


Biosorption of 5G blue reactive dye using waste rice husk

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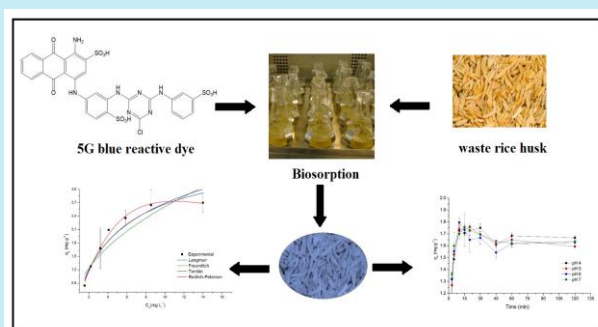
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ABSTRACT: In this study, the biosorption was used on the removal of 5G blue dye using rice husk residue. The influence of temperature and pH on the biomass pretreated with H₃PO₄ and NH₄Cl was evaluated on the sorption capacity. The tests were conducted in batch with previous determination of point of zero charge (PZC). Analytical measurements were performed by UV-VIS spectroscopy. A major influence of pH and temperature on the biosorption capacity of the dye was observed. The highest removal was obtained for the condition of pH 4 and temperature of 50 °C. The time for the biomass-dye system to reach equilibrium was around 45 min. Pseudo-first order kinetic model adequately represented experimental data and had a good correlation coefficient. In the equilibrium study, Langmuir isotherm best fitted the experimental data, with a maximum biosorption capacity of 3.84 mg g⁻¹. The use of rice husk as a biosorbent for the removal of reactive blue 5G dye can be considered promising for the abundance of this residue and the observed sorption capacity.



1. Introduction

In the industrial sector, several projects have been highlighted by the polluting potential, especially by the considerable amounts of residues rich in diverse types of substances highly harmful to water, air and soil. In this category, the textile industries are included as generators of environmental impacts and emitters of waste typically composed of the inputs used in its process, among which dyes, such as reactive blue dye 5G used on a large scale in the production of denim^{1,2}.

Reactive dyes have been used on a growing scale by the textile industries due to their reactivity with fibers and color stability. The reactive dye

molecule can be defined by the following structural systems: a chromophore system, responsible for the color phenomenon; a sulfonate group, responsible for the solubility and anionic character of the dye; and one or more reactive groups, which may form a covalent bond with the cellulose fibers by nucleophilic addition or substitution reaction³.

The increase of complexity and difficulty for the treatment of industrial effluents has led to the search of new methodologies for the removal of these wastes. The availability of innovative technologies and costs compatible with the need to reduce the environmental liabilities produced by industrial effluents is a fundamental task with repercussions in the short and medium term. As a measure to minimize the impacts caused by the

discharge of effluents rich in specific pollutants such as dyes, companies have the option of using tertiary treatments, mainly physical and chemical. Currently, due to the cost and operational complexity, these systems have been neglected by alternative systems or the use of biomass through the processes of bioaccumulation and biosorption^{4,5}.

Biosorption is a passive process where the capture is carried out by inactive (dead) biomass. The capture of the contaminants by biomass occurs through physical-chemical interactions between the ions and the functional groups present on the biomass surface⁶.

A variety of biosorbents have been investigated such as banana peel, chitosan, orange peel, aquatic plants, cotton fibers, wood sawdust, sugarcane bagasse, corn cob, babassu coconut, among others^{7,8}. Aiming for efficiency, kinetic and equilibrium studies are required to better understand the mechanisms involved. The pseudo-first and pseudo-second order models are commonly applied for kinetic evaluation. For the biosorption equilibrium, isotherms are used to describe the experimental data accurately within a set of imposed conditions⁹. The commonly used models are Langmuir, Freundlich and Henry^{10,11}.

Rice husk is a lignocellulosic compound formed, basically, by: i) cellulose (35%), a semi-crystalline polymer of anhydrocellulose, the units of which are interconnected via β -1 \rightarrow 4 bonds; (ii) hemicellulose (13.1%), a heterogeneous polymer composed of the combination of three hexoses: β -D-glucose, β -D-mannose and β -D-galactose, three pentoses: β -D-xylopyranose, β -D-arabinopyranose and β -D-galactouronic acid; and (iii) lignin (13.27%), an amorphous aromatic polymer (methoxy-phenols forming a resin species in plants), consisting of two types of basic units: guaiac and syringyl¹². This biomass is insoluble in water, has good chemical stability, high mechanical strength and has several functional groups in its structure such as COOH, -OH, SiOH, CH, C=O, C=C, CH₂, CH₃, CO, Si-O-Si, Si-H, -O-CH₃, and therefore has potential to be a good adsorbent material^{13,14}.

Biosorbents prepared with rice husk have been used in the adsorption of heavy metals, dyes and other organic compounds due to the large renewable production and the low cost for these adsorbents¹⁵⁻¹⁸. Previous researches reveal that rice husk can be used for removing ionic dyes from aqueous solutions and presented promising results.

This biomass presents high adsorption capacity, which is significantly increased when chemically modified¹⁹⁻²¹.

