Removal of Methylene Blue from Aqueous Solution by Tunics of the Corm of the Saffron

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ABSTRACT: *Removal of Methylene Blue (MB) from aqueous solutions was investigated using low-cost, natural, and eco-friendly biosorbent, Tunics of the Corm of the Saffron (TCS). Effect of various parameters including pH, contact time, adsorbent dose, initial dye concentration, and temperature on the adsorption was studied. TCS was characterized using SEM, TGA, and DTA. The adsorbent surface functional groups were identified with Fourier Transform InfraRed (FT-IR)spectroscopy. pHpzc of TCS was determined (5.8). The adsorption data of MB ontoTCS followed the Langmuir isotherm with a biosorption capacity of 137mg/g. The kinetic data were evaluated using pseudo-first-order and pseudo-second-order model equations and the data were fitted well with the pseudo-second-order kinetic model ($R^2>0.99$). Thermodynamic parameters revealed that the adsorption process was feasible, spontaneous, and exothermic ($\Delta H<0$). The findings of the present study indicated that TCS can be successfully used for the removal of MB from an aqueous solution.*

KEYWORDS: *Tunics of saffron corm; Adsorption; Isotherm; Kinetic; Thermodynamic.*

INTRODUCTION

Water pollution is considered a serious menace to the environment, especially to human health [1]. Colored effluent can affect the photosynthetic processes of aquatic plants, reducing oxygen levels in water [2]. Dyestuff industries produce millions of tons of colored effluents which cause adverse effects on the environment [3]. Methylene Blue (MB) is an example of these dyes. It is a heterocyclic aromatic chemical compound having dimethylamino groups in its structure [4]. MB is basic and cationic dye. This dye can cause serious problems in the environment [5]. Due to the presence of the benzene rings in the structure of this dye, it causes to allergies, dermatitis, skin irritation and cancer [6, 7]. Hence the need to remove this dye from industrial and other effluents.

Many physical, chemical and biological methods have been developed to remove pollutants from aqueous solution, such as coagulation and flocculation [8], membrane separation [9], activated carbon adsorption [10] electrochemical removal [11], photochemical degradation [12], biological degradation [13], and adsorption [3]. Among several chemical and physical methods, the adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater [14]. However, the elimination of organic

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pollutants by adsorption onto this material is an expensive process because of the high cost of the adsorbent and its regeneration [15]. In this context, there are much research concerning other adsorbents especially those made up of inexpensive materials and locally available in abundant quantities [16]. The use of natural biomaterials is a promising alternative due to their relative abundance and their low commercial value.

This study explores the possibility of utilizing tunics of saffron corm as low-cost biomaterial for the removal of methylene blue dye from polluted wastewater. The aim of this study was also to valorize the tunics of saffron corm, which is only an agricultural waste.

EXPERIMENTAL SECTION

Materials and instruments

All chemical compounds used were analytical reagent grade and supplied by Sigma Aldrich. Stock solutions of the test reagents were made by dissolving Methylene Blue, in distilled water. The structure of this dye is shown in Fig. 1.

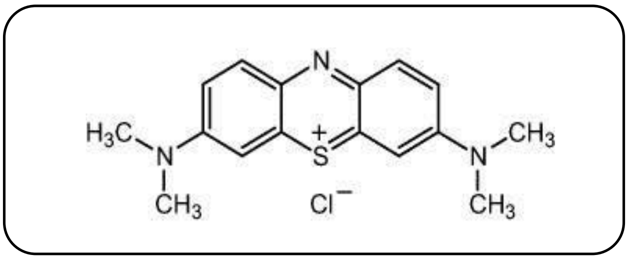

Fig. 1: The structure of methylene blue.

The tunics of the corm of the saffron (Fig. 2) used in the present investigation were collected locally from Taliouine, Morocco, and extensively washed with tap water to remove water-soluble impurities and other foreign particles.

