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Study of the Biosorption Equilibrium of the Yellow Dye Reafix B2R by Sugarcane Bagasse

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The production in the textile industry involves several steps, the water is used in great volume throughout the process. In the dyeing stage, the color is checked and the dyes that do not bind to the fabric fiber are discarded in the washing step. In addition to presenting a varied composition, the effluents generated have a strong coloration. Among the various chemical, physical and biological methods used in the treatment of these residual waters, the sorption processes are presented with high efficiency and simplified application in the removal of color. In this way, studies are carried out seeking economically viable and efficient adsorbents in the removal of pollutants from the water. In this context, the present work evaluated the ability to remove the yellow dye Reafix B2R in aqueous solution, using as biosorbent sugarcane bagasse, through equilibrium experimental data and adsorption isotherm models. At the end of 36 hours of reaction, the system showed a color removal of approximately 69%. However, within 24 hours of the reaction, the removal was approximately 66%. In relation to the applied adsorption isotherms, the model that best fits the data obtained experimentally was the Freundlich model, revealing a tendency of sorption in multilayers and in a heterogeneous surface. From the results obtained experimentally in this study, it can be stated that sugarcane bagasse biomass, when under favorable conditions, has a significant potential for the treatment of effluents containing Yellow Reafix B2R dye.

1. Introduction

The textile industry plays a significant role in the industrial sector, transforming raw materials into several everyday articles. In this context, the textile processes serve a great importance, and production involves several steps, being the water applied in great volume throughout the process.
In the dyeing step, color is imparted to the fabric what characterizes it as a very important phase in the processing of the material. Dyes that do not bind to the leather fiber are discarded in the wash step (Orts et al., 2018). Dyeing a fabric depends on factors like the type of textile fiber, dyes that are used, among others.
Synthetic dyes are widely used in this process of dyeing, and reactive dyes are the most used by the textile processing industries due to their high solubility in water, chemical stability, besides obtaining several shades and good coverage, however, they present effluents with intense staining (Orts et al., 2018).
In addition to presenting a strong staining, the effluents generated in the textile industries may present high chemical and biological oxygen demand, total dissolved solids among other components that cause this effluent to require previous treatments before being discarded (Bashiri et al., 2018; Norsyazwani et al., 2018; Rubio et al., 2018). Among the various chemical, physical and biological methods used in the treatment of these residual waters, the sorption processes are presented with high efficiency and simplicity of application in the removal of color. Activated charcoal is widely used as adsorbent in this sorption process, however it presents a high cost which can make the process unfeasible (Scheufele et al., 2014).
Other processes have already been reported in the literature, with emphasis on the discoloration of waters with dyes, for example, photocatalysis combined with adsorption (Nguyen et al., 2019) and electrochemical

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process (Nidheesh et al., 2018). As for the adsorption studies, tests are carried out in search of economically viable adsorbents that are effective in the removal of pollutants from water, such as dyes. Potential adsorbents are silenced at low cost, abundant in the environment and difficult to use (Silva et al., 2019). In this context, the present study had the study of sugarcane bagasse biomass.

Sugarcane is one of the main crops of Brazilian agribusiness. It is mainly used as raw material in the manufacture of alcohol and sugar. During and subsequent of the production of these products, some by-products are formed, one of the main ones being the sugarcane bagasse.

Sugarcane bagasse is produced in large quantities, and approximately 50% is used in power generation in distilleries and mills, but significant quantities still remain as surplus, presenting problems in their packaging and environmental concerns (Scheufele et al. 2014).

Therefore, utilizing the surplus volume of sugarcane bagasse in applications that are alternative to burning can have both financial and environmental gains. The sugarcane bagasse has already been applied as an adsorbent in other processes such as the adsorption of the drug diclofenac (Antunes et al., 2012) on the adsorption of the dye malachite green (Tahir et al., 2012), on the adsorption of cadmiun (Moubarik et al., 2014) among others. When sorption tests are performed, it is important to determine the equilibrium reaction time. The adsorption equilibrium allows to evaluate the adsorbate distribution between the fluid phase and the solid phase (adsorbent), that is, the adsorbent capacity to remove a mass unit of the adsorbate, which is the pollutant (Aksu and Gonen, 2004).