This study investigated the removal of 5G blue reactive dye by means of biosorption using the rice husk residue as a biosorbent. Kinetic and equilibrium studies were performed to evaluate this biomass as a low-cost alternative, when compared to traditional physicochemical systems.

2. Materials and methods

2.1 Reagents, solutions and analytical determinations

All reagents used in this work were analytical grade, phosphoric acid 85% (Merck), sodium hydroxide 97% (Merck), hydrochloric acid 37% (Merck), ammonium chloride P.A. (VETEC) and sodium chloride P.A. (VETEC). Reactive dye 5G (TEXPAL) of commercial nature was used in powder form.

Solutions were prepared at the concentration of 1.0 mol L⁻¹ for biomass treatments and for determination of the point of zero charge (PZC). From a stock solution of the 1000 mg L⁻¹ dye and distilled water, working solutions were prepared with 20 mg L⁻¹ used in the adsorption experiments.

The determination of the concentration of dye in the tests occurred by external calibration. For this, a six-point analytical curve was obtained using stock solution in the range from 0 to 50 mg L⁻¹. Measurements were performed using a UV-VIS spectrophotometer (Perkin Elmer Lambda 45) at 589 nm. The pH measurements were performed in bench potentiometer (Hanna 21).

2.2 Preparation of the biosorbent

Approximately 1.5 kg of rice husk were cleaned with distilled water by immersion for 24 h. Subsequently, the material was drained and oven dried (Quimis) for 24 h at 60 °C. Subsequently the biomass was ground in a knife mill and divided into three equal portions. One of them was reserved as experimental blank. To evaluate the influence of chemical pretreatments, one of the portions of the dried rice husk was immersed in 1.0 mol L⁻¹ H₃PO₄, and the other was immersed in 1.0 mol L⁻¹ NH₄Cl for 24 h. After rinsing again with distilled water, they were again dried in an oven and packed in sealed containers.

2.3 Point of zero charge (PZC)

The adsorption processes are strongly dependent on the pH, which affects the surface charge of the adsorbent, the degree of ionization and the adsorbate species. The pH_{PCZ} allows to predict the charge on the surface of the adsorbent as a function of pH. For the determination of the pH_{PCZ} , samples composed of 0.5 g of rice husk were placed in Erlenmeyer flasks with 50 mL of NaCl 0.1 mol L⁻¹ solution and adjusted pH 2 to 12 with NaOH and HCl 0.1 mol L⁻¹. The plastic film sealed bottles were kept under constant stirring (120 rpm) in a shaker incubator (Lactea brand, model LAC-2000) at 25 °C. The pH was measured at intervals of 1 h until constant values were obtained. Stirring was continued for 24 h to ensure equilibrium of the solutions. The values were presented as a plot of $\Delta pH \times$ initial pH, and the PCZ value defined as the one that intercepts the x-axis ($\Delta pH = 0$)²².

2.4 Biosorption Study

For the pH effect evaluation, two values above and two below of the PZC were chosen. To study the temperature, tests were performed at 40 and 50 °C, in addition to the ambient temperature (25 °C). The assays were carried out in duplicate in a 125 mL Erlenmeyer flask, kept under shaking at 120 rpm in a shaker incubator. 0.5 g of biosorbent and 50 mL of dye solution (20.0 mg L⁻¹) were added to each flask for kinetic test and at concentrations of 1.0, 5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0 and 40.0 mg L⁻¹ for isotherm equilibrium test. After 4 h, the biosorbent was removed by filtration and the dye concentrations were measured by using the spectrophotometer mentioned before.

The concentration of the dye in the adsorbent (q_e), in mg g⁻¹, was calculated by Equation 1.

$$q_e = V \cdot \frac{(C_0 - C_e)}{m} \quad (1)$$

where V is the volume of the solution (L), C_0 is the initial concentration of the solution (mg L⁻¹), C_e is the concentration of the final test solution (mg L⁻¹). The dye concentration at equilibrium (q_e) was determined by the inspection of the graph time $q_e(t)$ versus (t), at the instant the removal was constant.

The equilibrium kinetic data were fitted to the

pseudo-first order models (Eq. 2), pseudo-second order (Eq. 3) and the intraparticle diffusion model derived from Fick's law assuming that diffusion of the liquid film surrounding the adsorbent is negligible and intraparticle diffusion is the rate-determining step of the adsorption process (Eq. 4)²³⁻²⁵.

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

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

$$q(t) = k_3 t^{\frac{1}{2}} + C \quad (4)$$

where q_e and $q(t)$ are the equilibrium adsorption and the adsorption capacity at the time t , respectively, in mg g⁻¹; t is the time in min; C suggests the thickness of the boundary layer effect (mg g⁻¹); k_1 (min⁻¹), k_2 (g mg⁻¹ min⁻¹) and k_3 (g mg⁻¹ min^{-1/2}) are the constants corresponding to the pseudo-first, pseudo second order and intraparticle diffusion models, respectively.