Fig. 2: The tunics of the corm of the saffron.

The biomass was dried in the sun for two days, ground into fine material and then washed several times with distilled water before drying in an oven at 90°C for 24 hours. The dried biosorbent was then cut into small pieces and powder using a domestic mixer and was stored in a glass bottle for further use without any pre-treatment.

Adsorption experiments

Effect of contact time

This study aims to determine the time value from which the adsorption reaction reaches equilibrium. For this reason, the influence of the time was studied at pH of the solution without adjustment, at room temperature, at a concentration of 100mg/L of MB, with a mass of 90mg of adsorbent and stirring speed of 150 rpm. The effect of the time was studied by varying the time between 5 and 120min.

Effect of the mass

The effect of the mass to remove the methylene blue from the aqueous solution was studied by varying the mass between 20 and 120mg, at the pH of the solution without adjustment, at room temperature, at a concentration of 100mg/L, and stirring speed of 150 rpm.

Effect of initial pH of dye solution

Effect of pH on dye removal at pH 2.8, 3, 3.5, 4.5, 5.7, 6, 7, 8.5, 9 and 10, mass of 90mg of TCS, initial dye concentration 100 mg.l^{-1}, room temperature, stirring time 60min and stirring speed of 150 rpm were studied.

Effect of temperature and initial concentration on the adsorption

The influence of the temperature of (MB) was studied from different temperatures (21, 31, 41, 50 and 60 °C), at the pH of the solution without adjustment, at different dye concentration (100, 200, 300, 400 and 500 mg/L) of MB, with a mass of 90mg of TCS, stirring time 60min and stirring speed of 150 rpm.

Point of zero charge (pHpzc)

The pH point zero charges (pHpzc) corresponds to the pH value at which the net charge of the adsorbing surface is zero. For the determination of pHzpc of the adsorbent, 50 mL of 0.01M NaCl solutions were taken in different

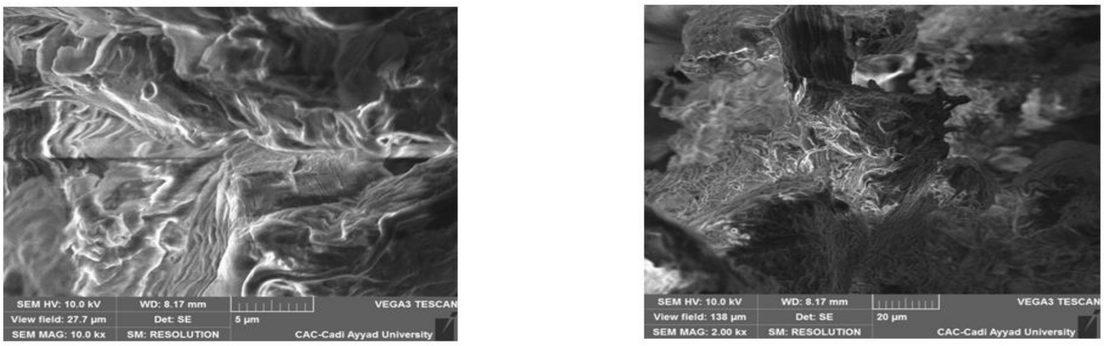

Fig. 3: Scanning electron microscopy of tunics of the corm of the saffron, a (5μm) and b (20μm).

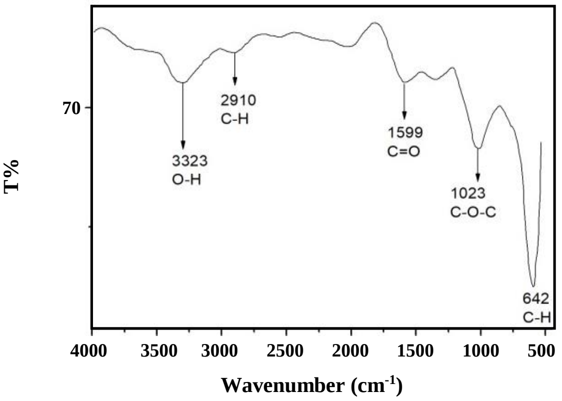

Fig.4: Infrared spectrum of the tunics of the corm of saffron.