The adsorption isotherms, which are mathematical equations, serve to define the theoretical adsorption capacity. It is very important to determine these isotherms experimentally, since with it it is possible to estimate the amount of solid (adsorbent) essential for the particular sorption process, and the design of the equipment to be used (Kaneko, 1994; Caprariis et al., 2018). The most widely used isotherms to describe the equilibrium of the system in sorption methods in water and effluent treatment are Langmuir and Freundlich isotherms (Wang et al., 2017). When the experimental data obtained do not adequately fit the Langmuir model, it says that the process was carried out in multilayers, however it may also indicate that the adsorption reaction involves more than one kind of bond, covalent and ionic (Avery; Tobim, 1993) . In this context, the present work evaluated the ability of the yellow dye Reafix B2R 134% (AR-B2R), in aqueous solution, using as biosorbent the sugarcane bagasse, through the experimental data of equilibrium and models of adsorption isotherms.

2. Experimental procedure

2.1 Preparation of biomass

The biomass used in the present study was the sugarcane bagasse washed in running water first and then with distilled water, that was cut into small pieces of approximately 6 cm each. Subsequently, the biomass was dried at a temperature of 30°C in a greenhouse with circulation and air renewal, and then milled in a macro knife mill.

2.2 Kinetic test

By means of the kinetic test it was possible to identify the equilibrium time for the removal of Reafix AR-B2R Yellow dye. The tests were carried out with 0.3 g of sugarcane bagasse and 50 mL of the synthetic solution of the Yellow dye Reafix B2R with initial concentration of 75 mgL^{-1} and pH 2, adjusted using solutions of HCl and NaOH. The system was kept under constant stirring at 110 rpm at 30°C in a shaker incubator. Samples were collected at predetermined times, centrifuged and the residual dye concentration readings in the solution were analyzed in a UV-Vis spectrophotometer (Femto 800 XI) at the wavelength of 410 nm.

2.3 Equilibrium test

The equilibrium test had as objective to verify the amount of sugarcane bagasse biomass necessary to reach the balance of dye removal present in the synthetic solution. The same operating conditions used in the kinetic test were applied here, however, the amount of biosorbent was varied from 0.2 to 0.9 g.

2.4 Adsorption isotherms

The application of the equilibrium test results in adsorption isotherms reveals the more probable behavior of the system in the process of dye uptake by bagasse. Eq. (1) determines the amount of dye adsorbed by sugarcane bagasse. On, C_o e C_{eq} is the concentration of sorvate in the fluid phase at time t=0 and at equilibrium time, respectively, and q_t is the amount of sorvate in the biosorbent.

$$q_t = \frac{V(C_O - C_{eq})}{m_s} \quad (1)$$

In this way, the Langmuir, Eq (2), and Freundlich, Eq (3) models were adjusted to the data obtained in the equilibrium test, thus identifying a possible system behavior.

$$\frac{C_e}{q_{eq}} = \frac{1}{q_{máx} b} + \frac{C_e}{q_{máx}} \quad (2)$$

In which, q_{eq} is the amount of adsorbate adsorbed in equilibrium (mg L^{-1}); $q_{máx}$ is the maximum sorption capacity (mg g^{-1}); b is the Langmuir constant related to adsorption energy (L mg^{-1});C_e is the concentration of adsorbate in equilibrium (mg L^{-1}). The values of $1/q_{máx}$ e $1/(q_{máx}b)$ are respectively coefficient and linear coefficient, obtained by the linear graph of C_e/q_{eq} versus C_e (Módenes et al., 2011; Ruthven, 1984).

$$\log q_{eq} = \log k_F + \frac{1}{n_f} \log C \quad (3)$$

In which, k_F and n_f are Freudlich constants related to adsorption capacity and adsorption intensity, respectively. C is the concentration of adsorbate in equilibrium (mg L^{-1}); q_{eq} is the amount of adsorbate adsorbed at equilibrium (mg g^{-1}); the values k_F and n_f can be obtained by the intersection and slope of the linear log q_{eq} versus log C (Módenes et al., 2011; Geankoplis, 2003).

