USE OF RICE HULL AS A BIOMASS SORBENT FOR ORGANIC POLLUTANT REMOVAL: ADSORPTION ISOTHERMS AND THERMODYNAMIC

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Abstract **- The present study describes the adsorption of textile dye on rice hull. The adsorption parameters were obtained from Langmuir and Freundlich isotherms utilizing linear regression plots to fit the data. The results showed that Langmuir equation was more suitable than the Freundlich one to predict the experimental adsorption isotherms, indicating that the adsorption of dye molecules is localized in a monolayer on the surface of the adsorbent. Thermodynamic parameters such as ΔH_a, ΔS_a and ΔG_a were determined in this work. The heat evolved during adsorption is endothermic. The maximum sorption capacity of rice husk was satisfactory when compared to capacities of other low-cost adsorbent materials.**

Keywords **– Adsorption, dye, rice hull, isotherm, thermodynamic.**

I. INTRODUCTION

The discharge of dyes in aquatic environment generates severe pollution problems by inhibiting photosynthetic activity (Reife and Fremann, 1996). Conventionally, dye wastewater discharged by the textile industry is treated with various chemical and physical methods, such as chemical coagulation, biological treatment, adsorption, ultrafiltration and advanced oxidation processes (Papic *et al.*, 2000; Cassano and Alfano, 2000; Karadag *et al.*, 2006; Mohorcic *et al.*, 2006; Bielska and Prochaska, 2007; Alfano and Cassano, 2009; Foletto *et al.*, 2010). Among several chemical and physical methods, the adsorption has been found to be superior compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design (Tan *et al.*, 2008). Natural materials that are available in large amounts, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Removal of dye by agricultural by-products and other low-cost sorbents such as cotton fiber (Pal and Esteve, 1959), kaolin (Nandi *et al.*, 2009), coir pith (Namasivayam *et al.*, 2001), carbon (Pereira *et al.*, 2003), clay (Schoonheydt and Heughebaert, 1992), oxide (Foletto *et al.*, 2009), and rice hull (Kumar and Sivanesan, 2007) has been investigated.

In the Rio Grande do Sul state (Brazil), the greatest national rice producer, about 8,900 million ton of rice were produced in harvest 2010/2011 (Rice Riograndense Institute, 2011). Knowing that the hulls represent 20% of this value, the annual production of this residue is about 1.782 million ton. In the present study rice hulls has been used as adsorbent for the removal of red dye from its aqueous solution. Thus, the use of biomass sorbent may offer promising benefits for commercial purpose in the future.

Adsorption of dyes in aqueous solution is a surface phenomenon involving the removal of the coloring matter (the adsorbate) by means of a material (the adsorbent). Adsorption process has been usually classified into physical adsorption (physiosorption) and chemisorption. In the first type, the forces are the weak van der Walls, and the heat evolved during adsorption is less than 40 $kJ.mol^{-1}$. In chemisorption the molecules are chemically bound to the adsorbent surface. The heat evolved during this type of adsorption is comparable to that of a chemical reaction (more than 80 $kJ.mol^{-1}$) (Wedler, 1976).

Various types of adsorption isotherms have been reported in the literature to describe the adsorption of colored compounds on adsorbents, however the most commonly used are the Langmuir and Freundlich adsorption isotherms. The applicability of adsorption isotherms in the study of dyes removal from aqueous solutions has already been reported in the literature (Walker and Weatherley, 2000; Wong *et al.*, 2004; Allen *et al.*, 2004; Kumar and Sivanesan, 2007; Tanyildizi, 2011).

The objectives of the present study were to investigate the equilibrium of adsorption of reactive red dye in aqueous solution and to elucidate the forces between the rice hull and the dye molecules. The Langmuir and Freundlich models were used to fit the equilibrium isotherms, and thermodynamic parameters were evaluated to elucidate the extent of adsorption data.

II. METHODS

A. Materials

Procion red H-E7B dye (CI Reactive Red 141), azo dye extensively used in the textile industry, was used as model compound. The chemical structure of dye is given in Fig. 1. Dye was provided by a textile industry located in the Santa Catarina State (Brazil). The rice hull in the present investigation was obtained from a local rice mill. The whole rice hulls (seen image in Fig. 2) were washed thoroughly with distilled water to remove all the dirt particles. The material were then dried at 60 ºC for 24 h and stored in plastic bottles for use.

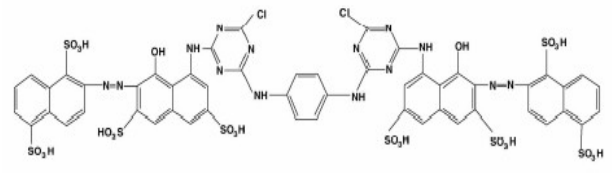

Fig. 1. Chemical structure of azo dye.

