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REMAZOL RED DYE REMOVAL IN WATER SOLUTIONS USING A MIXED ADSORVENT COMPOSED OF ASPERGILLUS NIGER AND ELEPHANT GRASS

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ABSTRACT

The disposal of untreated textile effluents in aquatic medium can guickly lead to the depletion of dissolved oxygen, resulting in an imbalance in this ecosystem. Several treatment methods are used to remove the color, and among them adsorption has been shown to be a simple, cheap and efficient method of treatment. The objective of this work was to evaluate the ability to remove the Remazol Red dye from a synthetic aqueous solution through the use of a mixed biomass of Aspergillus niger and elephant grass (Pennisetum purpureum Schum), under different temperature conditions (30, 40 and 50 °C), in concentrations ranging from 25 to 105 mg L⁻¹, time from 0 to 200 minutes and pH 2.0. The kinetic study was characterized by the pseudo-second order model. The Langmuir isotherm model presented the best fit to the linearization technique and presented and adsorption capacity of 3.42 mg g⁻¹ for the model. The spontaneity of the adsorption reaction was obtained by Gibbs free energy. The thermodynamic study indicated that the adsorption was favorable and spontaneous, and that the increase in temperature causes a reduction in the adsorptive capacity. These results using synthetic effluents show that the mixed adsorbent produced in this study is a promising alternative in the treatment of effluents contaminated by Remazol Red.

Keywords: Adsorption; Mixed biomass; Dye removal.

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REMOÇÃO DO CORANTE REMAZOL VERMELHO DE MEIOS AQUOSOS UTILIZANDO ADSORVENTE MISTO COMPOSTO DE *ASPERGILLUS NIGER* E CAPIM ELEFANTE

RESUMO

O descarte de efluentes têxteis não tratados nos meios aguosos pode ocasionar em um rápido esgotamento do oxigênio dissolvido, o que resulta em um deseguilíbrio no ecossistema. São vários os métodos utilizados na remoção de cor, e, dentre eles, a adsorção vem se mostrando como um método de tratamento simples, barato e eficiente. O objetivo deste trabalho consiste em avaliar a habilidade da biomassa mista de Aspergillus niger e capim elefante (Penissetum purpureum Schum) na remoção do corante Remazol Vermelho de uma solução aquosa sintética sob difrentes condições de temperatura (30, 40 e 50 °C), concentrações variando entre 25 e 105 mg L⁻¹, tempo de adsorção de 0 a 200 minutos e pH 2.0. O estudo cinético foi caracterizado pelo modelo de pseudo-segunda ordem. Já o modelo de Langmuir se mostrou o melhor ajuste linear das isotermas de adsorção, apresentando uma capacidade de adsorçãod e 3,42 mg g⁻¹. A esponteneidade da reação de adsorção foi avaliada através da energia lvire de Gibbs. O estudo termodinâmico indicou que a adsorção é favorável e espontânea, além de que o aumento da temperatura ocasiona em uma redução na capacidade de adsorcão. Estes resultados obtidos em efluentes sintéticos demonstram que o adsorvente misto produzido neste estudo é uma alternativa promissora no tratamento de efluentes contaminados com Remazol Vermelho.

Palavras-Chave: Adsorção; Biomassa mista; Remoção de corantes.

1. INTRODUCTION

Aquatic environments pollution caused by synthetic dyes have been causing serious damage to aquatic fauna and flora, since these complex organic molecules are stable, have low biodegradability and high toxicity when they are in water bodies (MONTEIRO et al., 2017). These contaminants are originated mainly from textile industry, pulp and paper manufacturing, food industry, pharmaceuticals and leather industry. Especially, the textile industries are the ones that most discard and produce effluents with color. It is estimated that approximately 10–25% of dye is lost during productive textile processing and 2–20% of dye is improperly disposed of in the environment (PÉREZ-CALDERÓN; SANTOS; ZARITZKY, 2020).

Among all textile dyes produced worldwide, it is estimated that 60-70% are azo dyes (-N=N-). This is due to their stability and the variety of colors available compared to natural dyes, thus making them the largest class of synthetic dyes released into the

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ecosystem. The azo dye Remazol Red when inappropriately disposed causes serious damage to the environment. In addition to that, it also cause public health problems, since it may exhibit toxic, carcinogenic and mutagenic properties (SARATALE et al., 2013). Thus, it is important to study efficient methodologies capable of removing these complex substances from the environment. In Brazil, The National Environment Council (CONAMA, 2005) recommends that all effluents must be treated previously in the 357th resolution of March 17, 2005. Therefore, all color should be removed before being released into the environment (CONAMA, 2005).

