

Evaluation of the adsorption process of remazol black b dye in liquid effluents by green coconut mesocarp

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Evaluación del proceso de adsorción del colorante Remazol Black B en efluentes líquidos por mesocarpio verde de coco

Avaluació del procés d'adsorció del colorant Remazol Black B en efluentes líquids per mesocarpi verd de coco

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RESUMEN

La industria textil es económicamente importante para el desarrollo de Brasil. Sin embargo, los efluentes generados por esta actividad contienen productos con una estructura molecular compleja que les confiere carácter recalcitrante en estas aguas residuales. Debido a esta realidad, se hace necesario desarrollar tecnologías viables de eliminación de estos compuestos, que en su mayoría son colorantes. En este estudio, se usa el mesocarpio verde de coco para eliminar el colorante Remazol Black B de una disolución acuosa utilizando la técnica de adsorción. Para realizar los experimentos, se seca el mesocarpio verde de coco a 60°C, se tritura en un molino, se tamiza, se limpia con agua destilada y se sumerge en albúmina durante 24 horas. El proceso de adsorción se optimiza en modo discontinuo, usando 0,5 g de adsorbente y 25 mL de solución sintética de 10 mg L⁻¹, a 30°C, pH 4,0, velocidad de agitación de 700 rpm y granulometría G_{0.149} mm. Seguidamente, se evalúa la influencia del pH de la disolución, de la granulometría del adsorbente y de la velocidad de agitación mediante un diseño de experiencias factorial. Se realizan experimentos de equilibrio y cinética de adsorción en matraces Erlenmeyer. Los resultados indican que, entre los efectos principales, el pH y la granulometría del adsorbente afectan significativamente el proceso de adsorción. Además, el equilibrio de adsorción se alcanza a los 60 minutos de contacto. Se ajusta el modelo de Langmuir a los resultados experimentales (R² = 0,9953), obteniendo una capacidad máxima de adsorción de 2,93 mg g⁻¹ y una constante de equilibrio de 0,26 L mg⁻¹. A partir de los resultados obtenidos, se puede concluir que el mesocarpio verde de coco podría ser una alternativa viable para el tratamiento de efluentes textiles.

Palabras clave: Industria textil, colorante, mesocarpio verde de coco, adsorción, Remazol Black B.

SUMMARY

The textile industry is economically important for the development of Brazil. However, the generated effluents from this activity present a complex molecular structure that gives a recalcitrant characteristic in its residuary waters. Due to this reality, it is necessary to develop viable technologies that remove those compounds, which are mostly dyes. In this study, the green coconut mesocarp was used to remove Remazol Black B dye of an aqueous solution using the adsorption technique. To perform the experiments, the green coconut mesocarp was dried at 60 °C, ground in a grinding mill, sifted, washed with distilled water and immersed in albumin for 24 hours. The process of adsorption was optimized in a batch mode, containing 0.5 g of adsorbent and 25 mL of synthetic solution of 10 mg L⁻¹, at 30 °C, pH 4.0, stirring speed of 700 rpm, and granulometry G_{0.149} mm. Afterwards, the influence of the pH of the solution, adsorbent granulometry and stirring speed were evaluated by means of factorial planning. Experiments of equilibrium and kinetics of adsorption were conducted in Erlenmeyer. Results indicated that among the main effects, the pH and the adsorbent granulometry significantly influenced the process of adsorption. Besides, the adsorption equilibrium was reached in 60 minutes of contact. The Langmuir model was adjusted to experimental results (R² = 0.9953) being obtained a maximum capacity of adsorption of 2.93 mg g⁻¹ and equilibrium constant of 0.26 L mg⁻¹. With the obtained results it could be concluded that the green coconut mesocarp could be a viable alternative for the treatment of textile effluents.

Key words: Textile Industry, dye, green coconut mesocarp, adsorption, Remazol Black B.

