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Removal of Remazol brilliant violet textile dye by adsorption using rice hulls

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Abstract

The release of industrial effluents into the environment causes widespread contamination of aquatic systems. Adsorption is seen as one of the most promising treatment processes, and lignocellulosic materials have gained prominence as adsorbents. This study investigates the potential of rice hulls, either *in natura* or treated with nitric acid, as adsorbents for removal of the dye. The adsorbents were characterized by infrared spectroscopy, solid state ¹³C-NMR, thermogravimetric analysis, and pH at point of zero charge. The dye adsorption experiments were carried out in batch mode, using different experimental conditions. The kinetic adsorption data could be fitted using the model of Elovich. The Freundlich model provided the best fit to the isothermal data. The thermodynamic parameters confirmed the spontaneity of the adsorption process. These adsorbents offer an alternative for dye removal, with advantages including biomass availability and low cost.

Keywords: *adsorption, remazol, rice hull.*

1. Introduction

The discharge of industrial effluents into the environment without adequate treatment is frequently a major problem, due to the problems of contamination of water resources. Many industries, such as those concerned with leather processing, rubber, paper, plastics, fabrics, and paints produce large volumes of wastewater containing various chemicals harmful to aquatic ecosystems^[1-3]. Among these, in the absence of adequate wastewater treatment, textile manufacturers produce (during the dyeing step) effluent with persistent coloration, which can contaminate natural waters, interfering in the passage of solar radiation and impairing processes of photosynthesis^[4,5].

Many processes are used in the treatment of wastewater containing dyes, such as biological oxidation and chemical adsorption^[5-7], photoelectrochemical processes^[8], treatment with zero-valent iron^[9] and zero-valent iron/H₂O₂^[10], heterogeneous photocatalysis combined with ozone treatment^[11], hydrogen peroxide combined with UV^[12], and others. However, many of these require appropriate conditions and have high operational costs. Adsorption has been shown to be very promising for the removal of textile dyes, since adsorbents can offer industrial practicality, low cost, high removal rates, and (in some cases) recovery of the species involved without losing their chemical identity^[13].

Adsorption is the removal of a chemical species from the fluid phase, with subsequent concentration on the surface of a substrate, usually a solid^[14]. Adsorbents are

generally highly porous and have a large surface area^[15]. One widely used material is activated carbon, which offers high efficiency due to its structural characteristics, high surface area, and chemical nature^[3]. However, its use has some disadvantages, such as low selectivity and efficiency for certain disperse dyes^[16], as well as losses during the recovery process^[17], resulting in a need to identify less expensive and more effective adsorbents. There are a variety of alternative low-cost materials that can be used for the removal of textile dyes, and other contaminants. Agricultural residues are an abundant and inexpensive renewable source of potential adsorbents. Examples include babassu coconut shell^[18], rice hull, rice straw^[19,20], and banana pseudostem^[21], amongst others. These agricultural residues can be used either *in natura* or modified with the insertion or release of active sites capable of improving the adsorption efficiency.

Rice hull is an agricultural waste biomass produced by the rice processing industry. This bulky byproduct represents about 23% of the weight of the grain^[22]. Few options for the use of this material have been reported in the literature, and it is still common to see deposits of the waste in the open and on the banks of rivers^[23], where it takes about 5 years to decompose, while emitting a high volume of methane, a greenhouse gas that is also harmful to the ozone layer^[24]. The aim of this study was therefore to analyze rice hull, *in natura* and treated with nitric acid, as an adsorbent for the removal of Remazol brilliant violet textile dye present in aqueous solutions.

2. Materials and Methods

2.1 Materials and reagents

The rice hull used in this work was collected in São Bento city (Maranhão-BR). All reagents used were of analytical grade. The Remazol brilliant violet textile dye was produced by DyStar and provided by Toalhas São Carlos (São Paulo-BR). The purity of the dye was not specified. The chemical structure of Remazol brilliant violet dye is shown in Figure 1^[18].

2.2 Preparation of the adsorbent

The rice hull was ground and washed with distilled water in a ratio of 10:1 (v/w) for 30 min, with constant stirring, until the conductivity of the supernatant remained constant. The material was then dried at 333 K for 24 h and sieved to obtain the particle size range between 0.088 and 0.177 mm. This *in natura* rice hull material was denoted RHI. Then, it was processed with acid, as described previously^[25], with small changes in contact time and temperature. RHI was placed in a solution of 2 mol L⁻¹ nitric acid, at a ratio of 1:200 (w/v), at 323 ± 1 K, for 5 h under constant stirring. It was then washed with distilled water until the supernatant conductivity remained constant, dried at 333 K, and sieved to obtain the 0.088-0.177 mm particle size fraction. The treated rice hull was denoted RHT.