To describe the adsorption equilibrium, the adsorption isotherms models were adjusted to experimental data. Langmuir model hypothesizes that adsorption occurs in a monolayer manner and that all active sites are evenly distributed on the adsorbent and are available at the same energy "cost". These facts are important for the description of the interaction adsorbent-adsorbate (Eq. 5).

$$q_e = \frac{q_m \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (5)$$

where q_m is the adsorption capacity of the studied material (mg g⁻¹); and b is the constant that measures the adsorbent-adsorbate affinity related to adsorption-free energy^{26, 27}.

The Freundlich model (Eq. 6) considers the heterogeneous solid and the exponential distribution to characterize the diverse types of adsorption sites, with different adsorptive energies²⁸.

$$q_e = k_L \cdot C_e^{1/n} \quad (6)$$

where k_L and n are empirical constants²⁹ and can be related to the changes in the adsorbed concentration with the changes in the solute concentration.

The Temkin model (Eq. 7) considers the effects

of the indirect interactions between the adsorbate molecules and the decrease of the heat of adsorption with the increase of the rate of removal³⁰.

$$q_e = B \cdot \ln k_T C_e \quad (7)$$

where B is the Temkin constant relating the heat of adsorption to the total number of sites (mg g^{-1}) and k_T is the Temkin constant (L mg^{-1}).

The Redlich-Peterson model (Eq. 8) is used to represent equilibrium of adsorption over a wide range of concentrations and may be applied in homogeneous and heterogeneous systems, due to its versatility³¹.

$$q_e = \frac{k_R C_e}{1 + a_R C_e^\beta} \quad (8)$$

where k_R and a_R are the Redlich-Peterson constants (L mg^{-1}) and β is the exponent with values from 0 to 1. The parameters of the models were obtained from non-linear regression using

Origin 8.5[®] and the regression was assessed by ANOVA at the 95% level of significance.

3. Results and discussion

3.1 Point of zero charge (pH_{PZC}), pH and temperature effect

Figure 1 shows the variation of pH as a function of the initial pH for the three adsorbents: untreated, treated with H_3PO_4 and treated with NH_4Cl . The pH at the point of zero charge was approximately 5.0 for the natural rice husk, 2.5 for the treatment with H_3PO_4 and 5.0 for treatment with NH_4Cl . Below these values the solid presents a positive surface charge favoring the adsorption of anions. Then, it is expected better adsorption on the studied biomass at pH s below pH_{PZC} due to the anionic characteristic of 5G blue reactive dye in aqueous solution.

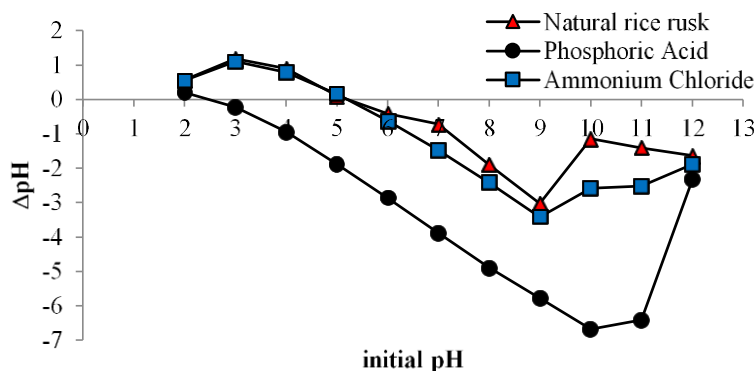


Figure 1. pH_{PZC} values for biosorbent rice husk natural and treated with H_3PO_4 and NH_4Cl .

Considering the value of the pH_{PZC} , the objective was to determine the pH range where the biosorbent adsorb more dye. Figure 2 presents the quantity of adsorbed dye (per adsorbent unit mass)

as a function of time, at different pH conditions and different adsorbents.