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RESUM

La indústria tèxtil és econòmicament important per al desenvolupament de Brasil. Tanmateix, els efluents generats per aquesta activitat contenen productes amb una estructura molecular complexa que els confereix caràcter recalcitrant en aquestes aigües residuals. Donada aquesta realitat, es fa necessari desenvolupar tecnologies viables d'eliminació d'aquests compostos, que majorment són colorants. En aquest estudi, s'empra el mesocarpi verd de coco per eliminar el colorant Remazol Black B d'una dissolució aquosa utilitzant la tècnica d'adsorció. Per realitzar els experiments, es seca el mesocarpi verd de coco a 60°C, es tritura en un molí, es tamisa, es renta amb aigua destil·lada i se submergeix en albúmina durant 24 hores. El procés d'adsorció s'optimitza en mode discontinu, emprant 0,5 g d'adsorbent i 25 mL de solució sintètica de 10 mg L⁻¹, a 30°C, pH 4,0, velocitat d'agitació de 700 rpm i granulometria G_{0.149} mm. Seguidament, s'avalua la influència del pH de la dissolució, de la granulometria de l'adsorbent i de la velocitat d'agitació mitjançant un disseny d'experiències factorial. Es realitzen experiments d'equilibri i cinètica d'adsorció en matrassos Erlenmeyer. Els resultats indiquen que, entre els efectes principals, el pH i la granulometria de l'adsorbent afecten significativament el procés d'adsorció. A més, l'equilibri d'adsorció s'assoleix als 60 minuts de contacte. S'ajusta el model de Langmuir als resultats experimentals (R² = 0,9953), obtenint una capacitat màxima d'adsorció de 2,93 mg g⁻¹ i una constant d'equilibri de 0,26 L mg⁻¹. Amb els resultats obtinguts, es pot concloure que el mesocarpi verd de coco podria ser una alternativa viable per al tractament d'efluents tèxtils.

Mots clau: Indústria tèxtil, colorant, mesocarpi verd de coco, adsorció, Remazol Black B.

INTRODUCTION

Clothing represents the fourth largest economic activity in the world. In Brazil, the textile industry is considered as traditional in its development and in its historical role from the time of manufacture to industrialization. It was one of the first industrial sections to be implanted as a company in all the cities of the country. Textile industries have an important socioeconomic value when generating direct employment in production or indirect employment in the production of raw materials and other input [1]. They have executed a role of great relevance in the development of the country, with total revenue, for the year of 2004, equivalent to 4.1 % of the Brazilian Gross Domestic Product (GDP) and have been providing jobs for about 1.7 % of the economically active population [2].

Starting from 1950 the textile industry went through important transformations, incorporating technological innovations of other industrial sections, such as the chemical section [3]. The appearance of new synthesized dyes, introduced in the environment through textile industrial effluents, affected the natural equilibrium of ecosystems [4]. At the end of the 1990 decade, the total consumption of dyes just by these industries exceeded the mark of 10⁷ kg per year and it is estimated that 90 % of that total is used in textiles cloth [5].

Industrial laundry and textile dyeing companies are generating great amounts of effluents hard to discern due to the

raw material diversity, such as dyes and surfactants. Those effluents are generally thrown in the receptacles without the appropriate treatment, thus elevating the organic load of those sources and in some cases heavy metals such as chromium, nickel and copper are also thrown in, possibly alternating the alimentary chain and the life cycle of the aquatic beings [6, 7].

In a general way the dyes are divided in two large groups: natural (of vegetable or animal origin) and synthetic. The dyes are constituted of two main chemical components: the chromophore group responsible for the color that absorbs light and the functional group that allows the fixation of fabric fibers [8]. Among the chromophores, the most representative are the ones from the azo family dyes. The azo dye represents about 60 % of the world market of dyes, being largely used in dyeing textile fibers [9].

The versatility of the azo compositions is due to the easiness with which they can be synthesized and to the fact that they present good fixation characteristics and accessible cost. However, some are not degraded biologically. The conventional, physical, chemical and biological treatments used in effluents of the textile industry have been reducing large amount of pollutants. However, they are not very efficient in the reduction of color.