2.3 Characterization of the adsorbent

The adsorbents were characterized by Fourier transform infrared spectroscopy (FTIR), ¹³C nuclear magnetic resonance (¹³C-NMR), thermogravimetric analysis (TGA), and pH at point of zero charge (pHpzc). The FTIR spectra in the 4000-400 cm⁻¹ region were obtained using an MB series spectrometer Bomem-Hartmann & Braun, and resolution of 4 cm⁻¹. The KBr tablets were prepared using a press, by diluting the sample of interest in KBr at a ratio of 1:100 (w/w). The ¹³C-NMR spectra were obtained using a Bruker AC300 spectrometer, with 7 mm rotor, cross polarization and magic angle spinning (CP-MAS), and a contact time of 3 min. The repetition time was 3 s and the frequency was 4 kHz. The TGA were performed with a DuPont instrument (model 9900), heating from room temperature to 1273.15 K at 10 K min⁻¹, under an inert argon atmosphere. The pHpzc values of the adsorbents were estimated by placing 100 mg of the adsorbent (RHI or RHT) in contact with 25.0 mL of

KCl solution (0.1 mol L⁻¹), with initial pH (pH_i) ranging from 1 to 12, previously adjusted with HCl or NaOH. After 24 h of contact at room temperature and under constant agitation, the adsorbent was removed by filtration and the final pH (pH_f) of the supernatant was measured.

2.4 pH study, adsorption kinetics and isotherms

The study was carried out varying the initial pH of the Remazol brilliant violet dye solution. 100 mg of adsorbent (RHI or RHT) was placed in contact with 25 mL of dye solution (100 mg L⁻¹) for 24 h at 298 ± 1 K, under continuous stirring. This test was performed at six pH values (initial pH between 1 and 6, adjusted with HCl and NaOH). To obtain the adsorption kinetics, 100 mg of adsorbent was placed in contact with 25 mL of dye solution at two concentrations (100 and 1000 mg L⁻¹), using the optimum pH (the pH at which greatest adsorption was observed in the pH study), with constant stirring at room temperature. The contact time was varied between 5 and 600 min. Adsorption isotherms were obtained by placing 100 mg of adsorbent in contact with 25 mL of dye solution at various concentrations (100 to 1000 mg L⁻¹) and four temperatures (283, 298, 313, and 328 ± 1 K), using the optimum pH and stirring constantly during the equilibration time. At the end of the contact time, the adsorbent was separated by centrifugation and the new dye concentration in the supernatant was determined with a UV-Vis spectrophotometer (model 2550, Shimadzu) fitted with a 1 cm optical path quartz cell, using the absorbance at 560 nm. The amount of adsorbed dye, *q* (mg g⁻¹), was obtained using Equation 1^[26], where *C_i* and *C_f* (mg L⁻¹) are the initial and final dye concentrations, respectively, *m* (g) is the mass of adsorbent, and *V* (L) is the volume of dye solution.

$$q = \frac{(C_i - C_f)V}{m} \quad (1)$$

3. Results and Discussion

3.1 Infrared spectroscopy

Spectroscopy in the infrared region is a widely practiced characterization technique, because it allows qualitative evaluation of the presence of different functional groups.

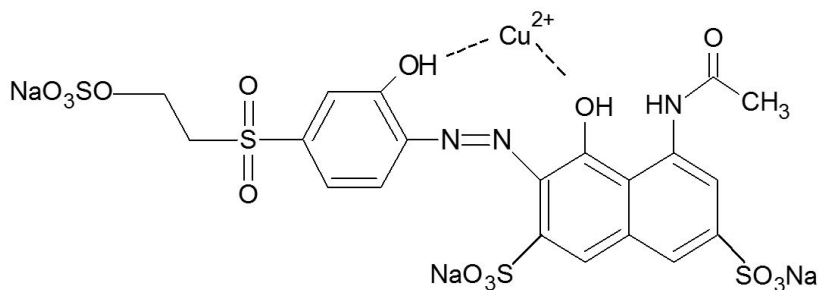


Figure 1. Chemical structure of Remazol brilliant violet dye.

Figure 2 illustrates the vibrational spectra of all the materials studied. The large numbers of peaks found for the *in natura* and treated rice hulls indicate the heterogeneous nature of the adsorbents.

The IR spectrum of the dye (see Figures 1 and 2a) presented many absorption peaks, including those corresponding to phenolic O–H, secondary amide N–H stretching, and aromatic C–H at 3671–3047 cm^{-1} ; aliphatic C–H_n at around 2925 cm^{-1} ; amide C=O stretching at 1639 cm^{-1} ; C=C stretching at 1532 cm^{-1} ; N=N stretching at 1436 cm^{-1} ; –SO (R–SO₂–R) stretching at 1309 cm^{-1} ; –SO stretching of R–SO₃[–] at 1207–989 cm^{-1} ; C–S stretching at 748 cm^{-1} (coupled with out-of-plane C–H and C=C bending) and at 626 cm^{-1} [27,28]. The spectra for the adsorbents (Figures 2c and 2e) exhibited the characteristic bands of lignocellulosic materials reported in the literature[18,29–30], and did not differ in terms of the nature of the functional groups present. Broad stretching bands occurred between 3100 and 3600 cm^{-1} , indicating the presence of –OH groups on the surfaces of the matrices. These were mainly due to glycosidic structures, the presence of silanol groups (Si–OH), and water adsorbed on the surfaces of the hulls[31]. A band between 2900–3000 cm^{-1} corresponded to CH stretching of the methyl groups that are common in the structures of lignocellulosic materials. A band located at 1730 cm^{-1} was characteristic of stretching of C=O of ketones, aldehydes, and carboxylic acids. A band at 1640 cm^{-1} could be attributed to adsorbed water, while a band at 1500 cm^{-1} corresponded to aromatic C=C vibrations. A band at 1370 cm^{-1} was due to CH plane deformation vibration, and a band at 1240 cm^{-1} was associated with CO stretching of the pyran ring. A band at 1060 cm^{-1} was due to the vibration of methoxyl (C–O–C) and β-1,4 bonds. Bands near 790 cm^{-1} were due to out-of-plane δ (CH) deformation of the aromatics present in lignin[32]. Comparison of the spectra for the *in natura* and treated adsorbents showed that the intensities of the bands at 3435, 1734, and 1067 cm^{-1} increased after treatment, as expected since these bands correspond to oxygen-containing groups (–OH, –C=O, and –COC–, respectively) that may have been formed during the treatment with nitric acid[33].

