius equation. The thermodynamic parameters, ΔH and ΔS, were obtained by fitting the plot of lnK as a function of 1/T with the van't Hoff equation, where K is the equilibrium constant (q_e/C'_e) and C'_e is the concentration of the dye solution at equilibrium. From the parameters obtained in the van't Hoff equation, the Gibbs free energy, ΔG, was calculated at 25 °C. The values are provided in Table 5.

TABLE 5. Thermodynamic Parameters Calculated by Experimental Data Obtained at Different Temperatures

ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}	E_a/kJ mol^{-1}	ΔG/kJ mol^{-1}
2.52	25.3	13.8	−7.29

The positive value of the enthalpy change indicates that the adsorption process is endothermic, and the positive entropy change indicates that, contrarily from what is expected for gas adsorption, the randomness at the solid/solution interface increases with the uptake of complex dye molecules, which can be related with the release of cations that were electrostatically attached to the dye molecule (Khraisheh *et al.* 2002). The obtained value for the activation energy is within the expected range for the adsorption process (Weber and Morris 1963; Özcan and Özcan 2004).

3.10. Desorption Study

When the sorbent material presents some commercial value, such as the case of activated carbon, the regeneration and reuse of the material is an important issue for large-scale applications. However, with negligible cost materials, such as the one used in the present work, it would be more advantageous if the dye was retained, which would facilitate its disposal as a solid waste. Figure 12 presents the amount of adsorbed dye per mass of sorbent as a function of water wash cycles for sawdust with and without treatment with formaldehyde.
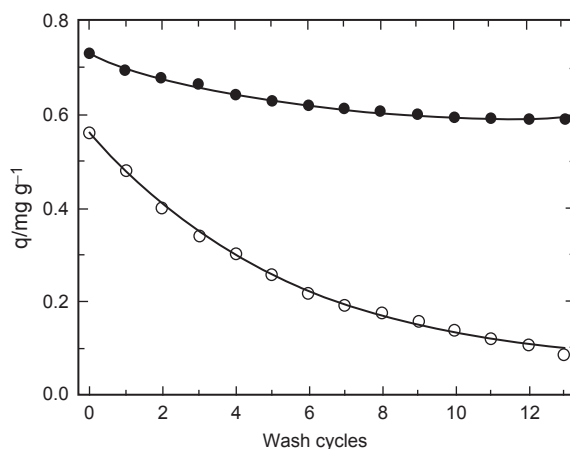

Figure 12. q as a function of water wash cycles for sawdust with (closed circles) and without (open circles) formaldehyde treatment. Adsorption conditions: Dye solution concentration: 70 mg l^{-1}, Sorbent dosage: 83.3 g l^{-1}, pH: 1.6, temperature: 25 °C, stirring speed: 400 rpm.

The results indicate that, for the treated sorbent, after 13 cycles of washing, there is a retention of 87% of the adsorbed material, which indicates that the dye molecules are strongly attached to the modified sawdust. For the untreated sorbent, the retention after the same number of washing cycles is only 18%. These results reveal that the formaldehyde treatment not only increases the dye adsorption capacity but also increases the dye–sorbent bond strength. This behaviour can be attributed to the stronger interaction of dye in the pores that were formed by the formaldehyde treatment.

4. CONCLUSIONS

In this study, the effects of several experimental conditions on the kinetics of dye adsorption on carra sawdust treated with formaldehyde were studied. IR spectroscopy, FESEM images and dye uptake experiments before and after treatment indicated that the formaldehyde attacks the sawdust surface to create pores on its surface, which increases its surface area. No chemical modification was observed in the IR spectra before and after treatment, which suggests that only morphological modifications occurred. Experimental data were fitted well with the pseudo-second-order kinetic model. The results indicated that the increase of the concentration of the solution and the ionic strength have a positive effect on the uptake of the dye. Stirring positively affects the adsorption of the dye, but no effect on the adsorption capacity was observed by increasing the stirring speed. Increasing the dosage of sorbent has a negative effect on q_e, which can be attributed to a decrease in the surface area that is available for adsorption. The increase of the solution pH negatively affects the adsorption process because it reduces the amount of positive charged sites on the surface of the sorbent.

Results of thermodynamic studies indicated that the adsorption process is endothermic and spontaneous at room temperature. From the analyses using the Langmuir and Freundlich models, it was possible to observe that both models fit well with the experimental data; therefore, it was possible to obtain the isotherm parameters. The maximum dye uptake was approximately 15 mg g^{-1}. Desorption studies revealed that the dye molecules are more strongly attached to the sawdust that was treated with formaldehyde compared to the untreated sorbent. This result is advantageous because this material has negligible commercial value, which enables the disposal of the dye as a solid waste.

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