The minimization of dye contents in effluents has demanded the development of cost-effective processes to be implemented in treatment systems. In searching for an alternative to treat textile industrial effluents, this study intends to evaluate, through kinetic and equilibrium constants of adsorption, the use of green coconut mesocarp as an adsorbent of the Remazol Black B dye (azo dye group). As the green coconut mesocarp is an abundant residue in Brazil, its utilization as adsorbent would be a good alternative to recycle this material. The molecular structure of Remazol Black B dye can be observed in Figure 1.

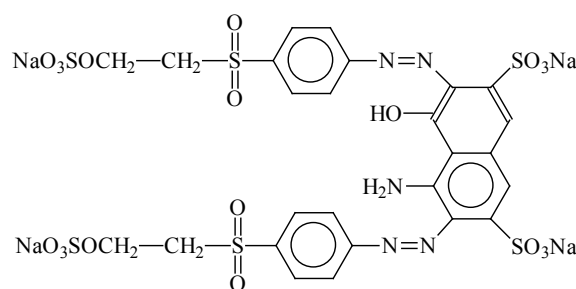


Figure 1 – Molecular structure of the Remazol Black B dye

2. MATERIALS AND METHODS

The studied parameters were pH of the Remazol Black B dye solution, stirring speed and adsorbent granulometry. For the kinetic and equilibrium adsorption study, an IKA KS 130 basic table agitator and a RADELKIS model OP-265 pH meter were used for evaluation of the pH of the solution. The solution of Remazol Black B dye was maintained at pH 4.0, with 0.5 mol L⁻¹ phosphate solution.

2.1 Adsorbent preparation

The coconut was collected at a ranch located in the municipal district of Olinda, Pernambuco - Brazil. Initially, the mesocarp was separated from the endocarp and dried at

60 °C. Then, it was ground in an FRITSCH-pulverisette 14 grinding mill and later classified in a series of Tyler (< 0.149 to 0.42 mm) sieves, washed exhaustively in distilled water and dried again at 60 °C.

Once the interaction tannin-protein is largely used for tannin removal in this type of material, the tannin content was removed using commercial albumin. This procedure was carried out due to studies accomplished in the laboratory verified that the tannin present in the green coconut mesocarp hindered the adsorption of azo compounds and besides its presence produced a brown coloration when in solution.

To perform that treatment, 40 g of the dry green coconut mesocarp was weighed and placed in NEO-NUTRI albumin solution (dehydrated pasteurized white egg) in a concentration of 20 g L⁻¹ for 24 hours, and then the mesocarp was washed exhaustively with distilled water and dried at 60 °C.

2.2 Evaluation of the humidity and ashes of the green coconut mesocarp

The evaluation on humidity of the green coconut mesocarp was accomplished in a (FANEM) sterilizer at 105 °C up to constant weight (Analytical Balance AND, HR-120) and the contents of ashes in an (ALTRONIC) muffle at 550 °C for 30 minutes. The volatile solids were obtained through the difference between the total solids, the humidity and the contents of ashes.

2.3 Evaluation of the adsorptive capacity of the green coconut mesocarp

The application of factorial planning in two levels had the objective of evaluating the variables that exhibit significant effects in the biosorption process in a batch system and that can be adjusted to improve the efficiency of the method. Three factors were identified as those that possibly influence the efficiency of the dye sorption process, the pH of the solutions of 10 mg L⁻¹ of Remazol Black B, the stirring speed and the granulometry of the adsorbent material. A complete Factorial 2³ Planning was accomplished including a central point. The levels of the studied variables are presented in Table 1. In the central point the experiments were performed in triplicates.

Table 1 – Levels of the factors chosen for the factorial 2³ planning with a central point.

Variables	Levels		
	Inferior (-)	Central	Superior (+)
pH	4.0	5.6	7.2
Granulometry (mm)	<0.149	0.149-0.42	0.42-0.59
Stirring speed (rpm)	300	500	700

2.4. Experiments of adsorption kinetics

In each experiment, 0.5 g of the green coconut mesocarp was added to 25 mL of the solution of 10 mg L⁻¹ of Remazol Black B dye, then the Erlenmeyer was placed on a table agitator with a room temperature set at (30°C) during 1, 5, 10, 20, 30, 60, 90 and 120 minutes. After each time the samples were filtered and the residual concentrations of the dye were quantified. The experiments were carried out in duplicates, being used the average of the measurements.