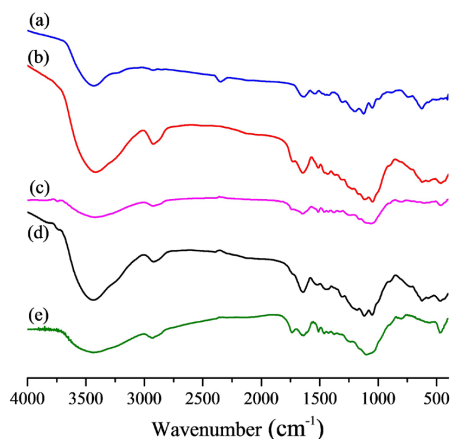


Figure 2. Infrared vibrational spectra of the RHI and RHT samples.

3.2 Solid state ¹³C nuclear magnetic resonance

The solid state ¹³C-NMR spectra for the RHT and RHI matrices indicated the presence of structures of cellulose and its derivatives (Figure 3). A peak at 105 ppm corresponded to the C1 carbon, with a large displacement due to the bonding to two oxygen atoms (CH(OR)₂). Signals at 90 and 83 ppm referred to C4, with a smaller displacement than C1 since the bond involves only one oxygen (CH(OR))[34,35]. A peak at 72 ppm was related to the C2, C3, and C5 secondary carbons attached to the hydroxyl (CH–OH). Peaks at 64 and 62 ppm were assigned to the C6 carbon, indicating regions of low crystallinity and amorphous character (see Figure 1A in the Appendix A)[36], confirming this characteristic for both matrices. The presence of methyl groups and carboxyl carbon-carbon double bonds were indicated at 21 and 172 ppm, respectively. A signal corresponding to lignin guaiacyl methoxy groups was found at 55 ppm, and signals corresponding to aromatic carbons could be seen between 120 and 150 ppm[37].

Comparison of the ¹³C-NMR spectra of the different matrices revealed increases in the peaks relating to C1, C2, C3, C4, and C5 after treatment (RHT sample) (see also Table 1A in the Appendix A). This could be attributed to the effectiveness of the treatment with nitric acid, forming active adsorption sites and increased intensities of peaks related to carbon atoms with oxygen groups. These results corroborated those obtained in the characterization by infrared spectroscopy, which were also indicative of an increase in oxygen-containing groups after treatment.

3.3 Thermogravimetric analysis

Thermogravimetric analysis was used to determine the thermal stability of the adsorbents and provide quantitative data on mass loss according to temperature. The thermogravimetric (a) and derivative (b) curves obtained for the RHI and RHT adsorbents, under an inert argon atmosphere, are shown in Figure 4.

The adsorbents showed similar behavior in terms of thermal decomposition, remaining stable up to about 473 K, as reported previously for other lignocellulosic materials[30]. Comparison of the percentage mass losses of the RHI and RHT adsorbents indicated that the *in natura* matrix showed greater weight loss corresponding to cellulose and hemicellulose, while the treated matrix showed greater loss of

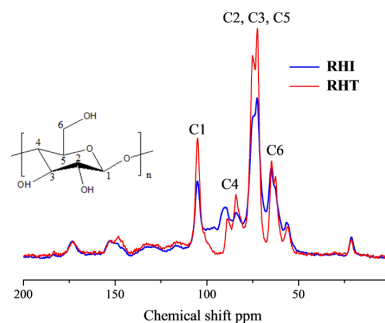


Figure 3. The solid state ¹³C-NMR spectra for the RHT and RHI.

mass corresponding to lignin. The thermogravimetric curve showed three distinct stages of decomposition. The first, at around 373 K, should not be taken into consideration in terms of thermal stability, because it was only due to the release of physically adsorbed water present on the surfaces of the adsorbents^[38]. The second stage, between 473 and 623 K, resulted in a greater loss of mass, due to the decomposition of hemicellulose and most of the cellulose. In the third stage (623–1043 K), which showed less mass loss than the previous stage, there was decomposition of lignin, which is structurally more stable than cellulose or hemicellulose^[32].

