

## STUDIES OF THE BIOSORPTION OF TEXTILE DYE ONTO WHEAT STRAW

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**Abstract:** The objective of this study is the valuation of a natural residue and its application for the removal of synthetic dye through the adsorption batch process. The determinations of the concentrations of dye have been performed using an UV–Vis spectrophotometer. The kinetics and thermodynamics of adsorption of Methylene blue by wheat straw were studied. Experimental data were analyzed by the Langmuir, Freundlich, and Temkin isotherms.

The Langmuir isotherm showed that the maximum value of adsorption capacity was  $85.47 \text{ mg}\cdot\text{g}^{-1}$ , and the coefficient of determination ( $R^2$ ) was 0.999. The experimental data fitted very well the pseudo-second-order kinetic model ( $R^2 = 0.998$ ), also the intraparticle diffusion rate constants vary from  $4.612$  to  $14.615 \text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$  for concentrations between  $10$  and  $120 \text{ mg}\cdot\text{L}^{-1}$ , whereas diffusion is not the only rate-control step.

The thermodynamic parameters were evaluated. The negative value of  $\Delta H^\circ$  ( $-13.850 \text{ kJ}\cdot\text{mol}^{-1}$ ) indicated that the adsorption of Methylene blue on wheat straw was exothermic, the reaction was accompanied by a decrease in entropy ( $-0.255 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ). The Gibbs energy increased from  $-13.770$  to  $-13.775 \text{ kJ}\cdot\text{mol}^{-1}$ . The studied system shows that the adsorption process is spontaneous.

**Keywords:** *biosorption, dye, modeling, thermodynamics, wheat straw*

## INTRODUCTION

Dye wastewater has a complex composition, high color content, high concentration of organic matter, and poor biodegradability, and poses a great threat to large bodies of water and human health [1 – 3]. Dye wastewaters represent the most amounts of the discharged industrial water [4]. The development of many treatment methods were the essential subjects of many articles. They can be physical, chemical or biological [5 – 7]. Biodegradation and adsorption were the two treatments widely used in the purification of waters [8, 9]. The treatment by adsorption consists of the retention of dyes onto a solid material called adsorbent by chemical or/and physical bonding. Several solid adsorbent materials such as activated carbon [10], clays [11], zeolite [12], biomasses, and industrial waste products are able to efficiently remove color from water [13].

The use of textile dyes is the essential cause of color in the discharged wastewaters [14]. Dye molecules present a considerable structural diversity, allowing them to be classified by several manners [15]. They can also be classified with respect to their solubility in water [16]. Acid, basic, reactive and direct dyes are soluble dyes, while dispersed pigments and oxidized dyes are insoluble in water. Over the last few decades, there has been an increase in the use of plant waste products for dye removal by adsorption from wastewater because of their natural availability and the high degree of dye removal achieved under laboratory conditions. Furthermore, most of these methods require high costs and are difficult to operate particularly on a great scale. Conversely, adsorption has attracted increasing interest owing to its lower cost [17 – 19].

Also there is no toxicity restrictions in the organism employed; they are simple to operate too. Various low-cost biomasses, including peel of fruit, potato plant wastes and dried algae and ferns, have been used as the potential biomass materials to remove dyes from aqueous solutions containing dyes [20].

Wheat straw has been found to be potentially proper adsorbent because of functional groups attach on the cell wall and their high binding affinity, fast growth and natural abundance around the world.

There are few reports on the adsorption of dyes from contaminated waters using wheat straw [21].

Methylene Blue (MB) is a basic blue dyestuff with the chemical formula  $C_{16}H_{18}N_3SCl$ . MB has several harmful effects in spite of being not strongly hazardous. It is harmful when it is swallowed and it can be harmful if it is breathed and in contact with skin.

Moreover, it causes severe eye irritation [22].

The aim of the present study was to investigate the removal of MB dye by dried wheat straw (WS) biomass. To obtain better understanding of the adsorption mechanisms, the isotherm, kinetic and thermodynamic of dye removal in batch system were studied. Furthermore, the effect of experimental conditions on maximum dye removal efficiency was investigated.

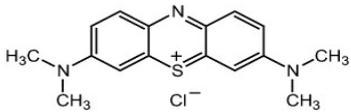
## MATERIALS AND METHODS

### Dye solution preparation

The basic dye used in this study was dye methylene blue (MB), purchased from Sigma Aldrich with a formula:  $C_{16}H_{18}ClN_3S$ . Its characteristics are summarized in Table 1. A

stock solution of  $1 \text{ g}\cdot\text{L}^{-1}$  was prepared by dissolving the appropriate amount (1 g) of MB in one liter of distilled water. The working solutions were prepared by diluting the stock solution with distilled water to give the appropriate concentration of working solutions. The *pH* of the solution was adjusted by adding either 0.1 M HCl or 0.1 M NaOH respectively.

