

Adsorption of reactive blue BF-5G dye by soybean hulls: kinetics, equilibrium and influencing factors

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ABSTRACT

The textile industry is known for the high use of chemicals, such as dyes, and large volumes of effluent that contaminate waters, a fact that has encouraged research and improved treatment techniques. In this study, we used unprocessed soybean hulls for the removal of reactive blue BF-5G dye. The point of zero charge of soybean hulls was 6.76. Regarding the speed of agitation in the adsorption process, the resistance to mass transfer that occurs in the boundary layer was eliminated at 100 rpm. Kinetics showed an experimental amount of dye adsorbed at equilibrium of 57.473 mg g⁻¹ obtained under the following conditions: dye initial concentration = 400 mg L⁻¹; diameter of particle = 0.725 mm; dosage = 6 g L⁻¹; pH 2; 100 rpm; temperature = 30 °C; and duration of 24 hours. The pseudo-second order best showed the dye removal kinetics. The adsorption isotherms performed at different temperatures (20, 30, 40 and 50 °C) showed little variation in the concentration range assessed, being properly adjusted by the Langmuir isotherm model. The maximum capacity of dye adsorption was 72.427 mg g⁻¹ at 30 °C. Since soybean hull is a low-cost industrial byproduct, it proved to be a potential adsorbent for the removal of the textile dye assessed.

Key words | adsorption, isotherms, kinetics, reactive dye, soybean hulls

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INTRODUCTION

Contamination of water by various types of dyes has awakened world concern, especially with respect to the textile industry. These effluents are generated in large amounts and have high contaminant potential, even at low concentrations. According to Venkatesha *et al.* (2012), about 125 to 150 L of water are used to produce 1 kg of textile products. In addition to affecting photosynthesis negatively, dyes have the tendency to sequester metals, causing micro-toxicity in organisms that came into contact with contaminated water (Nassar & Magdy 1997).

Ramakrishna & Viraraghavan (1997) state that most commercially used dyes are resistant to biodegradation, photodegradation, and oxidizing agents. This fact demonstrates the need for low-cost alternative methods in order to treat these effluents, which has been widely studied by several researchers (Bhatnagar & Sillanpää 2010).

Various treatment technologies are available for removing color, among which we mention coagulation and flocculation (Verma *et al.* 2012), nanofiltration (Khouni

et al. 2011), electrocoagulation (Phalakornkule *et al.* 2010), Fenton (Karatas *et al.* 2012), ozonation (Moussavi & Mahmoudi 2009), and adsorption (Crini 2006; Tanyildizi 2011; Kyzas *et al.* 2012). The adsorption process stands out among the other processes and it is considered the most convenient, due to ease of operation and simplicity of the project (Bhatnagar & Sillanpää 2010).

In order to make the operation of adsorption processes efficient, kinetic data and equilibrium are required to obtain models that describe the behavior. Various kinetic models have been reported in the literature to describe the adsorption process (Lagergren 1898; Ho & McKay 1998). Each model has its own characteristics and is derived according to certain conditions.

Another essential factor is the equilibrium isotherm, which plays an important role in predictive modeling for analysis and design of adsorption systems of different adsorbents (or various experimental conditions). The two models of the literature most often used to describe adsorption

isotherms in solid/liquid systems are Langmuir (Langmuir 1918) and Freundlich (Şener 2008).

The adsorption technique becomes more attractive when it uses a low-cost adsorbent material, with little processing, abundant in nature or available as a byproduct or industrial residue (Crini 2006). Soybean is the Brazilian crop that has expanded the most in the last decades, corresponding to 49% of the total grain-planted area, mostly on the central-western and south regions. A significant part of soybean production is destined for exportation, but approximately 30.7 million tons of soybeans are transformed by the national industry per year (Ministry of Agriculture 2015). In this context, soybean hull is a byproduct that represents a fraction of 8 to 10% of the total weight of grain processed in the soybean industry (Jia *et al.* 2011), a fact that enhances its application in the adsorption of dyes assessed in this work.

Studies using soybean hulls as adsorbent material showed good results for the removal of metals (Jia *et al.* 2011) and dyes (Chandane & Singh 2014). Regarding the removal of dyes, esterified soybean hull was an excellent adsorbent for basic dyes (Gong *et al.* 2008), as was soybean hull meal with respect to acid and reactive dyes (Arami *et al.* 2006).

This study aimed to assess the use of unprocessed soybean hulls in a batch system as adsorbent of commercial textile reactive blue BF-5G dye. The adsorbent was characterized, and the experiments assessed the influence of the pH of the solution and agitation speed. The experimental kinetic and equilibrium data obtained were adjusted using models available in the literature.

MATERIALS AND METHODS

Characterization of the adsorbent

We used soybean hulls from agri-industrial origin as adsorbent. It was donated by a company located in the western region of the state of Paraná, Brazil. The experiments were conducted with unprocessed soybean hulls (without washing). A certain amount of biomass was ground in a mill (Alfredo Villanova, ME 060) and separated in a vibratory equipment (Pavitest) in order to obtain the average particle size of 0.725 mm. Moisture and ash contents of soybean hull biomass were determined.