Thus, among the existing effluent treatments, adsorption has stood out because of its efficiency and low-cost procedure. In addition, the biosorbents are recyclable, biocompatible and are generally abundant in nature. Since the 1980s, the application of dead or live biomass for the capture of dyes has been successful. The biosorption technique consists of a wastewater treatment that uses organisms (algae, bacteria or fungi) and/or biomass to capture contaminants from the aqueous medium. Through this methodology, the adsorption process may occurs due to the following biosorbent mechanisms: chelation, physical adsorption, ion exchange, chemical adsorption and complexation (BAYRAMOĞLU; YAKUP ARICA, 2007; GÜL; TAŞTAN; BAYAZIT, 2019). Some low-cost fungal biomasses have been used as a biosorbent to remove dyes, such as: Lentinus sajor caju, Trametes versicolor, Lentinus edodes, and Aspergillus niger. In addition, plant biomass has shown promise because it can be obtained from various sources, such as agricultural and forest biomass residues (BAYRAMOĞLU; YAKUP ARICA, 2007; TAKSITTA et al., 2020). In this context of dye removal, the use of a mixed adsorbent is very promising. Cruz-Filho et al. (2016) e Cruz et al. (2016) evaluated the removal of the Remazol Black B dye by Aspergillus *niger* biomass grown in elephant grass and obtained a removal greater than 90%. Before studying the dye removal efficiency in a real effluent, which contains other pollutants besides dyes, the first tests to be carried out are with synthetic dyes. From this, it is possible to initially determine the best treatment conditions.

In this context, the present study aimed to evaluate the effectiveness of the removal potential of a mixed adsorbent (*Aspergillus niger*/elephant grass) against a toxic and highly sulfonated dye, Remazol Red (RR). The RR adsorption analysis was performed through isotherms, adsorption kinetics and thermodynamic study.

2. MATERIALS AND METHODS

2.1. REAGENTS

Sodium nitrate (NaNO₃; CAS: 7632-00-0; purity: 99.0%), monopotassium phospate (KH₂PO₄; CAS: 7778-77-0; purity: 99%), heptahydrate magnesium sulfate (MgSO₄.7H₂O; CAS: 10034-99-8; purity: 98%), heptahydrate ferrous sulfate (FeSO₄.7H₂O; CAS: 7782-63-0; purity: 99%), Sucrose (C₁₂H₂₂O₁₁; CAS: 57-50-1; purity: 99.5%), sulfuric acid (H₂SO₄; CAS 7664-93-9 purity: 99.9%), sodium hydroxide (NaOH; CAS 1310-73-2; purity: 98%), Remazol Red (CAS: 85585-89-3 purity > 98%). All reagents were acquired from Sigma-Aldrich Chemical Co. (USA).

2.2. MIXED ADSORBENT

The adsorbent was produced using a methodology proposed by Cruz Filho et al. (2016) and Cruz et al. (2016). The elephant grass (*Pennisetum purpureum Schum*) used in this work was collected in a specific grass bed, cultivated by the Department of Zootechnics of Federal Rural University of Pernambuco. It was cut, washed and dried at 75 °C. Then, it was crushed in a knife mill (SL-30, Solab), sieved in Tyler sieves (1.43 mm) and stored at 30 °C. The microorganism used was the filamentous fungus *Aspergillus niger* 5437-UFPEDA, belonging to the Collection of Microorganisms of the Department of Antibiotics of Federal University of Pernambuco, which was incubated in Czapec-Dox medium for approximately 7 days and dried in a drying oven TE-393/180L (Tecnal, Brazil) at 30°C.

For the preparation of fungal biomass, 5 mL of spore suspension (10^7 spore. mL⁻¹) was introduced into 250 mL of modified Czapec broth consisting of NaNO₃ (3.0 g), KH₂PO₄ (1.0 g), MgSO₄.7H₂O (0.5 g), FeSO₄ (0.01 g), sucrose (3.3 g) and elephant grass *in natura* (6.7 g). This system was kept under stirring of 200 rpm at 30 °C for 72 h through a C25KC0 shaker (New Brunswick Scientific, USA). The material produced was autoclaved through Autoclave CS 18 (Prismatec, Brazil) at 121 °C for 30 min, filtered and then washed with sterile water and dried in drying oven TE-393/180L (Tecnal, Brazil) at 75 °C.