2.5. Experiments of adsorption equilibrium

In the equilibrium experiments, 0.5 g of green coconut mesocarp was added in 25 mL of the solutions of Remazol Black B dye in concentrations that varied from 10 to 70 mg L⁻¹, at 30 °C, pH = 4.0, stirring speed of 700 rpm and granulometry G < 0.149 mm.

The system was under stirring for 120 minutes, then the samples were filtered and the residual concentrations quantified. The experiments were performed in duplicate, and the results were adjusted to the Langmuir model [10], according to equations 1 and 2.

$$\frac{q}{q_m} = \frac{kC_e}{1 + kC_e} \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{q_m \cdot k} + \frac{C_e}{q_m} \quad (2)$$

where:

q_e is the mass of the dye adsorbed per unit of adsorbent mass in equilibrium with the solute C_e concentration;

q_m represents the value of saturation of the monolayer in adsorbent mass per gram and it does not depend on the temperature in the absence of solvent interference;

k is a constant that relates to specific adsorption

(q_e / q_m) with the concentration of the solute in the liquid phase in a strip of very diluted concentration.

3. RESULTS AND DISCUSSION

3.1 Evaluation of the humidity and ashes of the green coconut mesocarp

The results obtained on humidity, ash contents and volatile solids for the green coconut mesocarp were 6.7, 91.8 and 1.5 % respectively. According to these results a high content of ashes can be observed, which indicates a strong predominance of inorganic matter. On the other hand, the low humidity favors the adsorption because it liberates the active sites.

3.2 Evaluation of the adsorptive capacity of the green coconut mesocarp

Table 2 presents the results obtained in the experiments accomplished according to the factorial 2³ planning with the central point.

Table 2 – Results of the experiments of the factorial 23 planning.

Experiments	pH	Granulometry	Stirring speed	q (mg.g ⁻¹)
01	-	-	-	0.318
02	+	-	-	0.196
03	-	+	-	0.324
04	+	+	-	0.057
05	-	-	+	0.455
06	+	-	+	0.153
07	-	+	+	0.321
08	+	+	+	0.067
09	0	0	0	0.253
10	0	0	0	0.251
11	0	0	0	0.238

The calculations of the effects of the factors and the interactions among them were accomplished according to Barros Neto et al. [11] and are presented in table 3.

Table 3 - Main effects and of interaction calculated for the factorial 23 planning with its respective standard errors, expressed in mg g⁻¹. Effect statistically significant at the confidence level of 95 %.

Effects	Estimate
Global average	0.239±0.002
Main effects	
pH	- 0.236±0.006
Granulometry	- 0.088±0.006
Stirring speed	0.025±0.006
Effects of Interaction	
pH x Granulometry	- 0.024±0.006
pH x Stirring speed	- 0.041±0.006
Granulometry x Stirring speed	- 0.021±0.006
pH x Granulometry x Stirring speed	0.048±0.006

Using the replications accomplished in the experiments of the factorial planning, the standard errors and the intervals of 95 % confidence level was calculated for the value of an effect. The effects whose absolute values exceed 0.026 (standard deviation versus t_{student}) are considered statistically significant.

Analyzing the values in Table 3, it is verified that only the main effect of the stirring speed and the interactions among pH x Granulometry and Granulometry x stirring Speed is not statistically significant.

The increase of the pH of 4.0 to 7.2 decreases the amount of dye adsorbed per adsorbent mass (q) on the average of 0.237 mg g⁻¹. The same observation can be made in relation to the effect of the granulometry that provokes a decrease in the value of q of 0.088 mg g⁻¹, on average.

Due to the presence of significant interaction effect (pH x Speed of Stirring) a joint interpretation of those ef-

fects is necessary, and these can be observed in the response surface graphic in figure 2.