Fourier transform infrared spectroscopy

The infrared spectroscopy is aimed at determining the frequencies of vibrations of the functional groups present in

soybean hulls, in the range of 400 to 4,000 cm^{-1} . The sample of unprocessed adsorbent was analyzed with average particle size of 0.215 mm. The analysis was performed by using Fourier transform infrared (FTIR) spectroscopy Bomem brand, model MB-100. The spectra were obtained with a number of 64 scans using KBr pellets.

Point of zero charge

The point of zero charge (PZC) is defined as the pH at which the surface of the adsorbent has neutral charge. The methodology used for its determination is called '11-point scale' (Regalbuto & Robles 2004). The procedure consists of putting 50 mg of adsorbent mixture in contact with 50 mL of an aqueous solution under different initial pH conditions (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12), adjusted with HCl or NaOH solutions of 1 mol L^{-1} at room temperature (25 to 30 °C), with an agitation of 180 rpm, and measuring the pH after 24-hour equilibrium. The difference between the initial and final pH ($\Delta\text{pH} = \text{initial pH} - \text{final pH}$) was represented graphically in relation to initial pH, and the point where $\Delta\text{pH} = 0$ was considered the PZC. The PZC corresponds to the range in which the final pH remains constant, regardless of the initial pH; i.e., the surface behaves as a buffer. The experiments were performed in duplicate.

Preparation of dye solution

For carrying out the experiments, we used commercial solutions of reactive blue BF-5G dye, named RABF-5G, produced by Texpal Química. Its molecular structure is formed by reactive vinylsulfonate and chlorotriazine groups. The molecular structure of the dye is patented until 2018 (CAS: 147826-71-9) and this is also called reactive blue 203. The solution was prepared using distilled water. The absorbance of the dye in solution was quantified by spectrophotometry (Shimadzu UV-1800) at 610 nm and the concentration determined using the Beer-Lambert equation. The effect of pH and agitation speed was assessed with solutions of 400 mg L^{-1} . For the adsorption isotherms, we prepared dye solutions varying from 25 to 1,000 mg L^{-1} .

Influence of solution pH

The effect of solution pH was assessed by varying its value from 1 to 12 (pHmetro MS Tecnopon, MPA-210), temperature of 30 °C, and agitation speed of 100 rpm. In each Erlenmeyer flask, 50 mL of the dye solution was put in contact with 0.3 g of adsorbent (dry basis), and the flasks were placed in an

orbital shaking incubator (Tecnal TE-424) for 48 hours. The samples were removed and centrifuged (Parsec CT-0603) for 3 minutes at 3,000 rpm, and the dye in the supernatant was quantified at 610 nm. The experiments were carried out in triplicate. The concentration of dye removed by the adsorbent was calculated using the Equation (1).

$$q_{eq} = \frac{(C_0 - C_{eq}) * V}{m} \quad (1)$$

where C_0 is the dye initial concentration (mg L^{-1}), C_{eq} is the remaining dye concentration at equilibrium (mg L^{-1}), m is the mass of the adsorbent, dry basis (g), Q_{eq} is the amount of dye adsorbed at equilibrium (mg g^{-1}) and V is the volume of dye solution in contact with the adsorbent (L).

Agitation speed

The adsorption kinetics of RABF-5G dye by unprocessed soybean hulls was held under the same experimental conditions described in the 'Influence of solution pH' section, with varying agitation speed (0, 50, 100, 140, and 180 rpm). The dye adsorption was assessed with pH 2 for a contact time of 24 hours. At regular intervals of time, the samples were removed and centrifuged for 3 minutes at 3,000 rpm. The remaining dye concentration was quantified at 610 nm. The experiments were performed in duplicate. The concentration of dye removed by the adsorbent in each time was calculated using Equation (2).

$$q(t) = \frac{(C_0 - C(t)) * V}{m} \quad (2)$$

where $q(t)$ is the amount of dye adsorbed with respect to time (t) (mg g^{-1}) and $C(t)$ is the remaining dye concentration with respect to time (mg L^{-1}).

We applied pseudo-first and pseudo-second order models, available in the literature, to the experimental data obtained, in accordance with Equations (4) and (6), respectively. The parameters of the models were obtained by using the Statistics software for Windows[®], version 7.0, nonlinear simplex method and objective function, and the error square sum (observed–predicted)².

Pseudo-first order kinetics

A simple analysis of the adsorption kinetics is the pseudo-first order model described by (Lagergren 1898).

$$\frac{dq(t)}{dt} = k_1(q_{eq} - q(t)) \quad (3)$$

where k_1 is the adsorption rate constant of the pseudo-first order model (min^{-1}).

Integrating Equation (3) so that $t = 0$ until $t = t$ and $q = 0$ until $q(t) = q(t)$, rearranging:

$$q(t) = q_{eq}(1 - e^{-k_1 t}) \quad (4)$$

Pseudo-second order kinetics

The pseudo-second order model can be represented by Equation (5) (Ho & Mckay 1998).

$$\frac{dq(t)}{dt} = k_2(q_{eq} - q(t))^2 \quad (5)$$

where k_2 is the adsorption rate constant of the pseudo-second order model ($\text{g mg}^{-1} \text{min}^{-1}$).