**Table 1.** Properties and characteristics of MB

<b>Chemical name (IUPAC)</b>	Dimethylamino-3,7 phenazathionium chloride
<b>Molecular weight [<math>\text{g}\cdot\text{mol}^{-1}</math>]</b>	373.90
<b>Molecular volume [<math>\text{cm}^3\cdot\text{mol}^{-1}</math>]</b>	241.9
<b>Molecular diameter [nm]</b>	0.8
<b>Chemical Structure</b>	

### Preparation of biosorbent

The WS was washed with boiling distilled water for 30 min. This WS was then placed in a solution of NaOH (12 %) for 15 min and washed again with tap water. They are whitened with bleach 12 % for 3 h at ambient temperature after which the straw is rinsed with distilled water several times. The WS was oven dried at  $105 \text{ }^\circ\text{C}$  for 120 min, then crushed and sifted. Samples are ready for adsorption.

### Adsorption experiments

Adsorption studies for the evaluation of the WS for the removal of MB from aqueous solutions were carried out using the batch contact adsorption. For these experiments, fixed amount of adsorbent 1 g were placed in a 500 mL glass Erlenmeyer flasks containing 300 mL of MB solutions  $10$ ,  $50$  and  $120 \text{ mg}\cdot\text{L}^{-1}$ , which were agitated for a suitable time 150 min from  $20$  to  $40 \text{ }^\circ\text{C}$  at *pH* 6.

For a given contact time corresponding to equilibrium, we recover the filtrate solution for passing the UV-visible spectrophotometer (Unicam 8625, Labexchange the world's N.1, France) at 664 nm.

Adsorption kinetic experiments were used to investigate the effect of contact time and determine the kinetic parameters. For these tests, 1 g of WS was added to 300 mL MB solutions with different initial concentrations. The mixture was agitated on an electromagnetic stirrer (Shinko Electric CO. LTD, Japan) at 350 rpm. At predetermined time intervals, 10 mL samples were taken out and filtered. The same methods were used to determine the residual MB concentration. Each measurement of dye concentration was repeated three times.

The adsorption amount at time *t*,  $q_t \text{ (mg}\cdot\text{g}^{-1})$  was calculated by the following equation:

$$q_t = \frac{(C_0 - C_t) V}{m} \quad (1)$$

$$\text{Percent removal} = \frac{(C_0 - C_t)}{C_0} \cdot 100 \quad (2)$$

where  $q_t$  is the amount of MB taken up by the adsorbent ( $\text{mg}\cdot\text{g}^{-1}$ ),  $C_t$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the concentration of MB solution at time,  $t$  (min),  $C_0$  ( $\text{mg}\cdot\text{L}^{-1}$ ) is the initial concentration of MB,  $V$  is the volume of dye solution (L), and  $m$  is the weight of adsorbent used (g).

### Adsorption isotherms

Adsorption isotherm models are widely used to describe the adsorption process and investigate mechanisms of adsorption. Adsorption isotherms were calculated based on the well-known Langmuir, Freundlich, and Temkin models. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, using uniform strategies of adsorption [23]. The linear form of the Langmuir isotherm equation is given as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \quad (3)$$

where  $C_e$  is the equilibrium concentration of the biosorbate ( $\text{mg}\cdot\text{L}^{-1}$ ),  $q_e$  is the amount of biosorbate adsorbed per unit mass of adsorbent ( $\text{mg}\cdot\text{g}^{-1}$ ),  $K_L$  is the Langmuir adsorption constant ( $\text{L}\cdot\text{mg}^{-1}$ ), and  $q_m$  is the theoretical maximum adsorption capacity ( $\text{mg}\cdot\text{g}^{-1}$ ).

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter [24],  $R_L$ , defined as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

The value of  $R_L$  indicates the shape of isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) [25].

The Freundlich isotherm, on the other hand, assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage [26]. The well-known logarithmic form of the Freundlich isotherm [27] is given by the following equation:

$$\text{Log}(q_e) = \text{Log}(K_F) + \frac{1}{n_F} \text{Log}(C_e) \quad (5)$$

where  $K_F$  ( $\text{mg}^{(1+1/n)} \cdot \text{g}^{-1} \cdot \text{L}^{-1/n}$ ) and  $1/n_F$  are the adsorption constants of Freundlich model generally related to the strength of interaction between adsorbate and sorbent.

Temkin's model rests on the assumption that during the adsorption gas phase, the heat of adsorption due to interactions with the adsorbate decreases linearly with the recovery rate  $\theta$ . From  $q_e$  plotted as a function of  $\text{Ln } C_e$ ,  $B_T$ , and  $K_T$  values can be determined [28].

$$q_e = \frac{RT}{B_T} \text{Ln}(K_T \cdot C_e) \quad (6)$$

where  $R$  is the perfect gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  $T$  is the absolute temperature (K),  $B_T$  is the variation in energy of adsorption ( $\text{J}\cdot\text{mol}^{-1}$ ), and  $K_T$  is the constant of Temkin ( $\text{L}\cdot\text{mg}^{-1}$ ).

### Adsorption Kinetics

The rate constant for surface adsorption of MB onto WS is also studied under the light of the pseudo-first-order rate expression of Lagergren model [29]. The integrated form of the Lagergren equation is given by:

$$\text{Log}(q_e - q) = \text{Log}q_e - \frac{k_1}{2.303}t \quad (7)$$

where  $q_e$  and  $q_t$  are the amounts adsorbed at equilibrium and at time,  $t$  ( $\text{mg}\cdot\text{g}^{-1}$ ), and  $k_1$  is the rate constant of the pseudo-first-order adsorption ( $\text{min}^{-1}$ ).