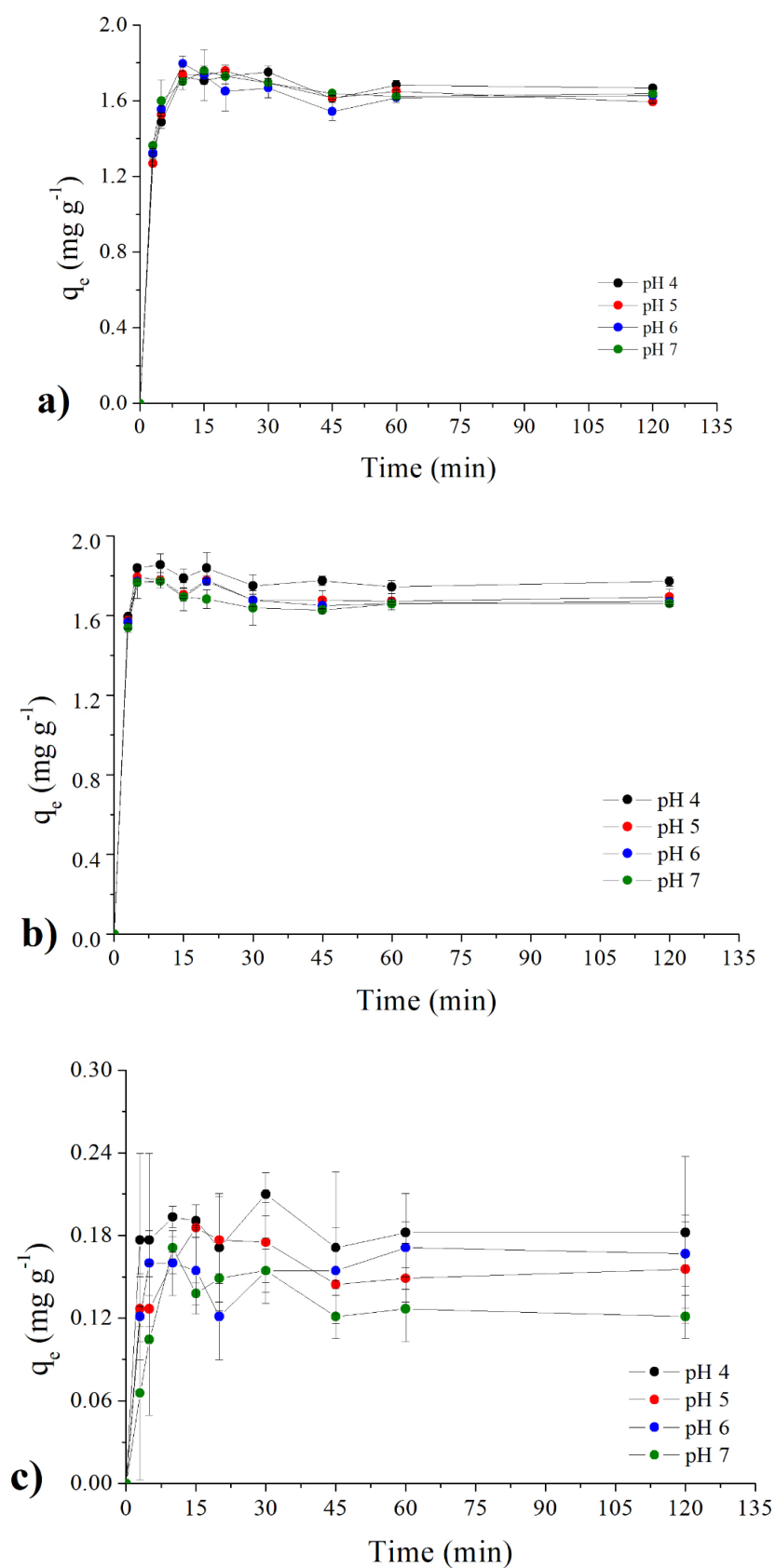


Figure 2. Influence of pH on biosorption (q_e) at 25 °C. a) natural rice rusk, b) H₃PO₄ and c) NH₄Cl.

It was observed that the biosorption of 5G Blue dye in solution by the rice hull is pH dependent. It was found that at pH 4 the natural biomass removed 81.3% of the dye, already for pH 5 it was 79.7%, for pH 6 it was 81.3% and pH 7 was 82.8%. In the pre-treatments the lower pHs were more efficient,

removing 88.6% of the dye by the biomass pretreated with phosphoric acid and 9.1% with ammonium chloride. Considering the time of 120 min the values of q_e were calculated for the studied pH values. These values are set forth in Table 1.

Table 1. Adsorption capacity of the study material (mg g^{-1}) at time 120 min for different pH values at 25 °C.

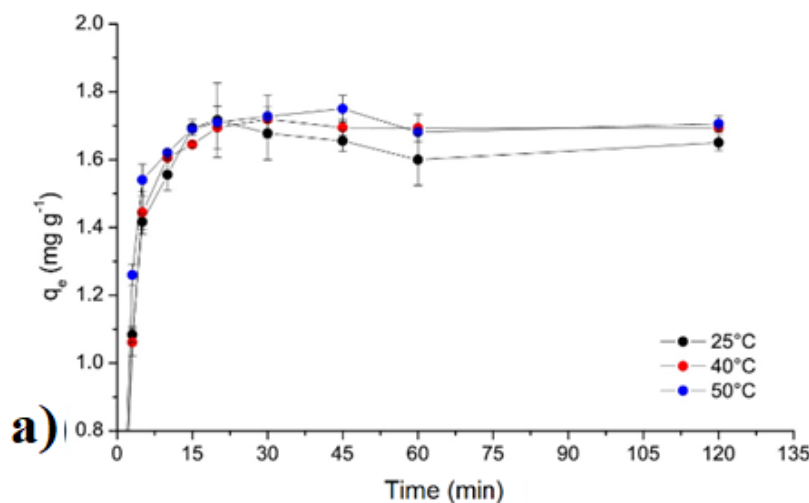
pH (A)	Treatments			t-test		
	Natural	H ₃ PO ₄ (B)	NH ₄ Cl (C)	AB	AB	BC
4	1.64(±0.03)	1.62(±0.01)	0.18(±0.02)	1.10	70.14	111.54
5	1.67(±0.04)	1.65(±0.04)	0.15(±0.01)	0.61	63.35	63.01
6	1.66(±0.01)	1.68(±0.02)	0.17(±0.01)	1.55	182.42	116.06
7	1.69(±0.03)	1.62(±0.01)	0.13(±0.03)	2.83	69.69	81.61