Integrating Equation (7) so that $t = 0$ until $t = t$ and $q = 0$ until $q(t) = q(t)$, rearranging:

$$q(t) = q_{eq} \frac{q_{eq} k_2 t}{q_{eq} k_2 t + 1} \quad (6)$$

Adsorption isotherms

Adsorption isotherms of RABF-5G dye for unprocessed soybean hulls were obtained by varying the initial concentration of the solutions (25 to 1,000 mg L^{-1}) at pH 2 and temperatures of 20, 30, 40 and 50 °C, at 100 rpm. The experimental conditions used are presented in the previous section on 'Influence of solution pH', with the exception of the 24-hour contact time. The experiments were performed in duplicate. The experimental data obtained were applied in the Langmuir and Freundlich models, available in the literature, in accordance with Equations (7) and (8). The parameters of the models were obtained by using the Statistics software for Windows[®], version 7.0, nonlinear simplex method and objective function, and the error square sum (observed–predicted)².

Langmuir isotherms

This model considers that the binding sites are evenly distributed on the surface of the adsorbent and that there is no interaction between the molecules of the adsorbent. The model can be extended to describe adsorption in a

multilayer system (Langmuir 1918).

$$q_{eq} = \frac{q_{max}K_L C_{eq}}{1 + K_L C_{eq}} \quad (7)$$

where K_L is Langmuir affinity constant (mg L^{-1}) and q_{max} is the maximum amount of dye adsorbed by the adsorbent (mg g^{-1}).

Freundlich isotherm

This empirical model should be only used for the range of concentration in which their parameters were set (Şener 2008).

$$q_{eq} = K_F * C_{eq}^{1/n} \quad (8)$$

where K_F is Freundlich empirical parameter and the parameter n has values between 0 and 1. For n equal to 1, the equation converts into the Langmuir isotherm (dimensionless).

RESULTS AND DISCUSSION

Adsorbent characterization

Unprocessed soybean hulls showed ash content of 4.14% and moisture of 9.11%. This moisture is in accordance with the values between 8 and 10% obtained by Karuppuchamy & Muthukumarappan (2009).

Infrared spectroscopy

Soybean hulls are primarily composed of cellulose (52%) and water (8 to 10%), and the remainder (38 to 40%) is composed of hemicellulose, lignin, protein, salts, and minerals (Karuppuchamy & Muthukumarappan 2009). The FTIR spectrum obtained for unprocessed soybean hulls showed a set of bands characteristic of lignocellulosic substances, as expected: broadband, with strong intensity, centered at $3,412 \text{ cm}^{-1}$, attributed to the symmetric stretch vibration of OH groups; one band at $2,925 \text{ cm}^{-1}$, characteristic of C–H stretching vibrations of saturated alkyl groups; a set of strong intensity bands between $1,000$ and $1,200 \text{ cm}^{-1}$, which is mainly attributed to stretching vibrations of C–O bond present in ligninic compounds and celluloses.

Other bands of lesser intensity were also observed. At approximately $1,700 \text{ cm}^{-1}$, we obtained a shoulder of

medium intensity, which can be attributed to stretching vibration of carboxylic groups. Close to $1,500 \text{ cm}^{-1}$, we observed another shoulder—as well as the band at $1,431 \text{ cm}^{-1}$ —which was probably due to stretching vibrations of the double bond between carbons (Alemdar & Sain 2008).

The set of bands shown in the spectrum of the infrared region indicates the presence of functional groups common to substances such as cellulose, hemicellulose and lignin, which are the major constituents of soybean hulls.

Point of zero charge

Figure 1 shows the result obtained for the PZC of soybean hulls.

Figure 1 shows the PZC ($\Delta\text{pH} = 0$), which is in a constant range of final pH represented by one row for varying values of initial pH. The calculation of PZC was made by the arithmetic mean of the points that were constants for final pH, i.e., between pH 4 and 10. This range corresponds to the buffer behavior in aqueous solution of soybean hull biomass (Regalbuto & Robles 2004). The value obtained for the pH_{PZC} of the adsorbent used was 6.76, as can be seen in Figure 1.

Regarding $\Delta\text{pH} = 0$ in values below $\text{pH}_{\text{PZC}} = 6.76$ of unprocessed soybean hulls, it is worth noting that adsorption should occur by attraction of anionic groups of reactive dyes in relation to the positive surface charge of solid materials, indicating that the process is favored with pH values of 1, 2 and 3.