The pseudo-second-order kinetic model (8) can be represented in the following form [30]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (8)$$

where  $k_2$  is the rate constant of the pseudo - second order adsorption ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ ).

The kinetics of adsorption of the adsorbate on the adsorbent was verified at different initial concentrations (10, 50, and  $120 \text{ mg}\cdot\text{L}^{-1}$ ).

The validity of each model was determined by the sum of squared errors (SSE), given by:

$$SSE = \frac{1}{N} \sqrt{\sum (q_{e,\text{exp}} - q_{e,\text{cal}})^2} \quad (9)$$

where  $N$  is the number of trials. Low value indicates a better SSE smoothing.

Most adsorption reactions take place through multi - step mechanism comprising (i) external film diffusion, (ii) intraparticle diffusion, and (iii) interaction between adsorbate and active site. Since the first step is excluded by shaking the solution, the rate - determining step is one of the other two steps. Weber and Morris [31] described the intraparticle uptake of the adsorption process to be proportional to the half power of time:

$$q_t = K_{dif} t^{1/2} + C \quad (10)$$

where  $C$  is the intercept and  $k_{dif}$  is the intraparticle diffusion rate constant  $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ .

### Adsorption thermodynamics

The original concepts of thermodynamics assumed that in an isolated system, where energy cannot be gained or lost, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy

change,  $\Delta G^\circ$ , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if  $\Delta G^\circ$  is a negative quantity.

The value of  $\Delta G^\circ$  can be determined from the following equation:

$$\Delta G^\circ = -RT \ln(k_L) \quad (11)$$

where  $K_L$  is the adsorption equilibrium constant,  $R$  is the universal gas constant ( $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ), and  $T$  is the absolute temperature.

A convenient form of the Van't Hoff equation then relates  $K_L$  to the standard enthalpy and entropy changes of adsorption,  $\Delta H^\circ$  and  $\Delta S^\circ$ , respectively [32]:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

(12) can be written as:

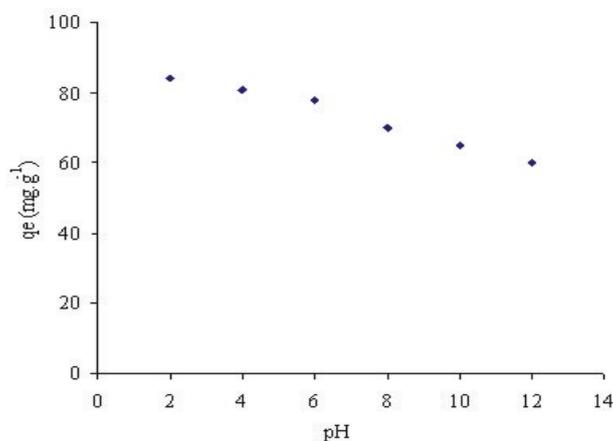
$$\ln(k_L) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} = -\frac{\Delta G^\circ}{R} \cdot \frac{1}{T} \quad (13)$$

## RESULTS AND DISCUSSION

### Effect of pH on the removal of dye

Many studies suggest that pH is an important factor in the biosorption process [33, 34], variations in pH could change the characteristics and availability of metal ions in solution as well as the chemical status of the functional groups responsible for biosorption. Some experiments were therefore performed at  $40^\circ\text{C}$  with  $120 \text{ mg}\cdot\text{L}^{-1}$  solutions to study the MB adsorption on WS as a function of solution pH.

The results for the study of the effect of pH on MB adsorption are shown in Figure 1. It is clear that a progressive increase in pH from 2 to 12 causes a lowering in the adsorption capacity.

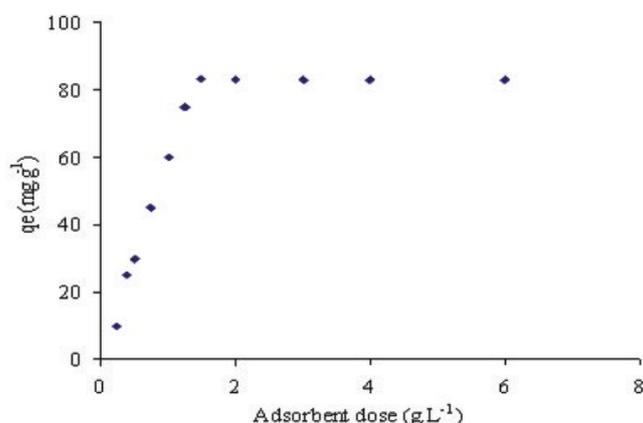


**Figure 1.** Effect of pH on MB adsorption:  $[MB]_0 = 120 \text{ mg}\cdot\text{L}^{-1}$ , WS dosage = 1 g,  $V = 300 \text{ mL}$ ,  $T = 40^\circ\text{C}$  and contact time = 30 min

This dye adsorption behavior can be explained by the fact that during the  $pH$  adjustment of the solution containing the dye MB, the wheat straw undergoes accordingly possible alteration of the ionic character of their surfaces and the aggregation state of the MB. A similar trend was observed for adsorption of MB onto wheat shells [35].