$t_{\text{critical}} (n=3; p=0.05) = 2.92$

For the comparison of the sorption capacity (q_e) between the treatments at each pH evaluated, the t-test was applied at a significance level of 95% (Table 1). Considering the degrees of freedom equal to 3, the critical value corresponds to $t_{(3; 0.05)} = 2.92$. All comparisons between the natural biosorbent and the H₃PO₄ (AB) treatment were considered statistically the same, since $t_{\text{critical}} > t_{\text{calculated}}$. However, for the biomass prepared with NH₄Cl, sorption capacity was different from the other treatments (AC and BC) because $t_{\text{critical}} < t_{\text{calculated}}$. Considering the lower values of q_e it can be considered that the application of NH₄Cl reduced the potential and sorption of the biomass studied and that the application of H₃PO₄ did not promote a statistically significant increase when compared to the natural biomass (Figure 2).

The pH can also affect the structural stability of the 5G blue reactive dye because, under an acidic condition, the dye molecule can be deprotonated within the solution, resulting in a polar molecule with a high negative charge density. Therefore, the electrostatic repulsion between the adsorbent site and the negatively charged dye ions was reduced at low pH. Consequently, positively charged functional groups could exert a strong electrostatic attraction on anionic dye molecules^{32, 33}.

An evaluation of the effect of the temperature considers a dye removal for each treatment at temperatures of 25, 40 and 50 °C. Figure 3 shows the experimental data of amount of dye adsorbed (q_e) versus time for each temperature studied at pH 4.



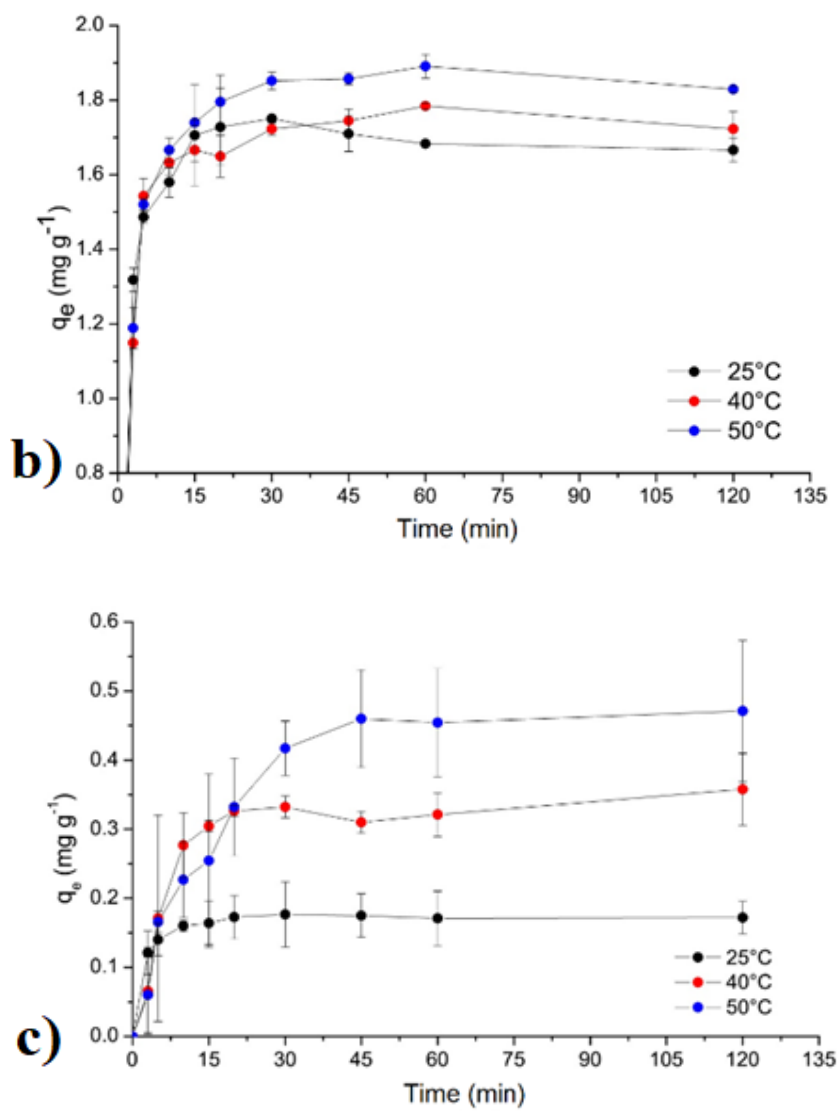


Figure 3. Influence of temperature on biosorption (q_e) at pH 4: a) natural rice rusk, b) H_3PO_4 and c) NH_4Cl .