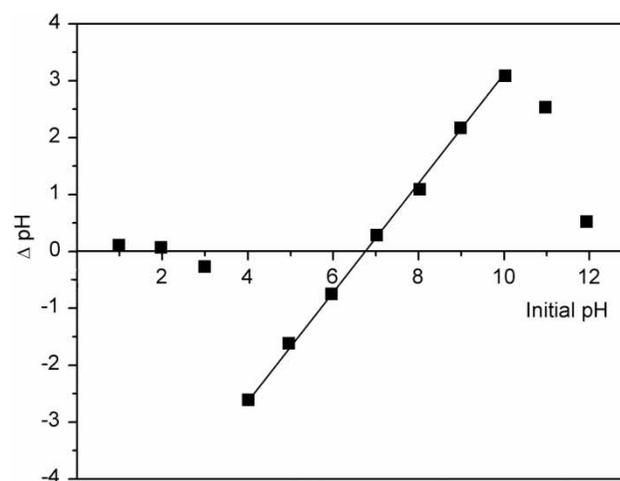


Figure 1 | Experimental data of PZC for soybean hulls (180 rpm; 30 °C; dosage = 1 g L⁻¹; 24 hours).

Influence of solution pH

Figure 2 shows the effect of the pH in the RABF-5G dye solution on the adsorption by unprocessed soybean hulls.

Figure 2 shows the strong influence of the pH parameter on the adsorption process, showing the best reactive dye removal at lowest pH values. For pH 1 and 2, the amount adsorbed was 58.716 mg g^{-1} and 60.440 mg g^{-1} , respectively.

There was a sharp decrease in reactive dye removal at pH higher than 2 (Figure 2). The presence of pH 2 in the process of reactive dye adsorption proves to be the most suitable regarding pH correction compared to pH 1, because the process is less costly.

Won *et al.* (2006) studied the adsorption of reactive black 5 dye in protonated *Corynebacterium glutamicum* biomass and showed that the removal was extremely dependent on the pH within the range from 1 to 11. The maximum dye adsorption occurred at $\text{pH} \leq 3$, in which 500 mg L^{-1} of the dye was totally removed. This behavior of pH was similar to that obtained in this study. According to Mittal *et al.* (2006), the increased protonation, due to the neutralization of negative charge on the surface of adsorbents, facilitates dissemination and provides more active surface to adsorbents, which improves adsorption.

Agitation speed

The agitation speed describes the influence on reducing the boundary layer formed by a stagnant fluid film (dye solution) around the adsorbent, which produces a resistance to the

external mass transfer in the fluid. The study of adsorption kinetics is fundamental; because it determines the equilibrium time – an essential parameter in the design of adsorption systems – and also describes the adsorption capacities at various time intervals.

Figure 3 shows the adsorption kinetics of RABF-5G dye by unprocessed soybean hulls at different agitation speeds.

Figure 3 shows a 24-hour contact time between the dye and soybean hulls for the system to reach equilibrium, with the exception of kinetics performed without agitation (0 rpm). Studies conducted by Peternele *et al.* (2006) obtained a 64-hour contact time to achieve equilibrium in blue 5G dye removal by using lignocellulosic materials (sugar cane bagasse, cupuaçu hulls (*Theobroma grandiflorum*), grábia sawdust (*Apuleia leiocarpa*), and açaí bunches (*Euterpe oleracea*)), at temperature of $\cong 26^\circ\text{C}$ and a pH value of 6.5.

This result demonstrates that, for the removal of the same reactive dye, unprocessed soybean hulls presented less contact time to ensure that the equilibrium in the system was reached, which makes it a suitable adsorbent for application.

The adsorption kinetics of the dye shows that between the non-agitation system and that with agitation of 50 rpm there was an increase of 25.2% in dye removal for a 24-hour period, corresponding to 39.531 mg g^{-1} and 54.176 mg g^{-1} , respectively. For rotations of 100, 140 and 180 rpm, the equilibrium of the system was reached almost at the same time and there were no relevant differences in

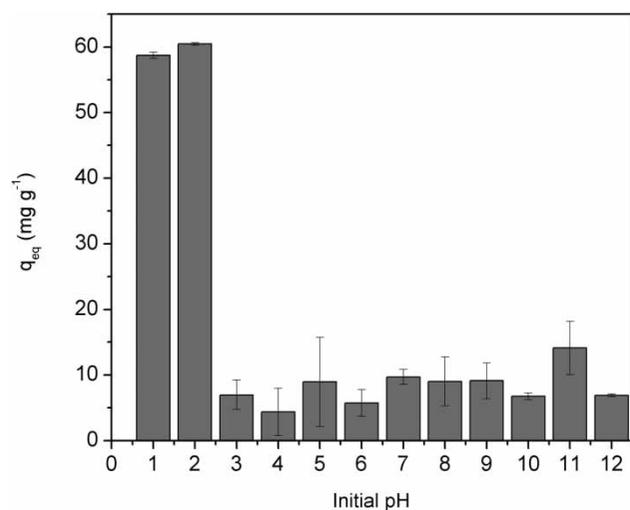


Figure 2 | Effect of pH on adsorption of the RABF-5G dye by unprocessed soybean hulls ($C_0 = 400 \text{ mg L}^{-1}$; particle diameter = 0.725 mm ; dosage = 6 g L^{-1} ; 100 rpm; 30°C ; 48 hours).