2.3. ADSORBATE

The Remazol Red dye has the azo group as a chromophore (Figure 1) (AKSU; TEZER, 2005). The maximum absorption wavelength ($\lambda_{max} = 518$ nm) was chosen to assess the remaining amount of unabsorbed dye (remaining solution) by monitoring the adsorption process in the UV/Vis spectrophotometer Agilent/HP 8453 (Hewlett-Packard, USA). The analytics curve y = 0.0119x + 0.3687, R² = 0.99, was determined by spectrophotometry at different concentrations of dye (1 - 105 mg L⁻¹).

Figure 1- Chemical structure of the textile dye Remazol Red (RR).



2.4. MATHEMATICAL MODELING OF ADSORPTION KINETICS

Kinetic study was performed under the same conditions previously determined by Cruz-Filho et al. (2016). The authors perfomed an optimization of the adsorption of Remazol Black B, which is also an azo dye, through the mixed biomass of elephant grass and *Aspergillus niger*. Therefore, in order to compare these results, the following experimental conditions were used: dye initial concentration of 25 mg L⁻¹, volume of 100 mL, pH 2.0, and 0.5 g of adsorbent. All experiments were realized under stirring of 150 rpm at 30, 40 and 50 °C through a shaker.

Aliquots were collected in the time interval from 0 to 200 min. Then, they were centrifuged at 5000 rpm for 3 minutes and analyzed in a spectrophotometer Agilent/HP 8453. Distilled water was used as blank of the equipment. The adsorptive capacity for each test was determined by Equation 1.

$$qt = \frac{V(C_0 - C_e)}{m} \tag{1}$$

Where qt is the adsorption capacity varying with time, C_0 is solute concentration in the initial solution (mg L⁻¹); C_e , refers to residual concentration in equilibrium (mg L⁻¹); V corresponds to the volume of the solution (L); and m is the amount of mass of the adsorbent (g).

The experimental data were adjusted to different kinetic models, these being: pseudo-first order (LAGERGREN; SVENSKA, 1898) (Equation 2), pseudo-second order (HO; MCKAY, 1998) (Equation 3), intraparticle diffusion (WEBER; MORRIS, 1963) (Equation 4) and Elovich (CHIEN; CLAYTON, 1980) (Equation 5).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2,303} t$$
(2)

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

$$q_t = k_{id} t^{0.5} + C$$
(4)

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$$
(5)

Where q_e the adsorptive capacity at the saturation point in mg g⁻¹; K₁ e K₂ are the velocity constants of the pseudo-first and pseudo-second order models in min⁻¹ and g g⁻¹ min⁻¹, respectively; K_{id} is the intraparticle diffusion constant in mg g⁻¹ min^{-0.5}; D is the constant related to the thickness of the diffusion layer in mg g⁻¹; β (g mg⁻¹) and α (mg g⁻¹ h⁻¹) are the Elovich constants and t is the contact time between species in min.

2.5. MATHEMATICAL MODELING OF ADSORPTION EQUILIBRIUM

Isotherms were determined through batch tests in a concentration range of 25 to 105 mg L⁻¹ and temperature of 30, 40 and 50 °C, controlled through the use of an SL-221 orbital shaker (Solab, Brazil). The fixed parameters of the process were: pH 2.0, mass of the adsorbent 0.5g, agitation of 170 rpm, volume of 100 mL and interaction time of 200 min. After the interaction, aliquots were removed and quantified by reading the absorbance in a UV-Vis spectrophotometer.

The experimental data were adjusted by the models of Langmuir (Eq 6), Freundlich (FREUNDLICH, 1906) (Equation 7), Elovich (ELOVICH; LARIONOV, 1962) (Equation 8), Temkin (TEMKIN, 1941) (Equation 9), Dubinin–Radushkevich (DUBININ; RADUSHKEVICH, 1947) (Equation 10) and the separation factor R_L (Equation 11).