The temperature significantly influences the kinetic energy of the molecules and interferes on the attraction and repulsion forces between the adsorbate and the adsorbent³³. In the range of temperature and conditions studied, an increase in the adsorbed amount was observed as the temperature increases, with 50 °C being the one that presented the best results. The biomass pretreated with H_3PO_4 at 50 °C showed the best dye removal, 91.5%. It was observed that an increase in temperature favorably influenced the ability of the 5G Blue dye to be removed by the rice husk biomass.

This behavior could be explained by factors such as an increased in 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 adsorbent³⁴.

3.2 Biosorption kinetic

Figure 4 shows the quantity of adsorbed dye per unit mass of adsorbent as a function of time, at pH 4 and 50 °C, for different pretreatments. The experimental data were adjusted to the models of pseudo-first order, pseudo-second order and intraparticle diffusion. The equilibrium time was about 20 min for *in natura* rice husk and about 35 min for both pretreated adsorbents.

Table 2 shows the fitted parameters and the determined coefficients for these experiments.

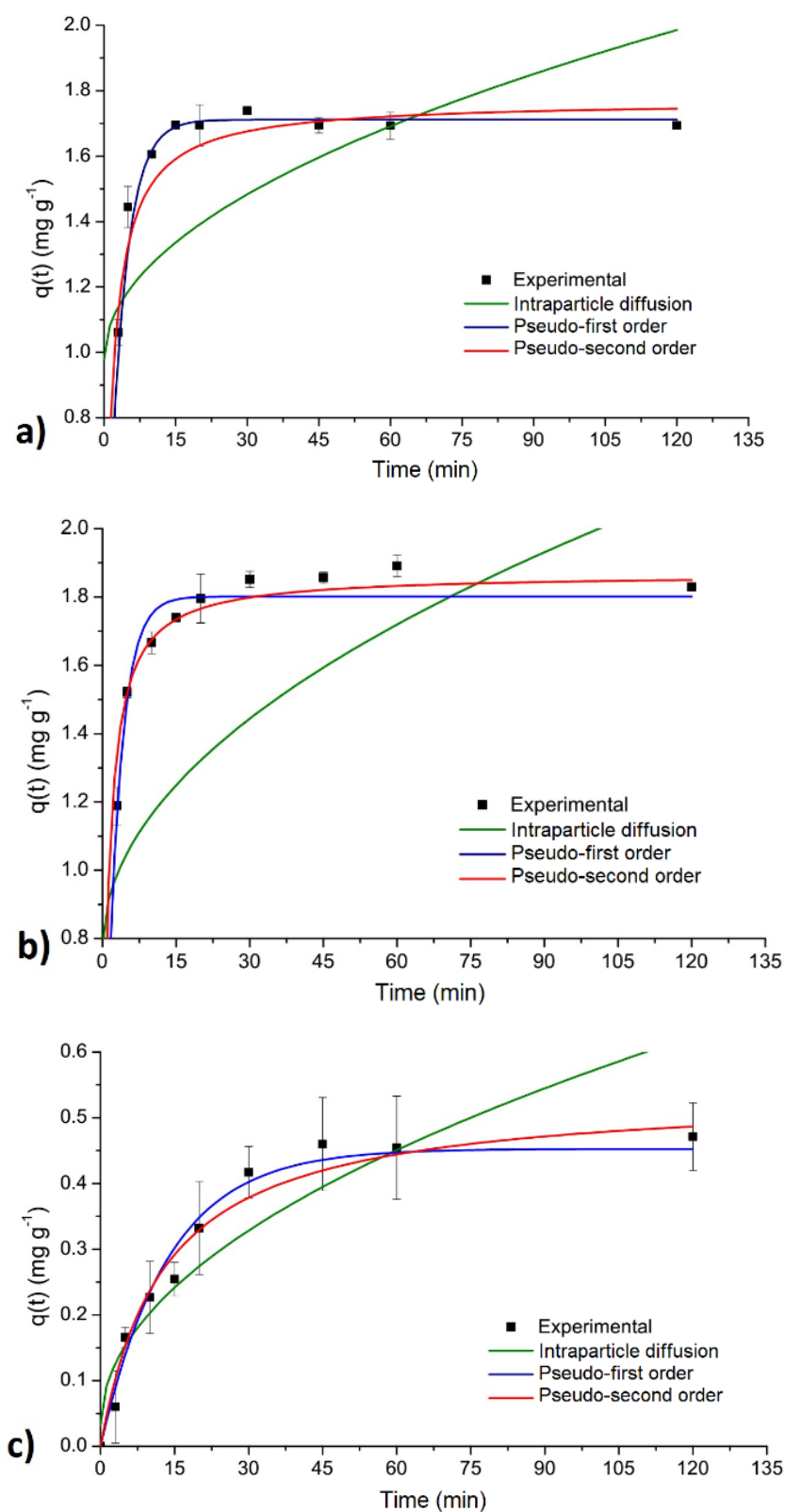


Figure 4. Experimental data and fit to intraparticle diffusion, pseudo-first and pseudo-second order models for the temperature of $50\text{ }^\circ\text{C}$ and $\text{pH } 4$: a) natural rice rusk, b) H_3PO_4 and c) NH_4Cl .