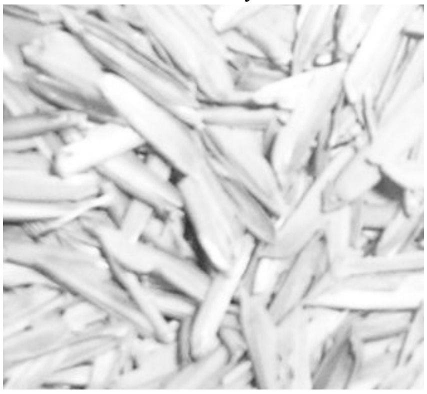

Fig. 2. Image of rice hulls used in the adsorption experiments.

B. Batch sorption experiments

For adsorption tests, different initial concentrations of rice hull (0.5, 1.0, 1.5 and 2.0 g) were added to 300 mL of the aqueous solution of dye at initial concentration of 30 $mg.L^{-1}$ and at an optimum pH 2.5 (showed in Fig.3). The pH was adjusted by using dilute H_2SO_4. The resulting solution was then magnetically stirred at 100 rpm in a thermostatic bath at constant temperature (293, 303, 313 and 323ºK) in the dark to achieve the adsorption equilibrium of dye on the solid. During the runs, 5 mL samples of solution were withdrawn at regular intervals and were filtered through a membrane to completely remove solid particles. All samples were analyzed using a Shimadzu 1650C UV spectrophotometer at $\lambda_{max.}$= 543 nm. The adsorption capacity of the dye was calculated as follows:

$$q_e = [(C_o - C_e)V]/W \quad (1)$$

where q_e ($mg.g^{-1}$) is the amount of dye adsorbed in the equilibrium, C_o ($mg.L^{-1}$) is the initial dye concentration, Ce ($mg.L^{-1}$) is the concentration of dye in the aqueous phase at equilibrium, W (g) is the adsorbent amount in the solution, and V (L) it the volume of the solution.

III. RESULTS AND DISCUSSION

The effect of pH on the adsorption of the dye was studied in the range 2.5-8.5 (Fig. 3). From the figure, it was observed that the adsorption was high in acid medium (pH 2.5). In pH 5.3 (the point of zero charge, pHpzc), the surface of rice hull had neutral charge (Costa *et al.*, 2009). However, at pH < pHpzc the solid surface present positive charge, favoring the adsorption of anionic molecules of the dye that is formed by several sulphonated groups charged negatively (Fig. 1). Similar trend of pH effect was observed for the adsorption of direct and acid dye onto soy meal hull, with maximum adsorption in pH 2.0 (Arami *et al.*, 2006), and for the adsorption of anionic dye onto babassu coconut mesocarpo (Vieira *et al.*, 2009).

Table 1. Adsorption capacity of dye (q_e) in the equilibrium on rice hull.

	q_e ($mg.g^{-1}$)			
Temperature (K)	0.5 g	1.0 g	1.5 g	2.0 g
293	8.06	4.44	4.13	3.40
303	10.10	5.85	4.29	3.69
313	11.76	6.94	5.46	4.16
323	12.66	7.35	5.55	4.25

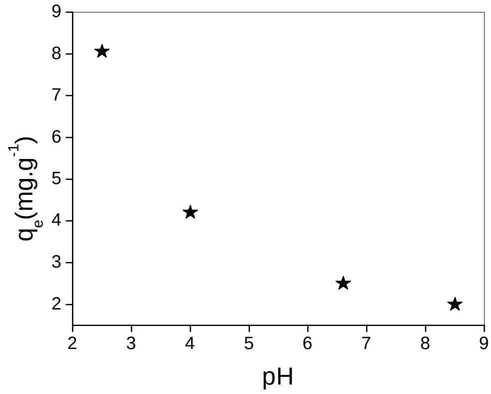

Fig. 3. Influence of pH on the adsorption of dye onto rice hull. Experimental conditions: $m_{adsorbent}$=0.5 g, Co = 30 $mg.L^{-1}$, T = 293K.

The amount of dye adsorbed at equilibrium on rice hull at different amounts (0.5, 1.0, 1.5 and 2.0 g) and temperatures (293, 303, 313 and 323ºK), at pH 2.5, are given in Table 1. The contact time (not shown here) required to attain equilibrium was about 40 min for all the experimental conditions used in this work. It is observed that the adsorption capacity increased with increasing temperature from 293 to 323 K, showing that this process is endothermic. Similar result was reported for the adsorption of cationic dye by activated carbon (Karaca *et al.*, 2008). But, it is noted that the adsorption capacity decreased with increasing the amount of rice hull. Similar result was observed for the adsorption of Acid Red 114 dye using activated carbon prepared from seed shells (Thinakaran *et al.*, 2008). This may be attributed to the aggregation of adsorbent particles at high dosage, which reduces the total surface area of the adsorbent and results in an increase in the diffusion path length (Shukla *et al.*, 2002).