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 q_e

1

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{6}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

$$\operatorname{Ln}\frac{q_e}{C_e} = \ln(K_E q_m) + \frac{1}{q_m} q_e \tag{8}$$

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \tag{9}$$

$$Ln q_e = \ln q_m - B(RT \ln(1 + \frac{1}{C_e}))^2$$
(10)

$$R_L = \frac{1}{1 + K_L C_0}$$
(11)

Where g_e is the adsorptive capacity at the saturation point in mg g⁻¹; C_e is the residual concentration in equilibrium; KL and qm represent the Langmuir constants and the adsorption capacity and K_f the Freundlich constant. K_E the Elovich constant, K_T the Temkin constant, R is the universal gas constant (8,314 J K⁻¹ mol⁻¹), T temperature (K), b_T the Temkin isotherm constant and B is the constant as a function of the average free energy of adsorption per molecule of adsorbate. The value of R_L indicates whether the adsorption is irreversible ($R_L=1$), unfavorable ($R_L > 1$) or favorable to balance (0 < R∟ < 1).

2.6. THERMODYNAMIC ADSORPTION VESTMENTS

Adsorption is a phenomenon that depends directly on the temperature of the system. Thus, evaluating the thermodynamic parameters involved in the process is extremely important, as they outline the viability of the process (SAHU et al., 2020). The thermodynamic characteristics of the process were obtained at different temperatures and concentrations. Through linearized Equations 12, 13 and 14 it is possible to determine the entropy (ΔS°), enthalpy (ΔH°), and Gibbs free energy (ΔG°) variations and activation energy of the adsorptive process (ALVES et al., 2020; CRUZ et al., 2016)

$$Ln(K) = \frac{-\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
(12)

$$\Delta G^{\circ} = -nRT \ln (K) \tag{13}$$

$$\mathrm{Ln}(K) = -\frac{\mathrm{Ea}}{\mathrm{RT}} + \mathrm{Ln}\,\mathrm{A}$$

Where K is the thermodynamic equilibrium constant (Lg⁻¹); R is the universal gas constant (8.314 J mol⁻¹ K⁻¹); T is the temperature (K), E_a corresponds to activation energy and A is the Arrhenius frequency factor.

3. RESULTS AND DISCUSSION

3.1. KINETIC STUDY

The adsorption kinetics studies are necessary to investigate the adsorption mechanism as well as the controlling steps of the process (NAUSHAD et al., 2019). The kinetic parameters are also necessary for choosing an optimal condition for possible applications on an industrial scale, since it allows the study of the speed that is directly related to the adsorbent/adsorbate interaction (SARUCHI; KUMAR, 2019). In this study it was used conditions previously optimized by Cruz-Filho et al. (2016), in which a mixed absorbent of elephant grass and *Aspergillus niger*. A removal of 96.8% of RR dye was achieved under the following conditions: pH 2, 0.5 g of adsorbent, and initial concentration of 25 mg L⁻¹. At an acidic pH, there is a protonation of the functional group on the adsorbent surface. Thus, since the studied dye is anionic, there is an electrostatic attraction between the biosorbent surface and the dye (Cruz Filho et al. 2016). The adsorption capacity of Remazol Red by the mixed adsorbent as a function of the interaction time for different temperatures is shown in Figure 2.

Figure 2- Study of the interaction time of the mixed adsorbent with the RR dye at different temperatures.



From the curves it is possible to observe that the adsorptive capacity increased quickly in the initial 80 minutes for all temperatures. After that time, the variation in capacity occurred slowly due to the saturation of the adsorption sites (NAUSHAD et al., 2019). Furthermore, it was observed that the temperature influences the adsorption process. That is, at higher temperatures the adsorptive capacity decreases, and thus decreasing the process efficiency (NASCIMENTO et al., 2017). This decrease with the increase in the temperature is an indication that the adsorptive system is exothermic, and does not require high temperatures for the adsorption of the dye by the adsorbent (AKSU; TEZER, 2005; SAHU et al., 2020). In addition, a high and fast removal of the adsorbent, and thus achieving equilibrium in a short period of time, indicates that the adsorbent under study is efficient (CRUZ et al., 2016).

The kinetic experiments, in addition to finding the time when the adsorption equilibrium occurs, aimed to evaluate the stage that controls the adsorption process. Four kinetic models were tested to fit the experimental data, namely, the pseudo-first and second order model (Figure 3A e B), Elovich (Figure 3C) and intraparticle diffusion (Figure 3D).