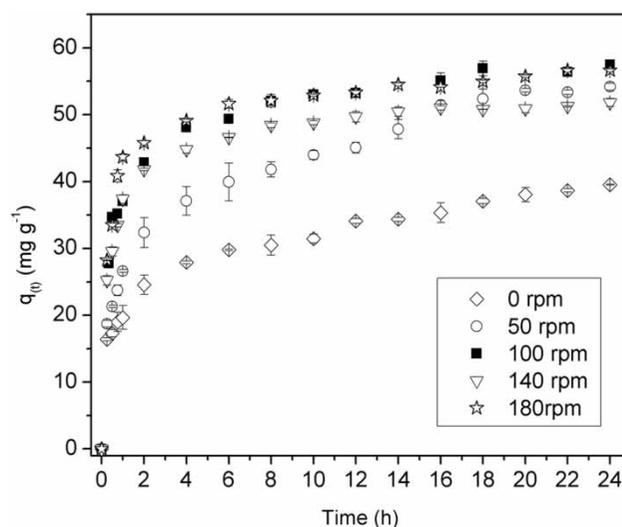


Figure 3 | Kinetics of the speed of agitation on the adsorption of RABF-5G dye by unprocessed soybean hulls ($C_0 = 400 \text{ mg L}^{-1}$; particle diameter = 0.725 mm ; dosage = 6 g L^{-1} ; 30°C ; pH 2; 24 hours).

the q_{eq} with respect to the adsorption kinetics (variation around 4 mg g^{-1}). Kyzas et al. (2012) used the industrial waste of coffee under the following conditions: 60 to 180 rpm; $100 \text{ mg L}^{-1} C_0$; dosage of 1 g L^{-1} ; temperature of $25 \text{ }^\circ\text{C}$; and 24-hour contact time. The authors did not observe any increase in reactive dye removal above 140 rpm.

This behavior is similar to that observed in this study. Rotations above 100 rpm ($q_{eq} = 57.473 \text{ mg g}^{-1}$) demonstrate that the resistance to mass transfer, which occurs in the boundary layer, is eliminated from the process and requires less energy in the operating system.

According to Figure 3, for the kinetics of 100 rpm in a 30-minute contact time, the adsorption of the RABF-5G dye by soybean hulls was 60.4% in relation to the amount adsorbed at equilibrium time ($q_{eq} = 57.473 \text{ mg g}^{-1}$), corresponding to 34.700 mg g^{-1} .

For the time of 8 hours, the removal of the dye reached 90.6% of the total quantity adsorbed at equilibrium ($q_{eq} = 52.063 \text{ mg g}^{-1}$). From this time on, the removal was slower until reaching equilibrium in 24 hours. In this experiment, it is possible to observe that the adsorption of the dye was fast in the initial phase of the contact period and decreased gradually until reaching equilibrium.

According to Kyzas et al. (2012), the rapid adsorption is due to the large number of free sites on the surface. As the sites are being occupied, there is repulsion between the solute molecules that are adsorbed in the solid phase, taking a longer time to reach equilibrium. The authors state that the fact of reactive dyes having large molecules, with little movement, means establishing equilibrium in the system takes more time.

Table 1 shows the parameters of the pseudo-first and pseudo-second order kinetic models for dye adsorption in

Table 1 | Parameters of pseudo-first and pseudo-second order kinetic models in the adsorption of RABF-5G dye by unprocessed soybean hulls

	Pseudo-first order	Pseudo-second order
k	0.028 ± 0.004 (min^{-1})	$7.60 \times 10^{-4} \pm 1.04 \times 10^{-4}$ (min g mg^{-1})
p -level	1.79×10^{-5}	6.03×10^{-6}
q_{eq} calculated (mg g^{-1})	52.585 ± 1.443	55.438 ± 0.985
p -level	1.82×10^{-14}	6.50×10^{-17}
q_{eq} exp. (mg g^{-1}) (24 hours)	57.473	57.473
R^2	0.962	0.989

a system agitated at 100 rpm. Figure 4 shows the adjusted experimental data.

The estimated parameters (Table 1) showed that the pseudo-second order model presented the best fit for the adsorption kinetics. The model showed small values for the standard deviations and p -level (<0.05), as well as a good coefficient of determination ($R^2 = 0.988$). The amount adsorbed in equilibrium was close to that obtained experimentally, indicating the proper adjustment of the experimental data (Figure 4). The q_{eq} estimated by the pseudo-second order model (55.438 mg g^{-1}) was closer to that obtained experimentally (57.473 mg g^{-1}) than was q_{eq} predicted for the pseudo-first order model (52.585 mg g^{-1}).

Won et al. (2006) and Tanyildizi (2011) studied the adsorption of reactive black 5 dye in protonated *Corynebacterium glutamicum* biomass and peanut hulls, respectively. The authors obtained a better representation of the experimental data by using the pseudo-second order model ($R^2 = 0.99$), which is an analogous result to that obtained in this study for the adsorption of the RABF-5G dye in unprocessed soybean hulls.