The adsorption data were analyzed according to the two frequently used isotherm models: Langmuir and Freundlich. The isotherms for adsorption from solutions are given by equations:

Langmuir:

$$\frac{C_e}{q_e} = \frac{1}{K_L.q_o} + \frac{C_e}{q_o} \quad (2)$$

Freundlich:

$$\log q_e = \log K_F + \frac{1}{n}.\log C_e \quad (3)$$

where q_o is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface ($mg.g^{-1}$), K_L is the Langmuir constant related to the energy of adsorption ($L.mg^{-1}$), C_e is the concentration of dye in the aqueous phase at equilibrium and K_F is the adsorption capacity (mg.g^{-1}) and *n* is a value that varies between 1 and 10 and is a measure the intensity of adsorption (Haghseresht and Lu, 1998; Tsai *et al.*, 2004).

The Langmuir constants q_o and K_L were calculated from the slope of plot between $1/qe$ versus $1/Ce$ (Fig. 4), while the values of Freundlich constants, *n* and K_F were obtained from of plot log q_e versus log C_e (Fig. 5). Parameters of the isotherms and correlation coefficients are given in Table 2. As seen from Table 2, the increase of q_o and *n* values with rise in temperature suggest that higher temperature creates more adsorption sites.

Comparing Fig. 4 and 5, it observed that the best fit was obtained by Langmuir isotherms, and this can be analyzed through of values of correlation coefficients (R^2) shown in Table 2. Langmuir model is more efficient than Freundlich equation to describe the phenomenon of dye adsorption on rice hull surface. The Langmuir model assumes that there is no interaction between the sorbate molecules and that the adsorption is localized in a monolayer. The values of *n* calculated from the Freundlich equation, are within the range 1-10 generally reported in the literature (Haghseresht and Lu, 1998; Tsai *et al.*, 2004), suggesting that the adsorption was favorable.

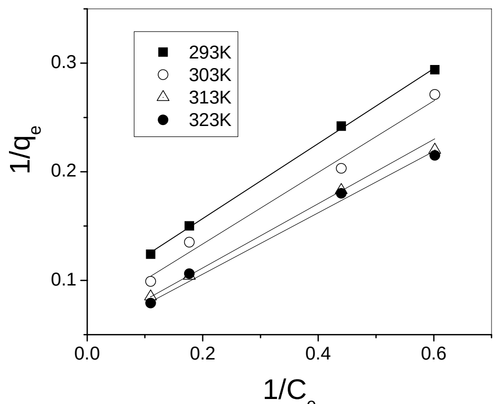

Fig. 4. Langmuir isotherms for the adsorption of dye on rice hull at different temperatures.

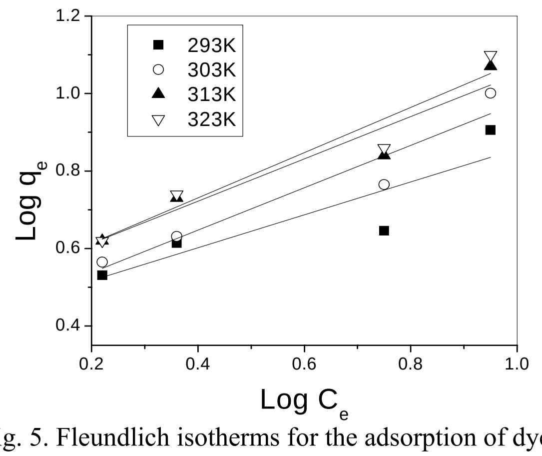

Fig. 5. Fleundlich isotherms for the adsorption of dye on rice hull at different temperatures.

Table 2. The values of constants evaluated from the isotherms at different temperatures with the correlation coefficients.

T (K)	K_L	q_o	R^2	*n*	K_F	R^2
293	0.256	11.40	0.999	2.354	2.707	0.680
303	0.204	14.81	0.980	1.822	2.684	0.885
313	0.176	19.16	0.999	1.831	3.189	0.884
323	0.173	20.36	0.992	1.713	3.143	0.892

Table 3. The maximum adsorption capacity (q_o) of dyes on various low-cost solid wastes.