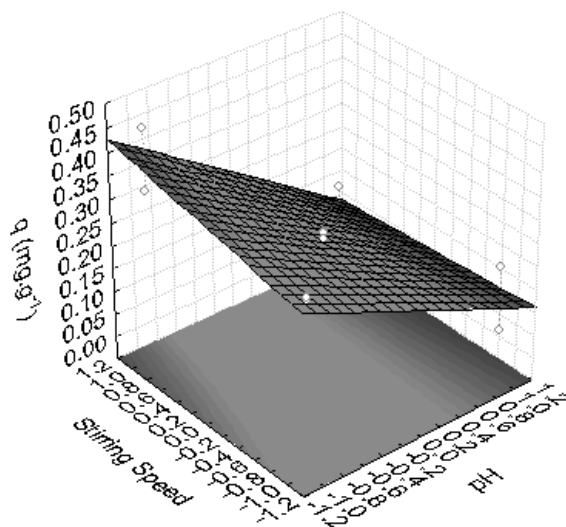


Figure 2 – Response surface for adsorption of Remazol Black B dye.

In figure 2 it is observed that the best results of the amount of adsorbed dye were obtained from experiments with smaller pH and larger stirring speed. However, for pH lower than 4.0 the increase of ions H⁺ occurs, which compete for the reactions centers.

3.3 Experiments of adsorption kinetics

The kinetic evolution of Remazol Black B dye removal by contact with the green coconut mesocarp was experimentally evaluated in discontinuous experiments up to 120 min (Figure 3). The time of equilibrium for adsorption of the dye starts from 60 min., being stabilized starting from 90 min. A time of 120 min was chosen for the equilibrium experiments in order to guarantee that the same could be reached.

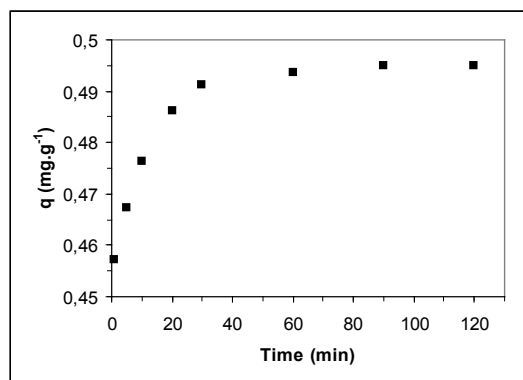


Figure 3 - Kinetic behavior of the adsorption of Remazol Black B. dye with an initial concentration of 10 mg.g⁻¹ and 0.5 g mesocarp treated with albumin. T = 30 °C, pH = 4.0, stirring speed = 700 rpm and granulometry £ 0.149 mm.

3.4 Experiments of adsorption equilibrium

The adsorption isotherm of Remazol Black B dye is presented in Figure 4A. The model used to represent the behavior of adsorption of this dye on the surface of the green coconut mesocarp was the one used by Langmuir. Linearizing the equation of the model (Figure 4B), the maximum capacity of adsorption q_m , could be evaluated as being the same as 2.93 mg g^{-1} and the equilibrium constant of Langmuir was equal to 0.26 L.mg^{-1} . In the linearization it was obtained r^2 of 0.9953.