3.4 pH_{pzc} and effect of pH

The pH at the point of zero charge (pH_{pzc}) is a parameter that indicates the pH value at which a particular solid does not have excess net charges on its surface. This parameter is important because it enables prediction of the surface charge of the adsorbent as a function of pH, since at pH lower than the pH_{pzc}, the surface charge of the solid is positive, while for pH values higher than the pH_{pzc}, the surface charge is negative. Figure 5a shows a graph of the variation of ΔpH (pH_i–pH_f), as a function of the initial pH (pH_i), for the *in natura* and treated adsorbents.

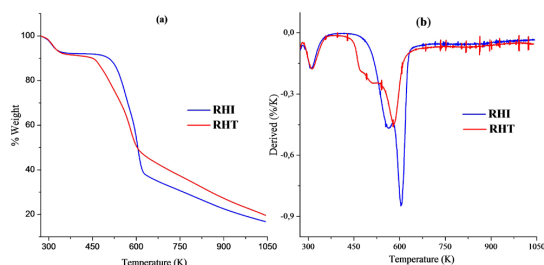


Figure 4. Thermogravimetric curves (a) and derived (b) of the RHI and RHT, obtained under an argon atmosphere, using a heating rate of 10 K min⁻¹ in the temperature interval 298.15–1273.15 K.

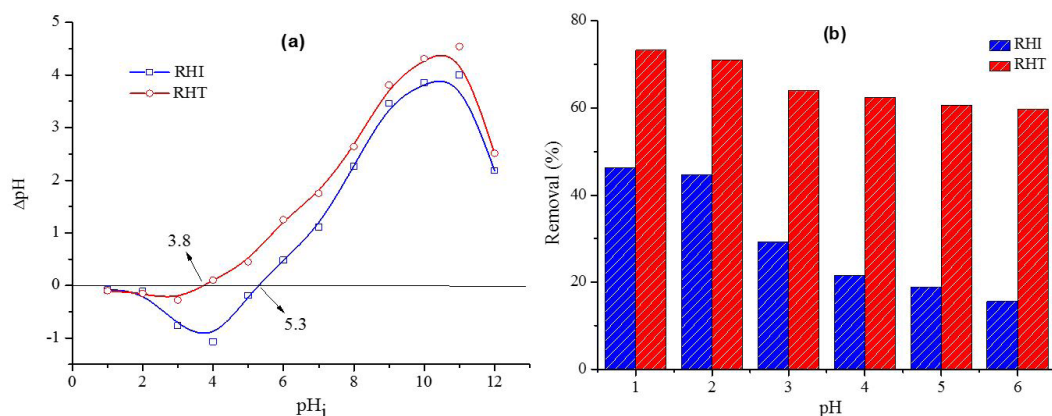


Figure 5. (a) pH_{pzc} of the RHI and RHT, (b) Influence of pH on adsorption of Remazol brilliant violet dye by the RHI and RHT adsorbents (m = 100 mg; C_i = 100 mg L⁻¹; t = 24 h; T = 298 ± 1 K).

The pH_{pzc} values obtained for the RHI and RHT adsorbents were 5.3 and 3.8, respectively. Hence, below these pH values, the surfaces of the adsorbents would be positively charged, favoring anion adsorption, while at higher values, the surfaces would be negatively charged, favoring the adsorption of cations. The pH_{pzc} value for RHI was very close to values reported in the literature for *in natura* rice hull (5.3)^[19] and babassu coconut epicarp (6.7)^[39,40]. In other work, it was found that *in natura* wood sawdust had a pH_{pzc} of 5.3, which decreased to 4.0 after treatment with hydrochloric acid^[41]. The decrease in the pH_{pzc} value of the adsorbent after treatment is an indication that there were changes in the surface characteristics, with an increased number of protonated sites. This is supported by the increased prevalence of peaks related to oxygenated groups in the infrared and ¹³C-NMR spectra.

The pH of the system is an important element in the adsorption process, because pH change alters the chemical balance of the ionic groups present in the adsorbent and the dye, influencing the electrostatic interaction. Figure 5b shows the removal percentages of Remazol brilliant violet dye by the RHT and RHI adsorbents. It can be seen that higher pH reduced adsorption of the dye, while at low pH there was greater protonation on the surfaces of the adsorbents, which favored anion removal.

The highest dye removal percentages were achieved at pH 1.0 and 2.0. At pH 1.0, the maximum amounts of dye adsorbed were 46.2 and 73.2% for RHI and RHT, respectively. Higher removal percentages of Remazol dyes at pH 1.0 and 2.0 were observed previously using adsorbents such as babassu coconut mesocarp^[42] and rice hull^[19]. Importantly, use of the RHT adsorbent significantly increased the percentage removal, compared to RHI, showing the effectiveness of the acid treatment. The adsorption by RHT improved between pH 3.0 and pH 6.0, suggesting that in addition to electrostatic attraction, other interaction mechanisms were involved in the adsorption process, since a decreased removal capability was expected between these pH values, as found for the RHI adsorbent. Another interesting finding concerned the contribution of protonation to dye

adsorption, with values of 66.3% and 18.4% obtained for RHI and RHT, respectively. These results provided further evidence of the effectiveness of the treatment, which resulted in dye removal being practically independent of the effect of protonation, due to the enhancement of other interactions that contributed to the adsorption.