3. Results

3.1 Kinetic test

The results of the AR-B2R dye biosorption test for sugarcane bagasse are presented in Figure 1 (a) concentration versus reaction time and (b) removal of the dye versus the reaction time.

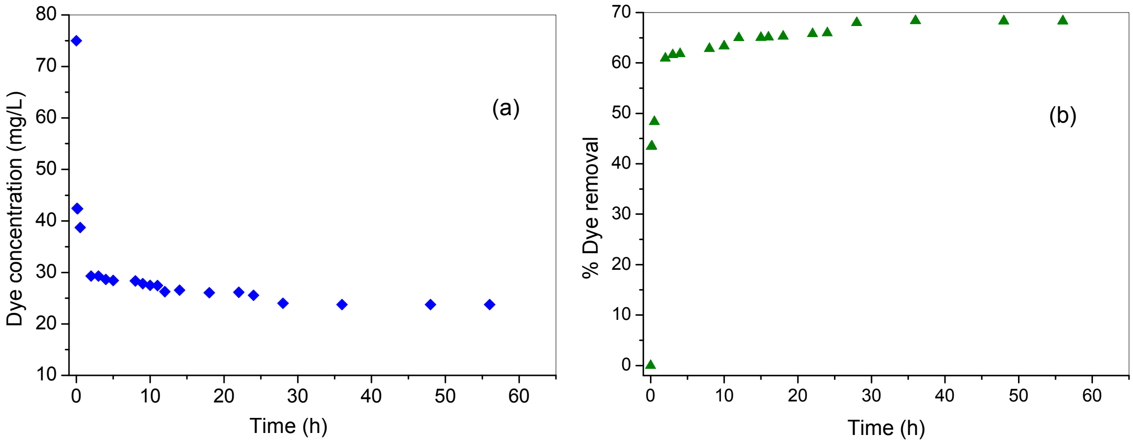

Figure 1: Yellow dye biosorption test by sugarcane bagasse.

3.2 Equilibrium test

Table 1 presents the experimental data obtained with the equilibrium test. Table 2 shows the parameters of the Langmuir and Freundlich models adjusted to the experimental data of the biosorption of the AR-B2R dye using sugarcane bagasse.

Table 1: Equilibrium test with surgacan bagasse and Yellow dye (Reafix B2R).

Mass of sugarcane bagasse (g)	Dye concentration (mg L^{-1})
0.2	28.00
0.3	22.24
0.4	13.75
0.5	11.81
0.7	08.49
0.9	06.99

Table 2: Values obtained with adsorption isotherms (Langmuir and Freundlich).

Adsorption isotherms	Parameters		Correlation coefficient (R^2)
Freundlich	k_F	0.8804	0.9805
	$1/n_f$	0.7303	
Langmuir	b (L mg^{-1})	0.0285	0.8227
	q_{max} (mg g^{-1})	21.85	

4. Discussion

4.1 Kinetic test

Figure 1 shows that the biosorption of the dye from the sugar cane bagasse was very marked in the first 3 hours of reaction, followed by a slower behavior in the later hours until reaching a steady state in 36 hours with a concentration of 22.24 mg L^{-1} dye. At equilibrium, the percentage of dye removal was approximately 69%. Although, the system equilibrium time was 36 hours, within 24 hours of the reaction, the removal was approximately 66%. This small difference (3%) led to the equilibrium tests in 24 hours.

When this study is compared with other studies involving textile dye biosorption, it is verified that the equilibrium time was higher as the information already captured in the literature, as in research Castro et al. (2017) that analyzed yeast slurry from brewery with adsorbent of textile dyes and found that the equilibrium time was 30 minutes for two dyes (reactive dyes) and 60 minutes for other dye (direct dye). Other study, by Silva et al. (2019), with biosorption test at the same textile dye (Yellow dye Reafix B2R) but with the malt bagace as biosorbent, the authors verified the equilibration time of the 360 minutes test with removal between 90 and 93%.