Table 2. Parameters of the adsorption kinetic models of the 5G blue dye by the biomass with different pre-treatments for the conditions of pH 4 and temperature of 50 °C.

Treatment	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	q_e^a	k_1^b	R^2	q_e^a	k_2^c	R^2	C	k_3^d	R^2
Natural	1.71	0.29	0.99	1.77	0.34	0.95	0.98	0.09	0.27
	(±0.01)	(±0.02)		(±0.01)	(±0.02)		(±0.28)	(±0.04)	
H ₃ PO ₄	1.80	0.35	0.99	1.87	0.47	0.99	0.78	0.12	0.44
	(±0.02)	(±0.03)		(±0.01)	(±0.05)		(±0.28)	(±0.04)	
NH ₄ Cl	0.45	0.07	0.96	0.54	0.15	0.97	0.03	0.05	0.88
	(±0.03)	(±0.01)		(±0.04)	(±0.03)		(±0.02)	(±0.01)	

^a q_e (mg g⁻¹); ^b k_1 (min⁻¹), ^c k_2 (g mg⁻¹ min⁻¹) and ^d k_3 (g mg⁻¹ min^{-1/2})

Determination coefficients (R^2) were obtained between 0.27 and 0.99, indicating that some models do not represent satisfactory experimental data (Table 1). The best fit was observed for the pseudo-first order model, being suitable for all pre-treatments. The pseudo-second order model was only suitable for the treatment with phosphoric acid. The intraparticle diffusion model presented a low correlation coefficient for all adsorption processes. Even though the correlation coefficient for the intraparticle diffusion model, using NH₄Cl-treated rice husk, was rather high (0.88), the C parameter presents a large standard deviation (66% of the mean value), which might impair its statistical significance.

The pseudo-first and pseudo-second order models presented similar performance in the fitting of the data. The removal values (q_e) predicted by the pseudo-first order model agrees with the equilibrium experimental data. This model considers that the occupation rate of the active sites is proportional to the number of active sites available in the adsorbent material³⁵.

The pseudo-first-order model also showed a better fitting in the biosorption of the 5G blue dye in a study using orange bagasse as a biosorbent prepared by dehydration at different temperatures. A k_1 in the value of 0.32 min⁻¹ at pH 2 and initial

concentration of 25 mg L⁻¹ has been reported³². The removal of reactive blue 5G (RB5G) dye in solution, 72 mg L⁻¹, using the drying biomass of banana pseudo stem was investigated at pH 1 and 30 °C. For the pseudo-first order model a k_1 of 0.84 mg g⁻¹ was obtained. This value is due to the higher concentration of dye applied in the test³⁶.

3.3 Equilibrium biosorption

Figure 5 shows the quantity of adsorbed dye per unit mass of adsorbent at equilibrium conditions as a function of the concentration of the supernatant solution at equilibrium conditions, at pH 4 and 50 °C, for *in natura* rice husk and H₃PO₄-treated rice husk. Equilibrium analyses with NH₄Cl-treated rice husk were not carried out due to the low removal of the dye. The observed result for this treatment should be at least similar to the *in natura* biomass. It is suggested that the ammonium ion was adsorbed by the material and thus limiting the biosorption capacity of the biomass, which would lead to low retention of the dye as verified.

The adjusted parameters for adsorption isotherms and ANOVA of regression are shown in Table 3.