### Effect of adsorbent dosage

The effect of the adsorbent dose on the amount adsorbed of MB was studied at  $40\text{ }^{\circ}\text{C}$  and  $pH$  of 6 by varying the adsorbent amounts from  $0.25$  to  $6\text{ g}\cdot\text{L}^{-1}$ . For all these runs, initial concentration of dye was fixed at  $120\text{ mg}\cdot\text{L}^{-1}$ . The analysis showed that the adsorption of MB increased as the adsorbent dosage increased from  $0.25$  to  $6\text{ g}\cdot\text{L}^{-1}$  due to the limited availability of the adsorbing species number for a relatively larger number of surface sites on the adsorbent. The significant increase in adsorption capacity was observed when the dose was increased from  $0.25$  to  $1.25\text{ g}\cdot\text{L}^{-1}$ , any addition of the adsorbent at this dose would not result in any significant change in the adsorption capacity. These results clearly indicated that the WS dosages must be fixed at  $1.25\text{ g}\cdot\text{L}^{-1}$  (Figure 2) which is the dosage that corresponding to the minimum amount of adsorbent that led to constant MB removal for the entire experiments. Similar results were previously reported by some researchers [35 – 37].

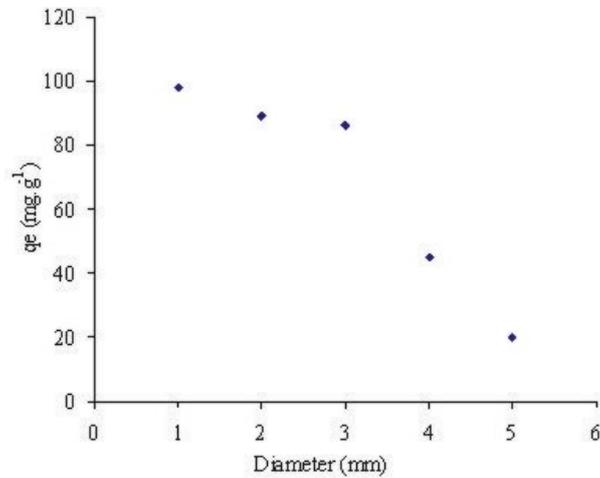


**Figure 2.** Effect of adsorbent dosage on the MB adsorption onto WS  $V=300\text{ mL}$ ,  $T=40\text{ }^{\circ}\text{C}$ ,  $C_0 = 120\text{ mg}\cdot\text{L}^{-1}$ ,  $pH\ 6$ , contact time = 150 min and agitation rate = 350 rpm

### Effect of particles size

The particle size of the adsorbent can greatly influence the external surface of the adsorbent, thus impacting on its interaction with the solution through the effect of resistance to the film diffusion. As a consequence, a variation in the adsorbent particle size modifies the accessibility and the availability of reactive groups present on its surface [38]. As expected, it was found that the MB adsorption decreases with increasing the particle size of the adsorbent (Figure 3). This is due to larger surface area of smaller particles for the same amount of the adsorbent. For larger particles, the diffusion resistance to the mass transport is higher, and most of the internal surface of

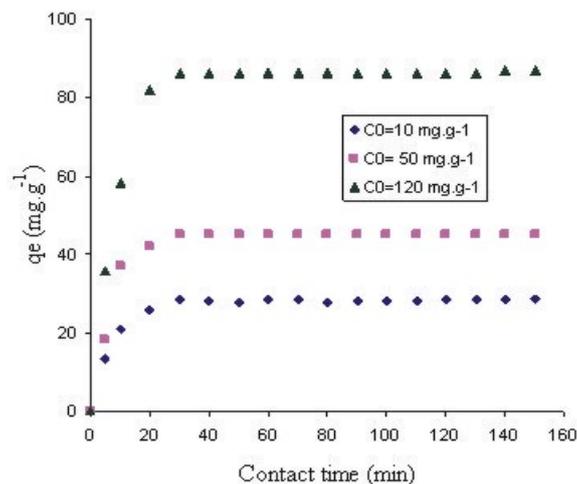
the particle is not utilized for adsorption. Consequently, the amount of MB adsorbed is small. Similar results were reported by other researchers with coniferous brown macroalga *Stoechospermum marginatum* [39], *Pinus brutia Ten* [40] and *Luffa cylindrica* [41].



**Figure 3.** Effect of the diameter of biosorbent particle on MB adsorption onto WS  $C_0 = 120 \text{ mg}\cdot\text{L}^{-1}$ ,  $\text{pH}=6$ ,  $m=1\text{g}$ ;  $T = 40 \text{ }^\circ\text{C}$ ,  $t = 150 \text{ min}$  and agitation rate = 350 rpm

### Effect of contact time

The dye adsorption was measured at given contact times for three different initial dye concentrations of 10, 50 and 120  $\text{mg}\cdot\text{L}^{-1}$ . Figure 4 shows that the amount of MB removed is higher at the beginning.