Adsorption isotherms

The quantitative assessment of the adsorption process was carried out by using adsorption isotherms at different temperatures. Figure 5 shows the experimental equilibrium data

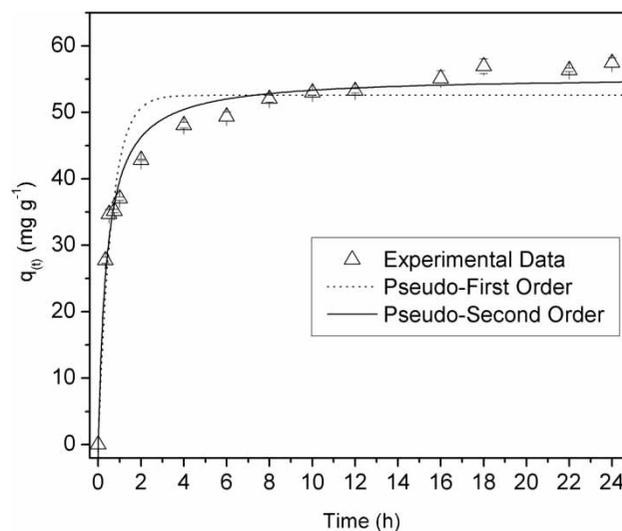


Figure 4 | Kinetic data and models for the adsorption of the RABF-5G dye by unprocessed soybean hulls ($C_0 = 400 \text{ mg L}^{-1}$; particle diameter = 0.725 mm ; dosage = 6 g L^{-1} ; 100 rpm; $30 \text{ }^\circ\text{C}$; pH 2; 24 hours).

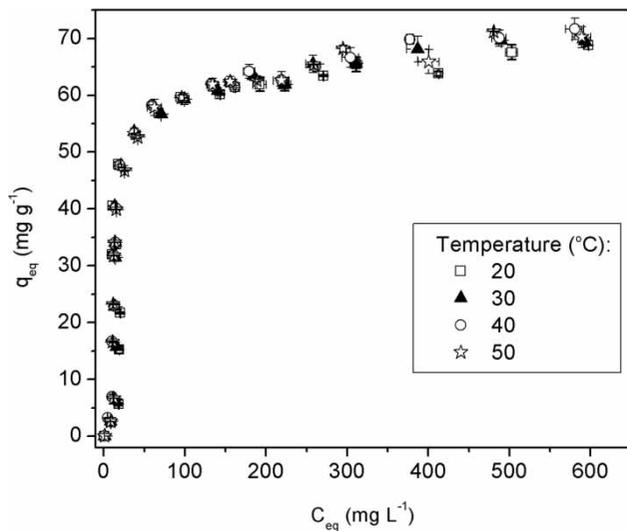


Figure 5 | Adsorption equilibrium data at different temperatures ($C_0 = 25\text{--}1,000\text{ mg L}^{-1}$; particle diameter = 0.725 mm; dosage = 6 g L⁻¹; 100 rpm; pH 2; 24 hours).

obtained for the unprocessed soybean hulls for RABF-5G dye removal.

The data of the dye adsorption equilibrium (Figure 5) show that the process had little variation due to temperature (>1 mg g⁻¹ up to $C_0 = 650\text{ mg L}^{-1}$), characterized by the overlap of the points up to a C_{eq} of $\approx 250\text{ mg L}^{-1}$. One of the main advantages of this behavior is that it is not necessary to spend on energy in order to adjust the temperature to achieve the best efficiency of the system. Another fact is that adsorption may occur at the temperature of the effluent, or at room temperature.

A favorable behavior was observed on the isotherms represented by Figure 5. For equilibrium concentration of 8.3 mg L⁻¹, the soybean hull presented an adsorbed amount of 2.6 mg g⁻¹. When compared to the amount in equilibrium at a higher concentration (20.8 mg L⁻¹), the adsorbed amount in equilibrium rises considerably, reaching 47.6 mg g⁻¹. For remaining concentrations over 100 mg L⁻¹, the adsorbed amount in equilibrium reached saturation between 60 and 70 mg g⁻¹.

Table 2 shows the adjustment parameters of the experimental data according to the Langmuir and Freundlich models at the temperatures studied. Figure 6 shows the Langmuir and Freundlich models for experimental data of adsorption at temperature of 30 °C.

According to the results shown in Table 2 and Figure 6, it can be observed that the Langmuir isotherm at 30 °C described properly the equilibrium data with q_{max} of dye adsorption by soybean hulls (72.427 mg g⁻¹ and $R^2 = 0.931$). It was also found that Freundlich's model did not describe satisfactorily the experimental data.

Tanyildizi (2011) studied the adsorption of reactive black 5 dye in peanut hulls and found that Langmuir's model best described the adsorption process. This result is in agreement with results obtained in this study regarding the adsorption of reactive RABF-5G dye by unprocessed soybean hulls. The maximum amount adsorbed (q_{max}) in peanut hulls obtained by Langmuir's model went from 50 to 55 mg g⁻¹ with temperature increase from 20 to 60 °C, respectively.