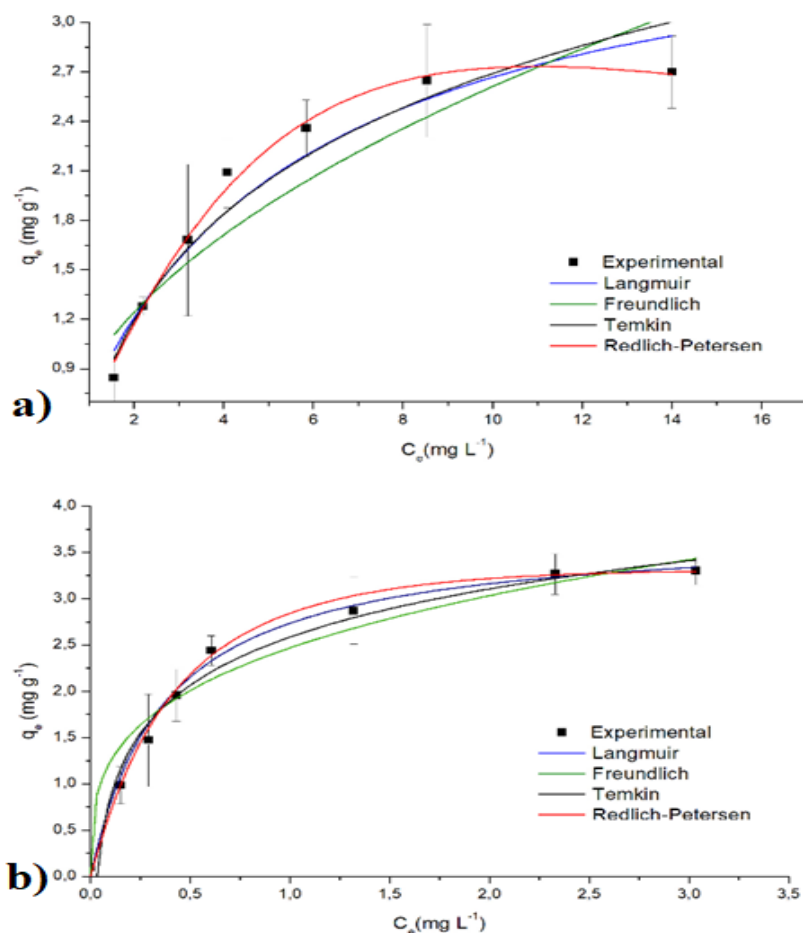


Figure 5. Experimental data and fit to Langmuir, Freundlich, Temkin and Redlich-Petersen isotherms at 50 °C and pH 4: a) natural and b) H_3PO_4 .

Table 3. Isothermal parameters (Langmuir, Freundlich, Temkin and Redlich-Petersen) and ANOVA of regression for fitting the experimental data of biosorption of rice husk dye natural and pretreated with H_3PO_4 .

Model		Treatment		ANOVA Regression			
		Natural	H_3PO_4	Natural		H_3PO_4	
				<i>F calc</i>	<i>p-value</i>	<i>F calc</i>	<i>p-value</i>
Langmuir	q_m	3.74 ± 0.09	3.8 ± 0.4				
	b	0.23 ± 0.04	2.7 ± 0.3	14.60	0.01	2.15	0.10
	R^2	0.98	0.95				
Freundlich	k_L	0.90 ± 0.09	2.5 ± 0.1				
	n	2.2 ± 0.3	3.4 ± 0.7	3.60	0.10	2.21	0.10
	R^2	0.86	0.89				
Temkin	B	0.93 ± 0.09	0.75 ± 0.06				
	k_T	1.8 ± 0.3	32 ± 9	3.20	0.10	2.16	0.20
	R^2	0.95	0.96				
Redlich-Petersen	k_R	0.64 ± 0.03	8.0 ± 0.8				
	a_R	0.03 ± 0.01	1.8 ± 0.3	60.00	0.00	11.17	0.04
	β	1.6 ± 0.1	1.13 ± 0.07				
	R^2	0.99	0.99				

$$F_{critical} (2.5; 0.05) = 5.8$$

Determination coefficients between 0.86 and 0.99 were observed, which means that some models do not represent the experimental data satisfactorily. The best fit was verified for the Redlich-Petersen model, being suitable for both the natural and the pre-treatment with H_3PO_4 . This model predicts a heterogeneous behavior on the surface of the adsorbent. The ANOVA at the 95% significance level for the evaluation of the fit of the models to the experimental data confirmed that the Redlich-Petersen model was more adequate, since it presented $F_{calc} > F_{critical}$ for the two treatments studied (60.0 and 11.17) as well as $p\text{-value} < 0.05$. It should also be noted that the Langmuir isotherm presented a favorable adjustment to the dye adsorption in the natural rice husk, with $R^2 = 0.98$ and $F_{calc} > F_{critical}$. When the constant β of Redlich-Petersen approaches 1 this equation takes the form of Langmuir. This model considers that the adsorbent has a limited number of positions on the surface. The molecules can be adsorbed to the point where all the surface sites are occupied, and adsorption will only occur in free sites, and when the equilibrium is reached no more interactions occur between the adsorbed molecules, nor between them and the medium³⁷. The maximum adsorbed value (q_m) of 3.81 mg g^{-1} predicted by the Langmuir model for the pretreated rice husk corroborates the experimental values.

The application of natural and citric acid treated rice hulls was evaluated in the Direct Red 23 dye biosorption. A q_m value was obtained for the Langmuir isotherm of 2.4 and 4.3 mg g^{-1} , respectively³⁸. These values were like those observed for the natural husk and treated with phosphoric acid (3.7 and 3.8 mg g^{-1}) presented in our study.

Removal of the reactive blue dye 4B using natural rice husk verified that Langmuir isotherm also better fitted to or the biosorption experimental data. Thus, it can be suggested that monolayer adsorption is occurred in this study³⁹. This also suggests that the intermolecular forces decrease rapidly with distance and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent.

4. Conclusions

The best condition for the biosorption of the 5G blue reactive dye was the pretreatment with H_3PO_4 at pH 4 and $50 \text{ }^\circ\text{C}$, where there was removal of 91.5%. The process was favored in acidic media

and elevated temperatures. The kinetic models of pseudo-first and pseudo-second order satisfactorily described the experimental data with equilibrium time of approximately 20 min. The Langmuir and Redlich-Petersen isotherms satisfactorily described the experimental data indicating the maximum adsorbed value (q_m) of 3.81 mg g^{-1} . Thus, the results indicated that the rice husk showed a potential biosorbent for textile dye and could be used to control pollution.

5. Acknowledgments

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