Figure 3- Linear graphics of the first (A) and second Pseudo model (B), Elovich (C) and Morris-Weber (D).



A good correlation of the kinetic data proves the possible adsorption kinetic mechanism in the solid phase. Table 1 presents the kinetic parameters of all models for the adsorption process.

Kinetic models												
T(K)		Elovich	I	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	α	β	R ²	qe	K1	R ²	qe	K2	R ²	С	Kd	R ²
303	0.21	0.29	0.62	5.13	0.04	0.83	7.6	0.020	0.98	-0.15	0.64	0.77
313	0.22	0.32	0.70	4.27	0.06	0.93	6.2	0.017	0.98	-0.09	0.59	0.82
323	0.17	0.47	0.71	2.47	-0.01	0.16	5.3	0.023	0.99	0.03	0.43	0.85

Table 1- Kinetic parameters for the models of pseudo-first order, pseudo-second order, intraparticle diffusion and Elovich.

Based on the correlation coefficients (R²) shown in Table 1, it can be seen that the kinetics of the system is best described by the pseudo-second order model. The pseudo-second order kinetics model indicates that the controlling step of the process would be the adsorption of molecules on the surface, where there is sharing or electron transfer between the adsorbent and the adsorbent surface (HO, 2006; HO; MCKAY,

2000). However, the R² results for the analysis of the Elovich fit, as shown in Table 1,

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shows that there is a lower adjustment of the model. Therefore, it is not possible to state that chemisorption is the predominant mechanism in the proposed process (CHIEN; CLAYTON, 1980).

The pseudo-first order model did not show satisfactory correlations because it did not fit the entire contact time range (dye + adsorbent) (LAGERGREN; SVENSKA, 1898). The intraparticle diffusion model also did not show a good fit, which is due to the fact that this model considers diffusion as the predominant process (WEBER; MORRIS, 1963). Diffusion is a slow process of mass transfer, which was not observed in the experiments (WEBER; MORRIS, 1963). The adsorption occurred quickly, reaching equilibrium in a maximum of 80 min, and thus demonstrating that the mass transfer by convection is dominant in this process. Through the results obtained it was possible to compare these results with those obtained by other authors also removing Red Remazol dye, as shown in Table 2.

Adsorbent	Balance time (min)	Adsorptive capacity (mg g ⁻¹)	Kinetic model	Reference		
Mixed biomass Aspergillus niger / elephant grass	80	7.6-5.32	Pseudo second order	Present work		
Rice husk ash	30	0.86	Pseudo second order	(COSTA; PARANHOS, 2019)		
Wood (Bagassa guianensis Aubl)	480	1.22	Pseudo second order	(MONTEIRO et al., 2017).		
mesocarp (cocos nucifera) residues	480	2.68	Pseudo second order	(MONTEIRO et al., 2017)		
mesoporous sílicas	180	0.118- 0.428	Pseudo second order	(ASOUHIDOU et al., 2009)		
Modified clay	90	24.26 – 72.58	Pseudo second order	(KARACA et al., 2013)		
Magnetic particles of N- lauryl chitosan	420	374	Pseudo second order	(DEBRASSI et al., 2012)		
Treated Sawdust	120	2.36	Pseudo second order	(ARA et al., 2013) (ARMAGAN;		
Pistachio shell	10	6.057	Pseudo second order	TOPRAK, 2015)		

Table 2- Comparison of the results of mixed biomass obtained in this work compared to different adsorbents found in the literature for the removal of Remazol Red.

Table 2 shows different values of adsorptive capacity and equilibrium time. These differences are directly related to the experimental conditions (pH, dye concentration, agitation and temperature) and the chemical structure of the adsorbents (amounts of adsorption sites, porosity, thermal resistance among others) (CRUZ FILHO et al., 2016). However, even with these differences, the model that best fit the experimental data was the pseudo-second order, since it considers a whole range of contact time.

3.2. THERMODYNAMIC STUDY AND ADSORPTION ISOTHERMS

The adsorption isotherms are important to describe how the solute interacts with the adsorbent (GOPINATHAN; BHOWAL; GARLAPATI, 2019). Therefore, in order to define the adsorption model in this study, linearized equations were used for the linear regression of the experimental data. Figure 4 shows the linearization of experimental data for the models of Langmuir (Figure 4A), Freundlich (Figure 4B), Elovich (Figure 4C), Temkin (Figure 4D) and Dubinin-Radushkevich (Figure 4E).