4.2 Equilibrium test

According to Table 1, it was verified that at the end of the 24 hours of reaction it is possible to verify that the removal of Reafix B2R Yellow dye by the biosorption process has increased, as the amount of biosorbent mass was high. The evaluation of the results was performed by comparing the values of the correlation coefficients R^2, which indicates the adequacy of the data obtained experimentally to the proposed model, the closer to a unit is the coefficient, the closer to the model studied the results will be. Thus, the model that best fit the experimental data was the Freundlich model.

In the study by Caprariis et al. (2018) that analyzed activated biochars produced fom pine wood on the adsorption of the two dyes (methylene blue and rhodamine b) removal; the authors verified that the Langmuir and Freundlich isotherms presented a good fit to the experimental data, indicating that it would not be possible to say that there is a single adsorption mechanism in the removal of the dyes.

In the present study, the best adjustment to be made by the Freundlich model reveals a tendency for the removal of the Reactive Yellow dye B2R by the sugarcane bagasse to have occurred by adsorption in multilayer and heterogeneous surfaces.

In the study by Silva et al. (2019) that studied adsorption of the same dye but with malt bagasse, the autors found as adsorption the Langmuir isotherm was the one that best fit the experimental tests indicating that the surface of the adsorbent is likely to be homogeneous and a single layer sorption.

The occurrence of multilayer adsorption in systems involving textile dyes was also observed by Scheudele et al. (2016). The authors worked on the removal of the reactive blue dye 5G using the sugarcane bagasse as biosorbent. In their study, the researchers used more specific models in investigating the sorption mechanism and limiting steps in that process. They found that initially the dye adsorption occurs in a monolayer on the surface of the biosorbent, with indicative of chemical interactions with the material, then the adsorption occurs in multilayers, on dye previously sorbed, with strength of weaker bonds between species.

According to Módenes et al. (2011), Freundlich's model considers a multilayer structure and does not predict the surface saturation of the solid based on the adsorption process, so the model considers the existence of an infinite surface coverage.

In addition, the n_f parameter of the Freundlich model indicates the adsorption intensity. Values of $1/n_f$ which are in the range of 0 to 1 indicates that the adsorption is favorable. Table 2 shows that by the parameter $1/n_f$ the value indicates the adsorption favorability between the sugarcane bagasse and the reactive yellow dye B2R (Allen et al., 2003; Cheng et al., 2010).

In this study, the Freundlich's constant showed an intermediate result when compared to other studies such as de Filho et al. (2012) that evaluated the removal of the reactive yellow dye 200% by smectite clay and verified that when the fresh adsorbent was used it had a kF value of 4.806. However, in the analysis of

Fungaro and Bruno (2009) that investigated the use of zeolites synthesized from coal ash in the removal of dye in water, they found that the Frendlich isotherm better fit the study, in which one of the studied zeolites the k_F value was 0.78 and this was the material with the highest adsorption capacity.

5. Conclusions

In the present study, the capacity of removal of the Reactive Yellow dye B2R by the sugar cane bagasse was evaluated. The equilibrium time of the studied system was 36 hours with removal capacity of approximately 69%, however in 24 hours the removal was approximately 66%, due to the discrete difference the equilibrium test was performed in 24 hours. The Freundlich's Isotherm model better represented the data obtained experimentally in the equilibrium test. By this result, the heterogeneity of the biomass surface is assumed, as well as the adsorption may have occurred in multilayers. The parameter $1/n_f$ showed a value between 0 and 1, which shows the favorability of the dye adsorption by sugarcane bagasse. Through the results obtained experimentally in this study, it can be affirmed that sugarcane bagasse biomass when under favorable conditions has a significant potential for the treatment of effluents containing B2R Reactive Yellow dye.

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