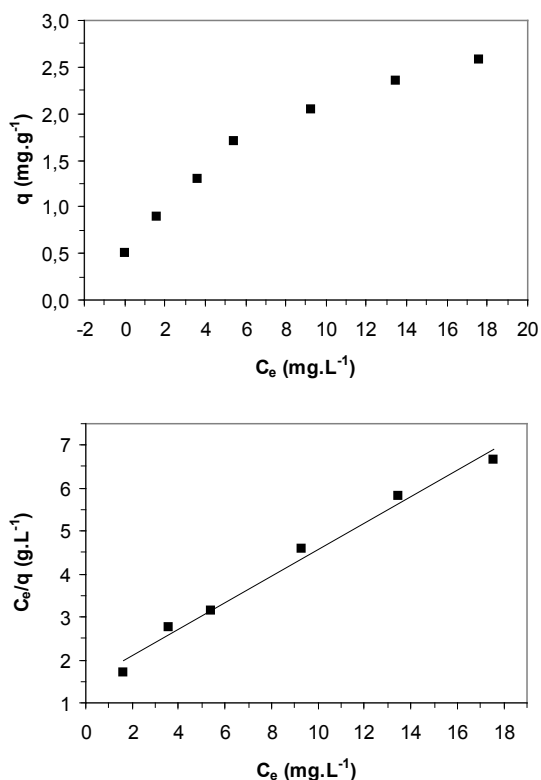


Figure 4 – (A) Adsorption isotherm of Langmuir and (B) Linearization of the model of adsorption Langmuir for initial concentration varying from 10 to 70 mg L^{-1} of Remazol Black B dye with 0.5 g green coconut mesocarp treated with albumin. $T = 30 \text{ }^\circ\text{C}$, $\text{pH} = 4.0$, Stirring speed = 700 rpm , granulometry £ 0.149 mm .

Table 4 presents a comparison between the results obtained in this research with results of some adsorbents found in literature used in the adsorption of Remazol Black B dye.

Table 4 - Comparison between the obtained results and the ones from literature with several adsorbents.

Adsorbent	Initial concentration mg.L^{-1}	q mg.g^{-1}	Reference
Fungus Rhizopus arrhizus	81.2	65.0	[12]
Green algae Chlorella vulgaris	79.3	55.3	[13]
Coal fly ash (high lime)	100	7.94	[14]
Cotton stalk	78.8	25.5	[15]
Cotton hull	75.8	39.0	[15]
Chitosan	100	1.89	[16]
Biomass fly ash	400	4.38	[17]
Mesocarp of the green coconut	70	2.93	This work

When the adsorbent used in this work is compared with some biomasses, it is observed that with a higher dye initial concentration, Chitosan presented smaller adsorption capacity. Biomass fly ash with concentration starting with Remazol Black B almost six times greater than that used in this work presented similar adsorption capacity. The q_{max} obtained in this study is relatively low when compared with the other adsorbents presented in table 4. However, the use of the green coconut mesocarp in dyes is interesting due to it is able to remove around 88 % for an initial concentration of 70 mg L^{-1} , in 120 minutes. Its use can be considered a potentially alternative once this is an abundant residue in Brazil.

3.5. Kinetic Modeling

Considering that the studied reaction occurred in the second order and the effects of resistance to the mass transfer were despised. It can be stated the following [18]:

$$r_{\text{ads}} = K_{\text{ads}} \cdot C \cdot (1 - \theta)^2 \quad (3)$$

$$r_d = K_d \cdot \theta^2 \quad (4)$$

Being known that:

$$r = r_{\text{ads}} - r_d \quad (5)$$

where: $\theta = q / q_m$

When equations 3 and 4 are substituted, then in equation 5, is obtained:

$$r = K_{\text{ads}} \cdot C \cdot (1 - \theta)^2 - K_d \cdot \theta^2 \quad (6)$$

$$r = K_{\text{ads}} \cdot C \cdot \left(1 - \frac{q}{q_m}\right)^2 - K_d \cdot \left(\frac{q}{q_m}\right)^2 \quad (7)$$

$$\text{With } K_d / K_{\text{ads}} = 1/k \quad (8)$$

Equation (7) can be presented in the following form:

$$\frac{dq}{dt} = K_{\text{ads}} \cdot \frac{1}{q_m^2} \cdot \left[C(q_m - q)^2 - \frac{1}{k} \cdot q^2 \right] \quad (9)$$

Thus:

$$q = \frac{(C_0 - C)}{m} \cdot V_L \quad (10)$$

When substituting equation (10) in (9), the following is obtained:

$$\frac{dq}{dt} = K_{\text{ads}} \cdot \frac{1}{q_m^2} \cdot \left[C \left(q_m - \frac{(C_0 - C)}{m} V_L \right)^2 - \frac{1}{k} \cdot \left(\frac{(C_0 - C)}{m} V_L \right)^2 \right] \quad (11)$$