Adsorbents	q_o (mg.g^{-1})	Dye	Ref.
Rice hull	11.40 to 20.36	Reactive Red 141	This study
Apricot stones-activated carbon	4.11	Methylene blue	Aygun *et al.*, 2003
Coir pith-activated carbon	6.72	Congo red	Namasivayam and Kavitha, 2002
Hazelnut shell-activated carbon	8.82	Methylene blue	Aygun *et al.*, 2003
Saklıkent mud	9.7	Brilliant Green	Kismir and Aroguz, 2011
Mango seed adsorbents	~ 10	Athraquinone and azo acid dyes	D.-Jiménez *et al.*, 2009

Table 3 gives the maximum adsorption capacity (q_o) values of dyes adsorption on vegetable waste adsorbents investigated by us and other researchers.

From Table 3, it is observed that the maximum sorption capacity of rice husk is satisfactory when compared to capacities of other low-cost adsorbent materials. Furthermore, as an agricultural by-product, rice husk is vast and cheap, so it shows potential for the removal of Reactive Red 141 from the solution.

The data obtained from adsorption isotherms were used to determine thermodynamic parameters such enthalpy of adsorption (ΔH_a), Gibbs free energy of adsorption (ΔG_a) and adsorption entropy (ΔS_a).

The enthalpy of adsorption (ΔH_a) and adsorption entropy (ΔS_a) were estimated by modified Vant Hoff equation:

$$\ln K_D = -\frac{\Delta H_a}{RT} + \frac{\Delta S_a}{R} \tag{3}$$

where *T* is the temperature in Kelvin, *R* is the universal gas constant (8.31414 J. mol^{-1}.K^{-1}) and K_D (q_e/C_e) is the linear adsorption distribution coefficient.

The Gibbs free energy of adsorption (ΔG_a) was evaluated using following equation:

$$\Delta G_a = \Delta H_a - T.\Delta S_a \tag{4}$$

The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the plot between ln K_D versus 1/T (Fig. 6), and are given in Table 3. The values of ΔG_a are also reported in Table 3. The positive values of ΔH_a indicate that the adsorption process is endothermic in nature. Bulut and Aydin (2006) found a value of 33.41 kJ.mol^{-1} for the heat (ΔH_a) involved in the adsorption of methylene blue dye on wheat shells, and Prado *et al.* (2004) found a value of 29.25 kJ.mol^{-1} for the heat involved in the adsorption of indigo carmine dye on chitin and chitosan. Values of (ΔH_a) varying between 11 and 45 kJ.mol^{-1} were found for the adsorption of

Table 3. Thermodynamic parameters for adsorption of dye on rice hull with different dosages of adsorbent at different temperatures.

Dosages (g)	ΔH_a ($kJ.mol^{-1}$)	ΔS_a ($kJ.mol^{-1}.K^{-1}$)	ΔG_a ($KJ.mol^{-1}$) Temperatures (K)			
			293	303	313	323
0.5	27.87	89.45	- 26.18	- 27.07	- 27.96	- 28.86
1.0	37.10	117.55	- 34.40	- 35.58	- 36.75	- 37.93
1.5	43.39	150.23	- 43.97	- 45.47	- 46.97	- 48.48
2.0	44.88	156.55	- 45.82	- 47.38	- 48.95	- 50.52

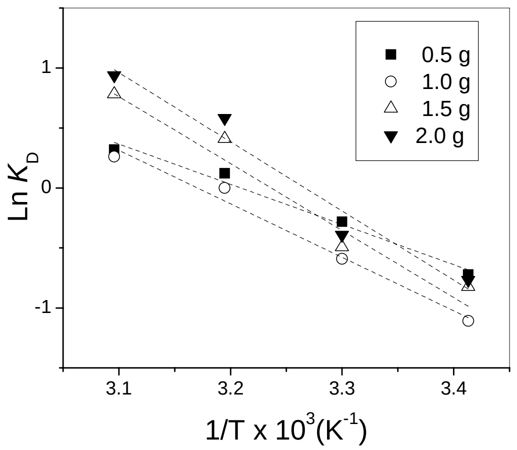

Fig. 6. Plot of ln K_D vs. $1/T$ for dye adsorption on rice hull at various dosages.

methylene blue dye on activated carbon (Tan *et al*., 2007). The negative values of ΔG_a show spontaneous nature of adsorption process and the positive values of ΔS_a indicate the affinity of the adsorbent for dye. Considering the total adsorption energy, the entropic contribution T. ΔS_a is much larger than the enthalpic contribution. This indicates that the adsorption process of dye on the adsorbent is entropically governed.

IV. CONCLUSIONS

In the present study, rice hull was used as adsorbent for removal of textile dye from the aqueous solutions. Adsorption of dye was studied by batch technique. The experimental data show that the Langmuir model was more applicable than the Freundlich model. The thermodynamic parameters were determined. Considering the total adsorption energy, the entropic contribution T.ΔS_a is much larger than the enthalpic contribution. This indicates that the adsorption process of dye on adsorbent is entropically governed.

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