Figure 4- Linear graphs of the models of Langmuir (A), Temkin (B), Freundlich (C), Elovich (D) and Dubinin-Radushkevich (E).



The values of the isotherm parameters from the experimental data were presented in Table 3.

Table 3- Isotherm parameters of the models of Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich.

Isotherms models

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	L	angmu	ıir	Fr	eundli	ch	Т	emkin			Elovich		Rad	Dubinin∙ dushkev	'ich
Т (К)	K∟	qm	R ²	Kf	n	R ²	Κτ	bτ	R ²	qm	Ke	R ²	qm	В (10 ⁻⁹)	R ²
303	0.37	3.42	0.98	11.9	4.81	0.14	1.009	2.13	0.17	3.64	1.2 10 ⁻²	0.02	2.14	1.6	0.14
313	0.10	1.67	0.96	23.9	2.23	0.31	1.006	1.30	0.44	2.69	8.4 10 ⁻³	0.33	0.62	3.3	0.31
323	0.07	1.13	0.95	36.8	1.64	0.20	1.006	1.36	0.32	2.28	7.010 ⁻³	0.41	0.20	4.5	0.20

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Through the correlation coefficient it is possible to affirm that the Langmuir model provides a more adequate description of the mixed adsorbent/RR adsorbent interaction. This suggests that in the mechanism of this system all adsorbent adsorption sites are equal and independent, each site accommodates only one adsorbent molecule (monolayer), the adsorbed molecules do not interact with each other and all sites have the same adsorption energy (that is, the surface is energetically homogeneous) (LANGMUIR, 1918; CRUZ et al. 2016; NASCIMENTO et al., 2017).

The degree of development and spontaneity of the adsorption process can be obtained from the assessment of the separation factor R_L , which indicates whether the adsorption reaction is favorable ($0 < R_L < 1$) or unfavorable ($R_L > 1$). As seen in Figure 5, as the temperature increases, the RL factor tends to increase, which indicates that the process becomes less viable. Thus, it suggests that the adsorptive process of this system is exothermic. In addition, in the three adsorption processes, adsorption reactions become more favored towards higher initial concentrations (PINHEIRO et al., 2013; WON et al., 2006).

Figure 5- Separation factor as a function of initial concentration and temperature.



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The models of Freundlich (multilayer adsorption) (FREUNDLICH, 1906), Elovich (adsorption sites increase exponentially with adsorption, which implies multilayer adsorption) (ELOVICH; LARIONOV,1962), Temkin (assumes that the heat of adsorption of all molecules decreases linearly with the increase in coverage of the adsorbent surface) (TEMKIN, 1941) and Dubinin-Radushkevich (considers that the size of the adsorbate molecule is comparable to the size of the adsorbent micropores, and that the adsorption equilibrium ratio for a given adsorbate-adsorbent combination can be expressed regardless of temperature) (DUBININ; RADUSHKEVIC, 1947) did not show good correlations.

The determined thermodynamic parameters were Gibbs free energy ΔG° , the enthalpy variation ΔH° and entropy ΔS° . Estimates of thermodynamic parameters ΔS° and ΔH° were possible to determine by linear regression Ln (K) as a function of T⁻¹ as shown in Figure 6. Table 4 shows the thermodynamic parameters obtained.

Figure 6- Variation of the Langmuir K_{L} equilibrium constant with the absolute temperature for the RR dye adsorption process in mixed adsorbent.



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Table 4- Thermodynamic data for the adsorption of the Remazol Red dye by the mixed adsorbent.

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (kJ mol ⁻¹ K ⁻¹)	Ea (kJ/mol)
303	+2.5	-68.12	-0.234	+5.66
313	+5.99			
333	+7.14			

The thermodynamic results reveal that the ΔH° is negative, which indicates that the adsorptive process under study is exothermic for the different temperatures investigated. Table 3 shows that the increase in temperature causes a decrease in the adsorption capacity, corroborating that the adsorption is exothermic. Negative values of ΔS° suggest a reduction in randomness at the solid-solution interface during RR adsorption by the mixed adsorbent *Aspergillus niger*/elephant grass. As temperature rise, there is an increase in free Gibbs energy. Therefore, this implies that the adsorption process is not spontaneous as the temperature increases (DIZGE et al., 2008; KABIR et al., 2015; UĞURLU, 2009).