For the mass equilibrium on the solute, there is:

$$-V_L \frac{dC}{dt} = m \frac{dq}{dt} \quad (12)$$

$$-\frac{dC}{dt} = \frac{m}{V_L} \frac{dq}{dt} \quad (13)$$

with the use of the equation (11), is found:

$$-\frac{dC}{dt} = \frac{m}{V_L} K_{ads} \cdot \frac{1}{q_m^2} \cdot \left[C \left(q_m - \frac{(C_0 - C)}{m} V_L \right)^2 - \frac{1}{k} \left(\frac{(C_0 - C)}{m} V_L \right)^2 \right] \quad (14)$$

The initial data and the values obtained experimentally starting from the Langmuir isotherm used for development of the kinetic model of adsorption were: mass of the adsorbent (m) of 0.5 g, volume of the solution of the dye (V_L) of 25 mL, initial concentration of the solution (C_0) of 10 mg L⁻¹, maximum capacity of adsorption (q_m), as being equal to 2.93 mg g⁻¹ and equilibrium constant of Langmuir (k_{eq}) equal to 0.26 L.mg⁻¹.

Based on numerical solution by the integration method of Runge-Kutta (4th order), followed by the application of the optimization method Box3, the minimization of the objective function between the calculated and experimental values of the adsorption components concentrations was intended.

Figure 5 presents the comparison between the results obtained experimentally and those generated from the second order model, obtained previously.

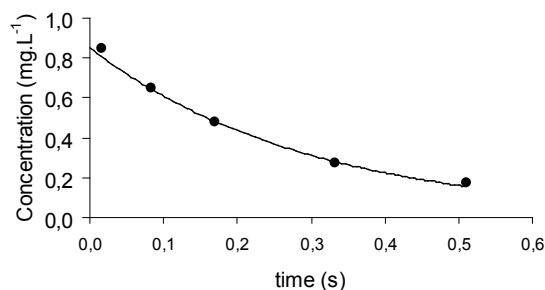


Figure 5 – Adjustments of the experimental values to the developed theoretical model. · experimental data; $\frac{3}{4}$ theoretical model.

The kinetic and equilibrium constants for the adsorption process, using the program mentioned previously were 3.31 Lg⁻¹.h⁻¹ and 0.26 L mg⁻¹, respectively. The correlation coefficient among these values was fully satisfactory ($r^2 = 0.9955$) and the relative error was very low (2.2%), indicating the good adjustment of the model.

4. CONCLUSIONS

The study of the equilibrium isotherm, at 30 °C, with pH = 4.0 stirring speed of 700 rpm, mass of the green coconut mesocarp of 0.5 g, Granulometry Φ 0.149 mm and concentrations from 10 to 70 mg L⁻¹, drives to experimental results satisfactorily presented by the Langmuir equation, being

the constant of equilibrium of adsorption k evaluated in those conditions at 0.26 L mg⁻¹. The kinetics of adsorption was identified as a reversible kinetics of 2nd order, with adsorption constant of 3.31 L g⁻¹ h⁻¹.

The green coconut mesocarp treated with albumin is presented as an alternative for the treatment of textile effluents due to its adsorbent capacity of 2.93 mg g⁻¹, reaching a dye removal of 88 % with initial concentration of 70 mg L⁻¹ in 120 minutes.

5. ACKNOWLEDGEMENTS

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6. NOMENCLATURE

C	solute concentration
C_0	initial solute concentration
C_e	equilibrium solute concentration
K	constant related to specific adsorption (q_e / q_m)
K_{ads}	adsorption kinetic constant
K_d	desorption kinetic constant
k_{eq}	equilibrium constant of Langmuir
q	cover fraction
m	adsorbent mass
q	mass of adsorbed dye per unit of adsorbent mass
q_e	mass of adsorbed dye per unit of adsorbent mass in equilibrium
q_m	value of monolayer saturation (adsorbent mass per gram)
r	reaction rate
r_{ads}	adsorption reaction rate
r_d	desorption reaction rate
V_L	volume of dye solution

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