In the present study, the soybean hull, an agricultural subproduct, demonstrated potential to be used as a low

Table 2 | Coefficient of determination and parameters of Langmuir and Freundlich models

	Langmuir model			Freundlich model		
	q_{max} (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2	K_F (L g ⁻¹)	n	R^2
20 °C						
Value	70.787 ± 4.795	0.040 ± 0.011	0.891	14.335 ± 3.451	3.788 ± 0.654	0.845
p-level	7.29×10^{-12}	1.78×10^{-5}		5.39×10^{-4}	1.39×10^{-5}	
30 °C						
Value	72.427 ± 3.824	0.041 ± 0.009	0.931	14.220 ± 3.120	3.691 ± 0.566	0.873
p-level	8.45×10^{-14}	1.48×10^{-4}		2.15×10^{-4}	3.04×10^{-6}	
40 °C						
Value	70.383 ± 2.782	0.050 ± 0.008	0.961	15.330 ± 7.171	3.825 ± 1.360	0.899
p-level	2.55×10^{-16}	5.44×10^{-6}		4.57×10^{-2}	1.11×10^{-2}	
50 °C						
Value	72.841 ± 3.170	0.043 ± 0.008	0.952	14.407 ± 2.942	3.695 ± 0.529	0.887
p-level	2.52×10^{-15}	1.83×10^{-5}		1.00×10^{-4}	1.17×10^{-6}	

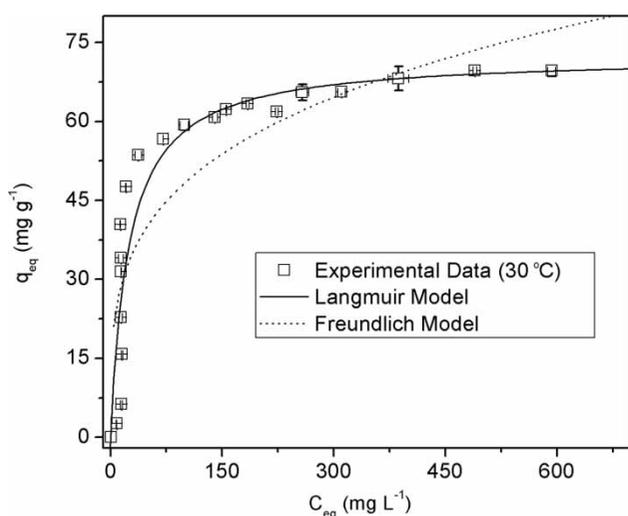


Figure 6 | Experimental data and models of adsorption isotherms ($C_0 = 25\text{--}1,000\text{ mg L}^{-1}$; dosage = 6 g L^{-1} ; 100 rpm; pH 2; 24 hours).

cost adsorbent for the removal of dyes. The investigated parameters (temperature, pH, contact time and equilibrium of adsorption) are the basis for dimensioning systems capable of treating great volumes of effluents containing reactive dyes, as a means of meeting legal discharge requirements. As for its applicability in column systems, the adsorbent is located in fixed bed columns and the effluent percolates through the bed. In this process, the dye is retained by the adsorbent and the treated effluent leaves the column. Also, saturated soybean hull may be replaced or regenerated with an appropriate eluent and reused in adsorption/desorption cycles.

CONCLUSION

By using unprocessed soybean hulls for RABF-5G dye removal, it was possible to observe that the process was favored by the following experimental conditions: pH 2; equilibrium time reached in 24 hours; and agitation speed of 100 rpm. Under these conditions, for the adsorption kinetics, an amount of 57.473 mg g^{-1} was removed from the dye. The pseudo-second order model best described the experimental kinetic data. The data of adsorption equilibrium showed little variation at different temperatures (20, 30, 40 and $50\text{ }^{\circ}\text{C}$) and an overlap of the points up to the C_{eq} of $\cong 250\text{ mg L}^{-1}$ was observed. The little influence of temperature on the adsorption process highlights the feasibility of the process, because it does not require energy expenditures and maintains the efficiency of the system, even applied at room temperature ($25\text{ to }30\text{ }^{\circ}\text{C}$).

The Langmuir isotherm model adjusted the experimental equilibrium data appropriately. This model showed a maximum capacity of adsorption (72.427 mg g^{-1}) at temperature of $30\text{ }^{\circ}\text{C}$. Soybean hulls proved to be an attractive alternative adsorbent, because it is an agro-industrial byproduct with potential ability for the removal of the textile dye studied.