**Figure 4.** Effect of contact time on MB removal onto WS  $\text{pH} 6$ ,  $m = 1 \text{ g}$ ,  $0.08 \leq dp \text{ (mm)} \leq 0.63$ ,  $T=40 \text{ }^\circ\text{C}$  and  $V = 300 \text{ mL}$

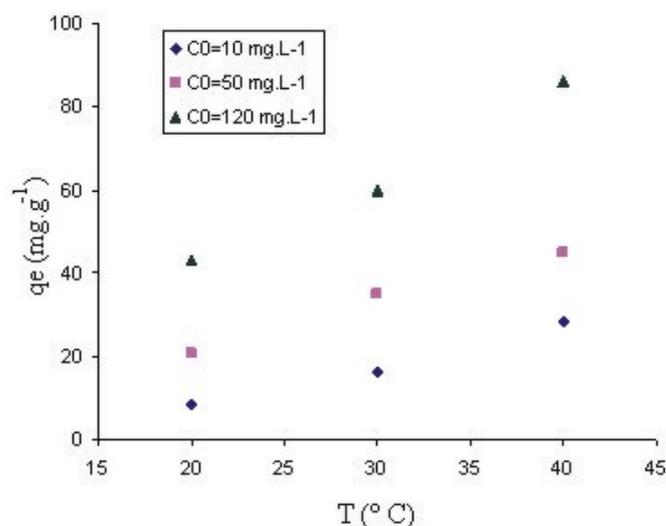
This is probably due to the presence of available sites in wheat straw for dye adsorption. When the surface adsorption sites are depleted, the rate of adsorption is controlled by

the rate at which the biosorbate is transported from the exterior to the interior sites of the adsorbent particles.

Most of the MB removal amount was attained after about 150 minutes stirring time at different initial concentrations. The adsorption capacity of MB increases with the contact time and then stabilizes and has equilibrium in 30 min for different initial concentrations. The same phenomenon was observed for other materials [35, 42].

### Effect of initial dye concentration on temperature dependent adsorption

The initial dye concentration provides an important driving force to overcome all mass transfer limitations of dye between the aqueous and solid phases. Therefore, a higher initial MB concentration will enhance the adsorption process. Figure 5 shows the effect of initial MB concentration on the equilibrium adsorption capacity ( $q_e$ ) of MB on WS at different temperatures. It was clear to see that the  $q_e$  values increase with the increase in the initial MB concentrations or the solution temperatures. The maximum equilibrium ( $q_e$ ) values were determined as 42.95, 60 and 86.4  $\text{mg}\cdot\text{g}^{-1}$  for 120  $\text{mg}\cdot\text{L}^{-1}$  initial MB concentrations at 20, 30, and 40  $^{\circ}\text{C}$ , respectively. Similar of the adsorption process has been reported for other adsorbent systems [27, 28, 35]. The adsorption capacity for the system (MB / WS) increases with increasing the temperature from 20 to 40  $^{\circ}\text{C}$ . The best removal efficiency (86.4  $\text{mg}\cdot\text{g}^{-1}$  and 96.5 %) was obtained at a temperature of 40  $^{\circ}\text{C}$ .



**Figure 5.** Effect of temperature on the amount adsorbed by the WS / MB  
pH 6, dosage = 1 g,  $0.08 \leq dp(\text{mm}) \leq 0.63$  and  $V = 300 \text{ mL}$

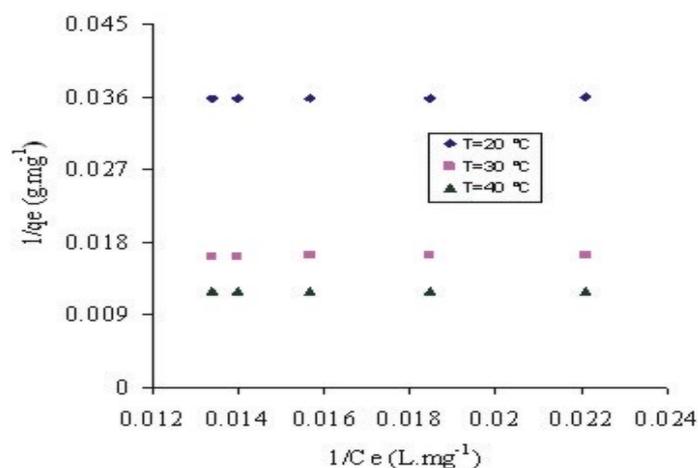
### Application of equilibrium models

The graphic representation of the rapport variation ( $1/q_e$ ) as a function of ( $1/C_e$ ) for the adsorption of MB at 20, 30, and 40  $^{\circ}\text{C}$  according to the linear form of Langmuir isotherm is showed at Figure 6. From this latter, the theoretic values such as  $q_m$  and  $K_L$  are calculated.

Table 2 summarizes the constants of the Langmuir, Freundlich and Temkin isotherms obtained from the slope and the interception of the plots of each isotherm at different temperatures.