The activation energy was determined through the Arrhenius equation and Figure 7 shows the Arrhenius graph of Ln K versus 1/T where K was obtained from the pseudo-second order model, because the equation allows to calculate the variation of the speed constant of a chemical reaction with temperature (SISMANOGLU et al., 2004). The adsorptive process presented an activation energy of $E_a = +5.66$ kJ.mol⁻¹, as noted in Table 4.

Figure 7- Variation of the pseudo-second order model constant with the absolute temperature for the RR dye adsorption process in the mixed adsorbent.



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The Table 5 presents works in which RR was removed through different adsorbents. The results found for removing the RR dye are directly related to the process conditions and the nature of the material (DIZGE et al., 2008; KABIR et al., 2015; UĞURLU, 2009).

m_{0} dol $(l_{1} m_{0} ^{-1})$ $(l_{2} m_{0} ^{-1})$ $(l_{2} m_{0} ^{-1})$	$a = b^{1} V_{c1} \rangle $ (b) $b = a + b^{1} \rangle$
	101'K') (KJ MOI')
Magnetic particles of N- lauryl Langmuir– 0.10 (25 °C)	(DEBRASSI et
chitosan Freundlich –1.64 (35 °C) 51.9 0.1	1738 Nd al., 2012)
−3.42 (45 ºC)	
(55 °C)	
-9.466(25 <u>°</u> C)	
Modified clay Langmuir -10.826 (40 °C) 31.03 -	-0.1 34.49 and (KARACA et al.,
-1.166 (60 ºC)	40.27 2013)
-4.5 (25 °C)	· · · · · · · · · · · · · · · · · · ·
Magnetic nanoparticles of O- Langmuir5.4 (35 °C) 34.3 0.	1294 Nd (DEMARCHI et
carboxymethyl chitosan-N- Freundlich -6.8 (45 °C)	al., 2019)
lauryl / y-Fe₂O₃ -9.5 (55 ºC)	, ,
-5.6 (25 °C)	
Babassu coconut mesocarp Freundlich -5.2 (35 °C) -17.8 -0	0.041 Nd (VIEIRA et al.,
-4.8 (45 °C)	2009)
-4.4 (55 °C)	/
-4.39 (20 ºC)	
Fly ash Langmuir and -4.95 (30 °C) 13.93 0.	.063 Nd (DIZGE et al.,
Freundlich -5.92 (40 °C)	2008)
-6.18 (50 ºC)	
-6.75 (30 ºC)	
Chitosan Langmuir -7.34 (40 ⁰C) 53.82 0. ⁻	7541 9.25 (KABIR et al.,
-7.33 (50 ºC)	2015)
Thermally activated sepiolite Langmuir 58.83 (20 °C) 10.81(20°C) -0.16	3(20ºC) 13.251 (UĞURLU, 2009)
60.61 (30 °C) 10.73(30°C) -0.16	54(30ºC)
62.65 (40 °C) 10.64(40°C) -0.16	6 (40ºC)
acid-activated sepiolite Langmuir 59.09 (20 °C) 23.89(20°C) -0.120	0 (20ºC) 26.332 (UĞURLU, 2009)
61.11 (30 ℃) 23.81(30℃) -0.12	23(30ºC)
63.13 (40 °C) 23.73(40°C) -0.12	25(40ºC)

Tabla 5 Adear	ntion ctudioc	of Domozol	Dod dyo	through	difforant	adcarbanta
Table 5- Ausur			neu uye	unougn	umerent	ausuineniis.

Note: Nd (not determined)

4. CONCLUSION

In this work, a mixed adsorbent produced from fungal and plant biomass was used to remove Remazol Red dye from effluents. Kinetic studies showed that RR adsorption is better adjusted to pseudo-second order model, which suggests a chemical adsorption. In regards to adsorption isotherms, the model which better describes the adsorption was Langmuir. This suggests that adsorption occurs in a monolayer and all adsorption sites have the same energy. In addition, through the thermodynamic study it was noticed that the interaction adsorbent-dye becomes unfavorable as the temperature increases ($q_m = 3,42 \text{ mg/g}$). Therefore, comparing with other materials presented in the literature, we can affirm that this mixed adsorbent is an efficient and low-cost alternative to remove the color of effluents contaminated by Remazol Red. Thus, it is an alternative for the treatment of a real effluent.

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