3.5 Adsorption kinetics

Study of the adsorption kinetics is important, because it provides information about the mechanism of adsorption. This work considered the contact time between the adsorbent and the adsorbate required for the system to reach equilibrium. The adsorption kinetics depends on several factors, including the adsorbent mass, concentration of adsorbate, temperature, pressure, and stirring speed of the system. Figure 6 shows the adsorption kinetics for two concentrations of the Remazol brilliant violet dye (100 and 1000 mg L⁻¹) at pH 2 (defined as optimal in the adsorption experiments), together with the fits obtained with the Lagergren (Equation 2)^[43], Ho (Equation 3)^[44], and Elovich (Equation 4)^[45] kinetic models.

$$q = q_e \left(1 - e^{-k_1 t}\right)$$
 (2)

$$q = \frac{(q_e)^2 k_2 t}{1 + q_e k_2 t}$$
 (3)

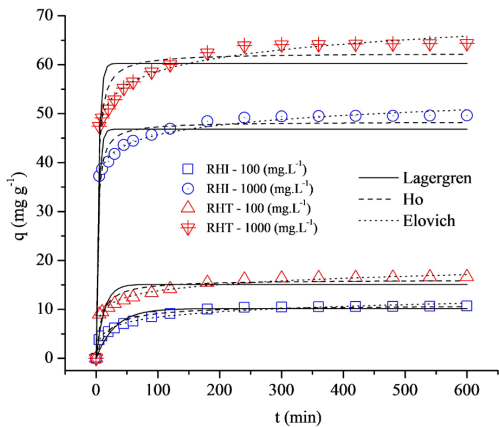


Figure 6. Adsorption kinetics of Remazol brilliant violet dye using RHI and RHT, at pH 2.0 and using initial dye concentrations of 100 and 1000 mg L⁻¹.

$$q = \frac{1}{\beta} \left(\ln(\alpha\beta) + \ln t \right)$$
 (4)

In the above equations, q_e (mg g⁻¹) is the amount adsorbed at equilibrium, k₁ (min⁻¹), k₂ (g mg⁻¹ min⁻¹), and α (mg g⁻¹ min⁻¹) are the Lagergren, Ho, and Elovich adsorption rate constants, and β (g mg⁻¹) is a parameter related to the activation energy. The equilibrium times were 180 and 240 min for dye concentrations of 100 and 1000 mg L⁻¹, respectively. At the lower concentration, the equilibrium time was shorter due to the smaller number of interactions between the dye molecules and the active sites of the adsorbent. Most of the adsorption occurred within 60 min, reflecting fast adsorption kinetics. The high adsorption rates in the early stages of the process were due to greater availability of active sites. Similar equilibrium times have been reported previously for the removal of Remazol dyes using lignocellulosic materials. Tunç et al.^[46] used cotton stem bark to remove Remazol B black dye and obtained an equilibrium time of 300 min.

The values of the fitting parameters for the Lagergren, Elovich, and Ho kinetic models are shown in Table 1. The closeness of R² (coefficient of determination) to unity indicates the high levels of explanation provided by the models, with the best results obtained using the Elovich model. This model has been successfully used previously for adsorption by materials with heterogeneous surface energy, and allows for a gradual decrease in removal rate with increasing concentration^[47]. The adsorbents used in this study presented several functional groups that could act as adsorption sites. Furthermore, Remazol brilliant violet dye also has many groups capable of interacting with adsorbents, so that the adsorption process was energetically heterogeneous, in agreement with the Elovich model.

3.6 Adsorption isotherms

After establishing the optimal pH and the equilibrium time, isotherms were constructed to determine the maximum amounts of dye that could be removed by the adsorbents. Figure 7 shows the dye adsorption isotherms for the RHI and RHT adsorbents, at four temperatures (283, 298, 313, and 328 ± 1 K). The isotherms can be represented by mathematical equations used to provide information on the mechanism of adsorption, surface properties, and the affinity of the adsorbent for the adsorbate. Several models

Table 1. Fitting parameters for the kinetic models.

Models	Parameters	RHI		RHT	
		C _i =100 mg L ⁻¹	C _i =1000 mg L ⁻¹	C _i =100 mg L ⁻¹	C _i =1000 mg L ⁻¹
Lagergren	q _e (mg g ⁻¹)	10.17	46.83	15.12	60.26
	k ₁ (min ⁻¹)	0.033	0.261	0.079	0.249
	R ²	0.9091	0.9208	0.7955	0.9031
Ho	q _e (mg g ⁻¹)	10.88	48.35	16.06	62.40
	k ₂ (g mg ⁻¹ min ⁻¹)	0.0049	0.0093	0.0074	0.0065
	R ²	0.9684	0.9695	0.9157	0.9596
Elovich	α (mg g ⁻¹ min ⁻¹)	3	253181	31	90545
	β (g mg ⁻¹)	0.628	0.350	0.540	0.250
	R ²	0.9845	0.9967	0.9900	0.9961

have been reported in the literature, and in this work, the experimental data were tested using the Freundlich (Equation 5)^[48], Langmuir (Equation 6)^[49], and Temkin (Equation 7)^[50] models. The parameters of the models are given in Table 2.