**Table 2.** Parameters of different adsorption models for system MB / WS

T [°C]	Freundlich			Langmuir				Temkin		
	$K_F$ [mg <sup>1+1/n</sup> ·g <sup>-1</sup> ·L <sup>-1/n</sup> ]	1/n <sub>F</sub>	R <sup>2</sup>	q <sub>m</sub> [mg·g <sup>-1</sup> ]	K <sub>L</sub> [L·g <sup>-1</sup> ]	R <sup>2</sup>	R <sub>L</sub>	K <sub>T</sub> [L·g <sup>-1</sup> ]	B <sub>T</sub> [J·mol <sup>-1</sup> ]	R <sup>2</sup>
20	26.483	0.013	0.996	28.329	1.312	0.996	0.071	89.772	8.180	0.648
30	57.945	0.014	0.991	62.500	1.194	0.995	0.016	75.786	3.274	0.848
40	79.218	0.015	0.998	85.470	1.125	0.999	0.007	55.926	1.853	0.938

**Figure 6.** Linearization of the Langmuir equation for adsorbing MB / WS  
pH 6,  $C_0=120 \text{ mg}\cdot\text{L}^{-1}$ ,  $V=300 \text{ mL}$ , and  $m=1 \text{ g}$ 

From Table 2, the values of  $1/n_F$  were found to be less than 1. The low value of the linear correlation coefficient,  $R^2$ , indicated the unsuitability of Temkin isotherm model. The values of  $R^2$  for Freundlich model (0.996, 0.991, and 0.998 at 20, 30, and 40 °C, respectively) were high, indicating that this model can be used to characterize the equilibrium adsorption. However, Freundlich model was not the best model in this study. Langmuir models were fitting well with the isotherm data at various temperatures with the highest  $R^2$  values, compared to Temkin and Freundlich models.

The Langmuir fit is consistent with strong monolayer sorption onto specific sites. The maximum adsorption capacities ( $q_m$ ) of wheat straw for dye was 28.329, 62.50, and 85.47  $\text{mg}\cdot\text{g}^{-1}$  at 20, 30, and 40 °C, respectively. The similar phenomena are also observed in adsorption of textile dyes onto the filamentous green algal *Spirogyra* sp [20].

The  $R_L$  values were found to be less than 1 and greater than 0 for all experiments carried out at different initial concentrations and temperatures (Table 2). It is found that the adsorption of MB on wheat straw is a favorable phenomenon. Thus, wheat straw seems to have a good affinity for dye removal and its adsorption capacity increased as the temperature increases.

Similar results were found for the adsorption of MB onto wheat shells [35]. According to the  $R_L$  values, all the systems correspond to favorable adsorption processes (Table 2). The values tended toward zero, representing the ideal irreversible case, rather than toward unity, representing the completely reversible case [43].

By comparison of the results obtained in this study with those in the previously reported works (Table 3) on adsorption capacities of various low-cost adsorbent in aqueous solution for MB, it can be stated that our findings are extremely good.

**Table 3.** Previously reported adsorption capacities of various adsorbents for MB

Adsorbents	q [mg·g <sup>-1</sup> ]	Ref.
Yellow passion fruit	44.70	[44]
Teak tree bark	333.3	[45]
Cherry saw dust	39	[46]
Peanut hull	68.03	[47]
Banana peel	20.8	[42]
Sugarcane bagasse	34.20	[48]
Banane andorange peels	31.25	[49]
Sugarcane bagasse	96.56	[50]
Wheat shells	21.5	[35]
Wheat straw	86.45	This study

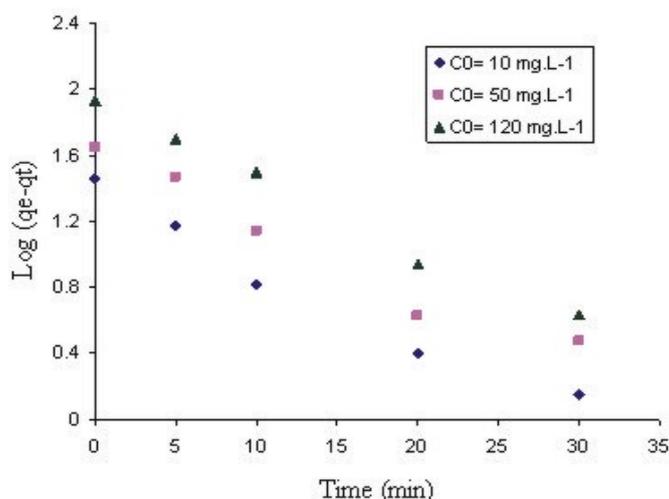
### Application of kinetics models

The kinetic parameters for dye adsorption presented in Table 4 were calculated from plots of  $\log(q_e - q_t)$  vs  $t$  (Figure 7), and the plots of  $t/q_t$  vs  $t$  (Figure 8).