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REFERENCES

- Alemdar, A. & Sain, M. 2008 Isolation and characterization of nanofibers from agricultural residues – wheat straw and soy hulls. *Bioresour. Technol.* **99**, 1664–1671.
- Arami, M., Limaee, N. Y., Mahmoodi, N. M. & Tabrizi, N. S. 2006 Equilibrium and kinetics for the adsorption of direct and acid dyes from aqueous solution by soy meal hull. *J. Hazard. Mater. (B)* **135**, 171–179.
- Bhatnagar, A. & Sillanpää, M. 2010 Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – a review. *Chem. Eng. J.* **157**, 277–296.
- Chandane, V. & Singh, V. K. 2014 Adsorption of safranin dye from aqueous solutions using a low-cost agro-waste material soybean hull. *Desalin. Water Treat.* DOI:10.1080/19443994.2014.991758.
- Crini, G. 2006 Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour. Technol.* **97**, 1061–1085.
- Gong, R., Sun, J., Zhang, D., Zhong, K. & Zhu, G. 2008 Kinetics and thermodynamics of basic dye sorption on phosphoric acid esterifying soybean hull with solid phase preparation technique. *Bioresour. Technol.* **99**, 4510–4514.
- Ho, Y. S. & Mckay, G. 1998 Kinetic models for the sorption of dye from aqueous solution by wood. *Trans. IChemE.* **76** (B), 183–191.
- Jia, L., Enzan, C., Haijia, S. & Tianwei, T. 2011 Biosorption of Pb^{2+} with modified soybean hulls as absorbent. *Chin. J. Chem. Eng.* **19** (2), 334–339.
- Karatas, M., Argun, Y. A. & Argun, M. E. 2012 Decolorization of antraquinonic dye, reactive blue 114 from synthetic wastewater by Fenton process: kinetics and thermodynamics. *J. Ind. Eng. Chem.* **18**, 1058–1062.
- Karuppuchamy, V. & Muthukumarappan, K. 2009 *Extrusion Pretreatment and Enzymatic Hydrolysis of Soybean Hulls*. American Society of Agricultural and Biological Engineers, Bioenergy Engineering, Bellevue, Washington, pp. 11–14.
- Khouni, I., Marrot, B., Moulin, P. & Amar, R. B. 2011 Decolourization of the reconstituted textile effluent by different process treatments: enzymatic catalysis, coagulation/flocculation and nanofiltration processes. *Desalination* **268**, 27–37.

- Kyzas, G. Z., Lazaridis, N. K. & Mitropoulos, A. Ch. 2012 Removal of dyes from aqueous solutions with untreated coffee residues as potential low-cost adsorbents: equilibrium, reuse and thermodynamic approach. *Chem. Eng. J.* **189–190**, 148–159.
- Lagergren, S. 1898 Zur Theorie der sogenannten Adsorption Gelöster Stoffe (On the theory of so-called adsorption of dissolved substances). *Kungliga Svenska Vetenskaps-Akademiens Handlingar* **24 Afd. II** (4), 1–39.
- Langmuir, I. 1918 The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **40**, 1361–1403.
- Ministry of Agriculture 2015 *Grain Crop: Soybean*. <http://www.agricultura.gov.br/vegetal/culturas/soja> (accessed 24 June 2015).
- Mittal, A., Mittal, J. & Kurup, L. 2006 Adsorption isotherms, kinetics and column operations for the removal of hazardous dye, tartrazine from aqueous solutions using waste materials – bottom ash and de-oiled soya, as adsorbents. *J. Hazard. Mater. (B)* **136**, 567–578.
- Moussavi, G. & Mahmoudi, M. 2009 Degradation and biodegradability improvement of the reactive red 198 azo dye using catalytic ozonation with MgO nanocrystals. *Chem. Eng. J.* **152**, 1–7.
- Nassar, M. M. & Magdy, Y. H. 1997 Removal of different basic dyes from aqueous solutions by adsorption on palm-fruit bunch particles. *Chem. Eng. J.* **66**, 223–226.
- Peternele, W. S., Costa, A. C. S. & Sallo, F. S. 2006 Remoção do corante Reativo Azul 5G por adsorção em diferentes materiais lignocelulósicos (Removal of Reactive Blue 5G dye by adsorption on different lignocellulosic materials). *Biomassa & Energia* **3** (1), 49–56.
- Phalakornkule, C., Polgumhang, S., Tongdaung, W., Karakat, B. & Nuyut, T. 2010 Electrocoagulation of blue reactive, red disperse and mixed dyes, and application in treating textile effluent. *J. Environ. Manage.* **91**, 918–926.
- Ramakrishna, K. R. & Viraraghavan, T. 1997 Use of slag for dye removal. *Waste Manage.* **17** (8), 483–488.
- Regalbuto, J. R. & Robles, J. 2004 *The Engineering of Pt/Carbon Catalyst Preparation – For Application on Proton Exchange Fuel Cell Membrane (PEFCM)*. University of Illinois, Chicago, USA, pp. 4–7.
- Şener, S. 2008 Use of solid wastes of the soda ash plant as an adsorbent for the removal of anionic dyes: equilibrium and kinetic studies. *Chem. Eng. J.* **138**, 207–214.
- Tanyildizi, M. Ş. 2011 Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. *Chem. Eng. J.* **168**, 1234–1240.
- Venkatesha, T. G., Viswanatha, R., Arthoba Nayaka, Y. & Chethana, B. K. 2012 Kinetics and thermodynamics of reactive and vat dyes adsorption on MgO nanoparticles. *Chem. Eng. J.* **198–199**, 1–10.
- Verma, A. K., Dash, R. R. & Bhunia, P. 2012 A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *J. Environ. Manage.* **93**, 154–168.
- Won, S. W., Kim, H. J., Choi, S. H., Chung, B. W., Kim, K. J. & Yun, Y. S. 2006 Performance, kinetics and equilibrium in biosorption of anionic dye reactive black 5 by the waste biomass of *Corynebacterium glutamicum* as a low-cost biosorbent. *Chem. Eng. J.* **121**, 37–43.

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