$$q_e = K_F C_{eq}^{1/n} \quad (5)$$

$$q_e = \frac{q_m C_{eq} K_L}{1 + K_L C_{eq}} \quad (6)$$

$$q_e = B \cdot \ln(K_T C_{eq}) \quad (7)$$

In the above equations, q_m (mg g^{-1}) is the maximum amount of dye adsorbed; K_F ($\text{L mg}^{-n} \text{g}^n$)^{1/n}, K_L (L mg^{-1}), and K_T (L mg^{-1}) are constants of the Freundlich, Langmuir, and Temkin models, respectively; n is a parameter related to the energy of the surface sites; B (mg g^{-1}) is a constant obtained from the expression $B = RT/b$, where b is a parameter related to the heat of adsorption, T is the absolute temperature (K), and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The parameter, n describing the degree of heterogeneity of the system showed values between 1 and 5, which indicates favorable adsorption for both adsorption systems^[51]. Application of the Freundlich model resulted in the highest value of the linear coefficient of determination (R^2), with values close to unity for all temperatures studied Table 2.

Previous studies of lignocellulosic materials used for adsorption of Remazol brilliant violet have also found good fits using the Freundlich model. The materials tested were babassu coconut mesocarp^[18], and coconut straw^[52]. The amount of dye adsorbed increased progressively with increasing temperature, suggesting that the system was endothermic. This behavior could be explained by factors such as increased mobility of the molecules present in the solution (increased kinetic energy caused by the temperature rise), increased diffusion of adsorbate on the surface of the adsorbent, and dilation of the pores of the adsorbent^[53].

3.7 Thermodynamics of adsorption

Knowledge of the adsorption thermodynamic parameters is important because it enables characterization of the process as spontaneous, exothermic, or endothermic, and provides information on the affinity of the adsorbent for the adsorbate. Additionally, these parameters can provide information concerning the heterogeneity of the surface of the adsorbent and whether the process involves physical or chemical adsorption. The thermodynamic parameters adsorption enthalpy (ΔH°), entropy (ΔS°), and Gibbs energy (ΔG°) were obtained by linearization of the van't Hoff equation, according to Equations 8, 9, and 10^[54].

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

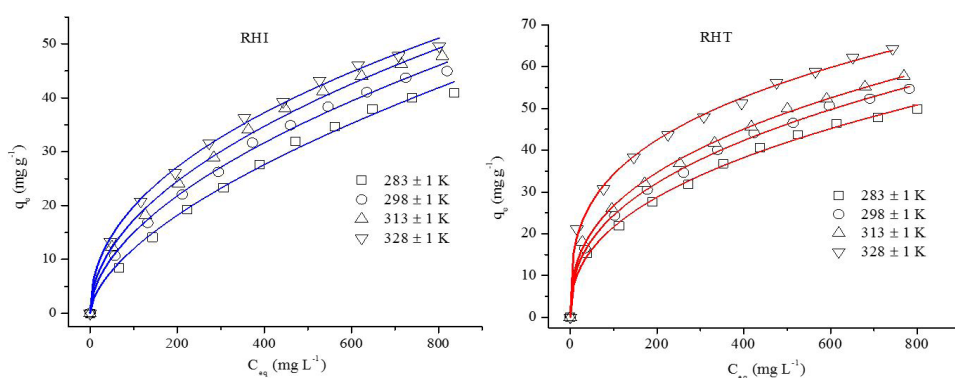


Figure 7. Adsorption isotherms for Remazol brilliant violet dye using *in natura* (RHI) and treated (RHT) rice hulls as adsorbents.

Table 2. Parameters of the isotherm models used to fit the adsorption equilibrium data for removal of Remazol brilliant violet dye by the RHI and RHT adsorbents. Temperature error = ± 1 K.

Isotherms	Parameters	RHI				RHT			
		283 K	298 K	313 K	328 K	283 K	298 K	313 K	328 K
Freundlich	n_F	1.663	1.854	1.990	2.196	2.433	2.519	2.647	3.211
	$K_F (\text{L mg}^{-n} \text{g}^n)^{1/n}$	0.751	1.250	1.709	2.432	3.260	3.924	4.685	8.156
	R^2	0.9941	0.9965	0.9958	0.997	0.9972	0.9985	0.9983	0.9978
Langmuir	$q_m (\text{mg g}^{-1})$	71.16	68.63	68.48	65.20	61.41	65.07	66.49	67.87
	$K_L (\text{L mg}^{-1})$	0.0017	0.0023	0.0028	0.0037	0.0047	0.0053	0.0060	0.0102
	R^2	0.9974	0.9943	0.9914	0.9901	0.9774	0.9728	0.9606	0.9394
Temkin	$B (\text{mg g}^{-1})$	13.80	13.74	13.77	13.44	12.13	12.68	12.40	11.52
	$K_T (\text{L mg}^{-1})$	0.0214	0.0287	0.0354	0.0448	0.0654	0.0781	0.1036	0.2568
	R^2	0.9777	0.9772	0.9757	0.9839	0.9771	0.9771	0.9708	0.9718