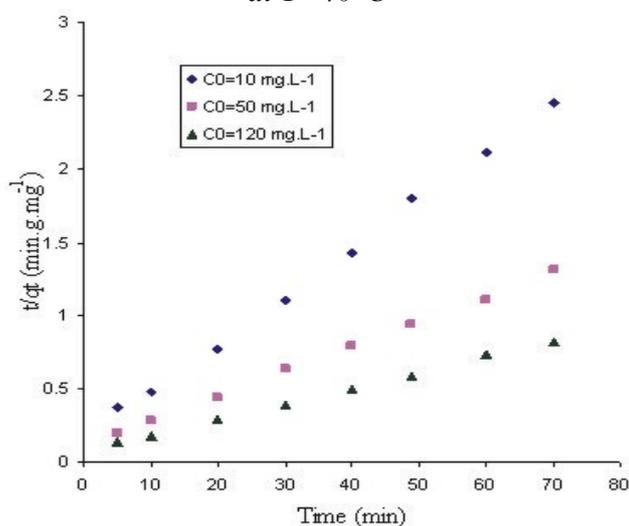
**Table 4.** Pseudo - first - order and Pseudo - second - order kinetic parameters for the adsorption of MB onto WS

	MB [mg·L <sup>-1</sup> ]	10	50	120
<b>Pseudo-first-order kinetic model</b>	$q_{e, \text{exp}}$ [mg·g <sup>-1</sup> ]	28.5	45	86.45
	$q_{e, \text{cal}}$ [mg·g <sup>-1</sup> ]	23.47	41.34	83.79
	$K_1$ [min <sup>-1</sup> ]	0.101	0.100	0.103
	$R^2$	0.968	0.959	0.990
	SSE [%]	22.58	24.75	20.65
<b>Pseudo-second-order kinetic model</b>	$q_{e, \text{cal}}$ [mg·g <sup>-1</sup> ]	30.58	59.17	93.46
	$K_2$ [g·mg <sup>-1</sup> ·min <sup>-1</sup> ]	0.007	0.002	0.001
	$R^2$	0.998	0.999	0.999
	SSE [%]	14.75	12.5	16.7
<b>Intraparticle diffusion</b>	$K_{\text{dif}}$ [mg·g <sup>-1</sup> ·min <sup>-1/2</sup> ]	4.612	7.486	14.615
	C	2.79	4.18	5.41
	$R^2$	0.931	0.900	0.944

The results of Table 4 show that the second-order rate constant  $k_2$  decreased with increasing concentrations. The correlation coefficients for the second-order kinetic model were between 0.998 and 0.999. Moreover, the experimental  $q_{e(\text{exp})}$  values agree well with the calculated ones. On the other hand, the correlation coefficients for the pseudo-first-order kinetics ( $0.959 < R^2 < 0.990$ ) were lower than that from pseudo second-order one.



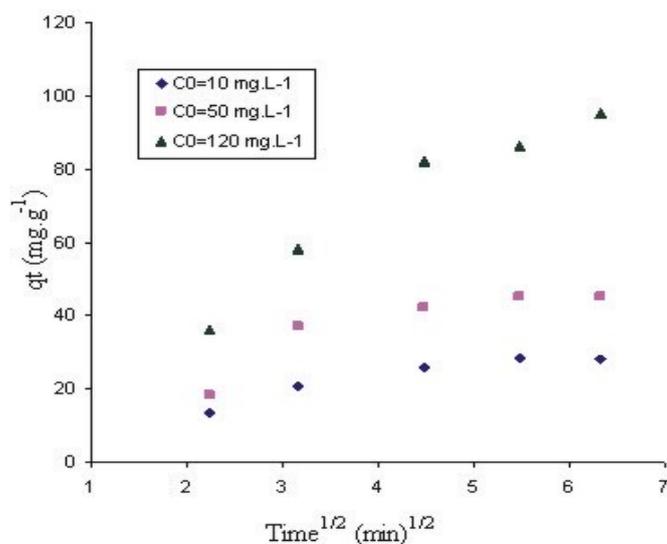
**Figure 7.** Linearization of the kinetic model of pseudo-first-order for (MB/WS), at  $T=40^{\circ}\text{C}$



**Figure 8.** Linearization of the kinetic model of the pseudo-second-order for (MB/WS), at  $T = 40^{\circ}\text{C}$

These results indicate that the adsorption system of dye obeyed a pseudo-second-order kinetic model. The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism. Similar phenomena have been observed in direct dyes onto orange peel [51], the sorption of MB onto rice husk [52], adsorption of basic dyes onto pumice powder [53] removal of MB from perlite [54] and MB on wheat shells [35].

The values of intercept give an idea about the boundary layer thickness, i.e., the larger the intercept, the greater the boundary layer effect [55]. The intraparticle rate constants calculated from Figure 9 are 4.612, 7.486, and 14.615  $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$  at 10, 50, and 120  $\text{mg}\cdot\text{L}^{-1}$ , respectively. From Table 4, it is observed that  $K_{\text{dif}}$  increased with increasing initial concentrations.

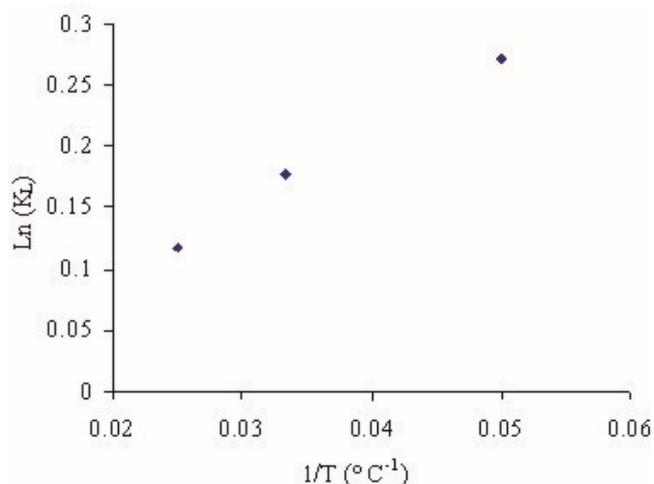


**Figure 9.** Application of simplified model intraparticle diffusion for the adsorption of MB on WS,  $T = 40^{\circ}\text{C}$

Kavitha *et al.* [56] reported that on the diffusion intraparticle for the methylene blue/Vitex negundo Stem system, the value of  $K_{\text{dif}}$  is equal  $1.59 \text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ . So we note that the coefficient  $K_{\text{dif}}$  ( $14.615 \text{ mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1/2}$ ) is 9 times greater than that of  $K_{\text{dif}}$ , found by Kavitha *et al.* [56] to the concentration  $C_0 = 125 \text{ mg}\cdot\text{L}^{-1}$  at  $T = 40^{\circ}\text{C}$ .

### Thermodynamic parameters

The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  can be determined from the slope and intercept of the plot between  $\text{Ln } K_L$  vs  $(1/T)$  (Figure 10). The values of  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ , and  $\Delta S^{\circ}$  for the biosorption of MB onto wheat straw at different temperatures (20, 30 and  $40^{\circ}\text{C}$ ) are given in Table 5. The negative values of Gibb's free energy changes approve a spontaneous nature of biosorption.



**Figure 10.** Relationship between Langmuir sorption equilibrium constant and temperature for MB / WS,  $C_0 = 120 \text{ mg}\cdot\text{L}^{-1}$

**Table 5.** Thermodynamic parameters for the adsorption of MB onto WS at different temperatures

T [°C]	$\Delta G^{\circ}$ [kJ·mol <sup>-1</sup> ]	$\Delta H^{\circ}$ [kJ·mol <sup>-1</sup> ]	$\Delta S^{\circ}$ [J·mol <sup>-1</sup> ·K <sup>-1</sup> ]
20	-13.775	-13.850	-0.255
30	-13.772		
40	-13.770		

The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$ , for the sorption processes are calculated to be -13.850 kJ·mol<sup>-1</sup> and -0.255 J·mol<sup>-1</sup>·°C<sup>-1</sup>, respectively. The negative  $\Delta G^{\circ}$  values indicates the feasibility and spontaneous nature of the adsorption process with a high preference of MB on WS, the negative  $\Delta H^{\circ}$  value suggests the exothermic nature of adsorption and the negative  $\Delta S^{\circ}$  value suggests a decrease in the randomness at solid - solution interface during the biosorption of dye on WS [30].

The growth temperature promotes mobility ions and dye produce a swelling effect of the internal structure of the wheat straw. It will also allow the dye molecules to penetrate further. Therefore, the adsorption capacity will depend largely on the chemical interaction between functional groups on the adsorbent surface and the adsorbed molecules (which should increase with increasing temperature). This can be explained by an increase in the rate of diffusion of the adsorbate in the pores [57]. The  $\Delta G^{\circ}$  values obtained in this study for the MB are < -10 kJ·mol<sup>-1</sup>, which indicates that physical adsorption was the predominant mechanism in the sorption process [58].

Boudechiche *et al.* [41] have reported that the values of  $\Delta G^{\circ}$  for the adsorption of the reactive dye on *L. cylindrica* were found to be -5,428, -4,912 and -4,396 kJ·mol<sup>-1</sup> for methylene blue at 20, 30 and 40 °C, respectively. These values are 3 times lower than  $\Delta G^{\circ}$  for our study at temperatures of 20, 30 and 40 °C. The adsorption of both processes is spontaneous.

## CONCLUSION

This study shows that wheat straw, an abundant natural source, can be used effectively and efficiently for the removal of synthetic dye (MB) from aqueous solutions. Equilibrium data were fitted to Langmuir, Freundlich, and Temkin isotherms, and the equilibrium data were best described by the Langmuir isotherm model ( $R^2 = 0.996$ ), with a maximum monolayer adsorption capacity of 86.45 mg·g<sup>-1</sup>, at 30 min. The adsorption kinetics was best described by the pseudo-second-order ( $R^2 = 0.999$ ).

The thermodynamic parameters for the adsorption of dye MB onto WS were also determined. The negative value of  $\Delta G^{\circ}$  confirms the feasibility and the spontaneous nature of the adsorption process and physical reaction.

The negative value of  $\Delta S^{\circ}$  shows the decreased randomness at the solid - solution interface during adsorption, and the negative sign of  $\Delta H^{\circ}$  indicates that the adsorption process is exothermic.

Therefore, the potential use of wheat straw for industrial wastewater treatment is real and represents interesting prospects to investigate, particularly for solutions containing organic species at very low concentrations.

## NOMENCLATURES

MB	Methylene blue
WS	Wheat straw
SEE	Sum of squared errors
vs	Versus

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