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

$$K_{eq} = \frac{q_e}{q_m - q_e} \frac{1}{C_{eq}} \quad (10)$$

In the above equations, q_e is the amount adsorbed (mg g^{-1}), q_m is the maximum amount adsorbed at each temperature (mg g^{-1}), C_{eq} is the equilibrium concentration of the adsorbate (mol L^{-1}), T is the temperature of the adsorptive system (K), K_{eq} are equilibrium constants, and R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). Figure 8 illustrates the linearization of the experimental data according to the van't Hoff equation, where linearity was observed between the points for the systems studied. The thermodynamic parameters for the adsorption of Remazol brilliant violet dye by the adsorbents are listed in Table 3. Negative values of the Gibbs energy (ΔG°) indicated that the interactions between the dyes and the RHT and RHI adsorbents were spontaneous and favorable, because the lower the value of ΔG° , the greater the driving force of the process, resulting in high adsorption^[53]. This was supported by the more negative values of ΔG° for RHT, which also showed greater adsorption of the dye, compared to RHI. Positive enthalpy (ΔH°) values indicated the endothermic nature of all the adsorption processes, with the amount of dye adsorbed at equilibrium tending to increase with increasing temperature. The positive entropy (ΔS°) values indicated that entropy increased during the adsorption process, so the process tended towards a higher degree of disorder.

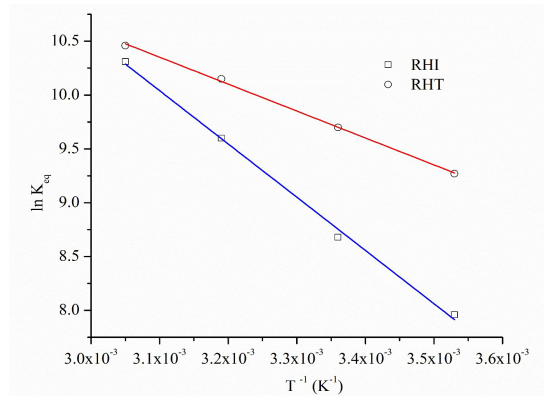


Figure 8. Van't Hoff plots for the adsorption of Remazol brilliant violet dye by the *in natura* (RHI) and treated (RHT) rice hull adsorbents.

Table 3. Thermodynamic parameters for the adsorption of Remazol brilliant violet dye by the RHI and RHT adsorbents.

Adsorbent	T (K)	$K_{eq} \times 10^{-4}$	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	R ²
RHI	283 ± 1	0.29	-18.60	40.95	210.41	0.9978
	298 ± 1	0.59	-21.75			
	313 ± 1	1.48	-24.91			
	328 ± 1	3.00	-28.07			
RHT	283 ± 1	1.06	-21.81	20.71	150.27	0.9989
	298 ± 1	1.63	-24.07			
	313 ± 1	2.56	-26.32			
	328 ± 1	3.49	-28.58			

Bekçi et al.^[55] reported that an enthalpy change of between 0 and 20 kJ mol⁻¹ was characteristic of a physisorption process, while a change of between 80 and 400 kJ mol⁻¹ reflected chemisorption. Alkan et al.^[56] found that an enthalpy change of between 40 and 120 kJ mol⁻¹ characterized a chemisorption process. However, Zhou et al.^[57] considered that these ranges were not sufficient to confirm the type of adsorption. In fact, under favorable conditions, these processes can occur simultaneously or alternately^[58], but the values obtained suggested that adsorption of the dye by the adsorbents occurred mainly due to physisorption.

3.8 Possible interactions between the dye and the adsorbents

Elucidation of the mechanism of dye adsorption is a major challenge, as many interactions can occur during the adsorption process. Remazol Brilliant Violet is an anionic dye that contains a sulfonic group in its structure (which ionizes in aqueous solution, forming colored anions), together with aromatic rings. The RHT and RHI adsorbents were lignocellulosic materials composed primarily of cellulose, hemicellulose, and lignin. Characterization of the adsorbents revealed heterogeneous surfaces and the presence of hydroxyl and carbonyl groups.

Comparison of the IR spectra for the dye and the rice hull surfaces (Figures 2a, 2c, and 2e) revealed that they were very similar, with the exception of bands at 1639 cm⁻¹ (amide I) and 626 cm⁻¹ (C–S stretching), which were only present in the dye spectrum. These bands were present in the spectra for the dye-saturated biomasses (Figures 2b and 2d), indicating that adsorption had occurred. Unfortunately, the characteristic N=N stretching band of the dye was overlapped with the C–H deformation vibration band, and could not be used for comparative analysis^[27]. No other new bands were present in the spectra for the materials with adsorbed dye, suggesting similar predominant functional groups after adsorption. This was in agreement with the better definition and intensity of the IR bands for the materials with adsorbed dye, as well as with the estimated values of the thermodynamic parameters (which were indicative of physisorption)^[58]. Some of the well-defined bands, such as those at 1100–1300 cm⁻¹, could be attributed to protonated sulfonic groups^[27,59] that probably resulted from interactions between the dye and the protonated surface, as illustrated in Figure 9.

The pH_{pzc} values showed that at pH below 5.3 (RHI) and 3.8 (RHT), the surfaces of the adsorbents were positively

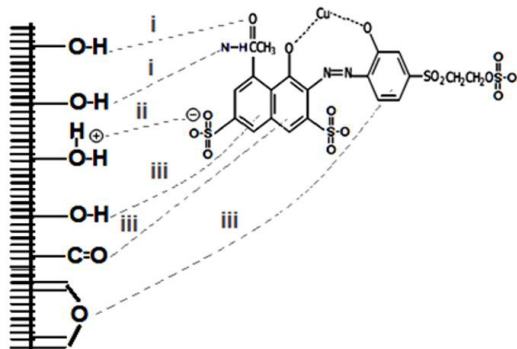


Figure 9. Possible adsorbent-dye interactions: (i) hydrogen bonds; (ii) electrostatic attraction; (iii) π electron resonance.

charged, with the presence of H^+ ions favoring adsorption of anionic species such as the dyes studied here. This was supported by the results obtained in the study of the influence of pH on the adsorption, with greater removal achieved at pH 1 and 2. These findings indicated that the mechanism of adsorption of the dye by the adsorbent occurred due to electrostatic attraction, with the adsorbents being protonated in an acid medium, hence attracting the negatively charged sulfonic groups of the dye.

The treated adsorbent showed greater dye removal efficiency, compared to the *in natura* material, especially at less acidic pH (pH 3-6), where the percentage removal remained essentially constant. However, a smaller influence of protonation was observed for the treated adsorbent. These findings confirmed that in addition to electrostatic attraction, other interactions were involved in the adsorption systems studied. The FTIR results showed that carboxyl, hydroxyl, and aromatic carbon functional groups could participate in dye adsorption. Considering all the information obtained in the experiments, three possible interaction mechanisms^[50,60] can be proposed for the adsorption of Remazol Brilliant Violet dye by the adsorbents at pH 2: (i) hydrogen bonding, (ii) electrostatic attraction, and (iii) π electron resonance (Figure 9).

4. Conclusions

The surface of rice hull was successfully modified by treatment with nitric acid, resulting in a decrease in the point of zero charge (pHpzc). Infrared and ^{13}C -NMR analyses showed that oxygenated groups were introduced in the rice hull surface after treatment. Thermogravimetric analysis indicated that the matrix remained stable up to temperatures close to 473 K, and that the treated adsorbent showed greater weight loss due to the decomposition of lignin. The points of zero charge (pHpzc) were pH 5.3 and pH 3.8 for the *in natura* and treated materials, respectively. Below the pHpcz, the surface was positively charged, favoring adsorption of the anionic dye.

Kinetic studies revealed that adsorption equilibrium was achieved within around 240 min. The Elovich kinetic model provided the best fit to the experimental data for adsorption of the dye, for the two concentrations employed

here. The adsorption isotherms obtained for different temperatures showed that the removal efficiency increased with increasing temperature. The Freundlich isotherm model provided the best explanation of the experimental results for adsorption of the dye. The thermodynamic parameters (ΔG° , ΔH° , and ΔS°) obtained for these adsorption systems (at the temperatures studied) revealed that the reactions were spontaneous, energetically favorable, and endothermic, with a high degree of disorder.

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Appendix A. Additional materials.

Table 1A. Percentages of carbon (C), hydrogen (H), and nitrogen (N) in the *in natura* (RHI) and treated (RHT) adsorbents.

Adsorbent	%C	%H	%N
RHI	35.87	5.04	0.54
RHT	39.73	5.37	1.46
Difference	3.86	0.33	0.92

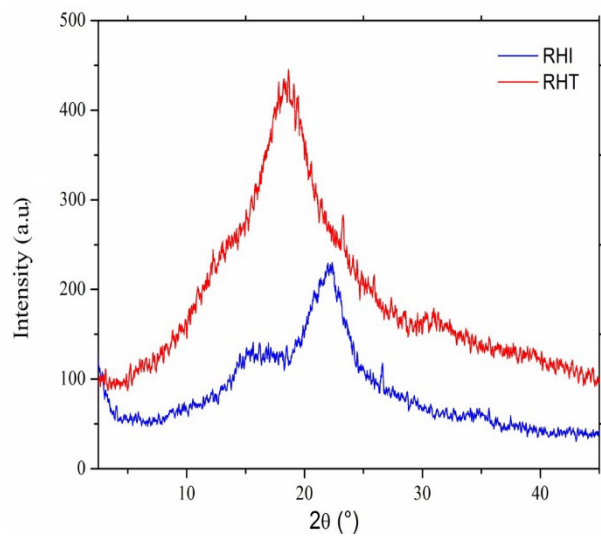


Figure 1A. X-ray diffractograms of the *in natura* (RHI) and treated (RHT) rice hulls.