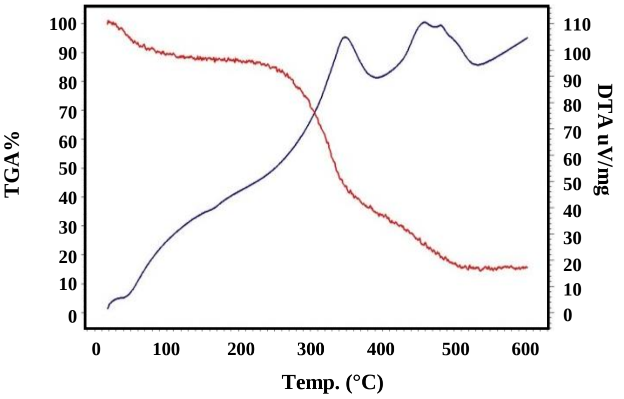

Fig. 5: TGA and DTA.

Erlenmeyer flasks of 250 mL and 90 mg of adsorbent was introduced in each of them. Now the pH values of these solutions were adjusted in 2 to 10 range by 0.1 M HCl/NaOH solutions [17]. These flasks were kept for 48 h and the final pH of the solutions were measured.

RESULTS AND DISCUSSION

Characterization

SEM micrographs for samples were obtained with a SUPRA 40 VP COLONNE GEMINI ZEISS using a maximum voltage of 20 kV. The SEM images of the Tunics of the corm of the saffron are shown in Fig. 3. It was observed the presence of the elongated fibers and vessels which contains the fibers. These forms would be very interesting for adsorption because of the amount of cavities and pores observed.

Also, FT-IR analysis was used for the determination of the presence of specific functional groups on the adsorbent Fig. 4. According to Fig. 4, peaks at 3323, 2910, 1599, 1023 and 642 (cm^{-1}) correspond to functional groups of OH, C-H, C=O, C-O-C, and C-H, respectively[18-20].

The TGA-DTA analysis of the material is presented in Fig. 5. The weight loss occurred in the following four steps: the first in the temperature range of 22–200 °C (15%) is due to the loss of physically adsorbed water. The second loss from 200 to 350 ° C (50%), which corresponds to the thermal degradation of cellulose [21]. The third exothermic loss between 350 to 400 °C, corresponds to the degradation of hemicelluloses [21]. The fourth loss between 400 ° C to 550 ° C (10%), which corresponds to the decomposition of lignin [22]. The rest mass at the temperature above 500°C may correspond to basic salt and ashes.

The results obtained are illustrated in Fig. 6. A rapid increase in the adsorption capacity of the dye and the percentage of fixation takes place within a few minutes, due to the adsorption of methylene blue to the surface of the particles of the adsorbent. In the second stage,

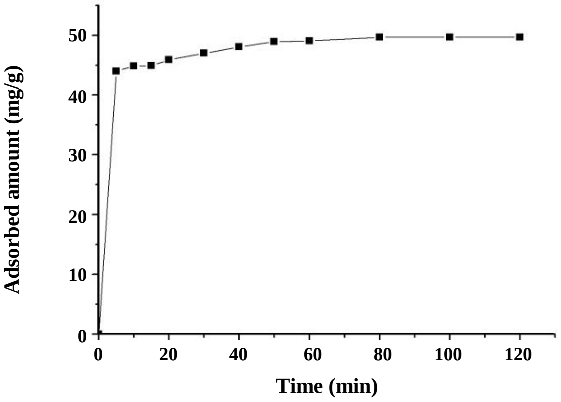

Fig. 6: Effect of contact time on adsorption.

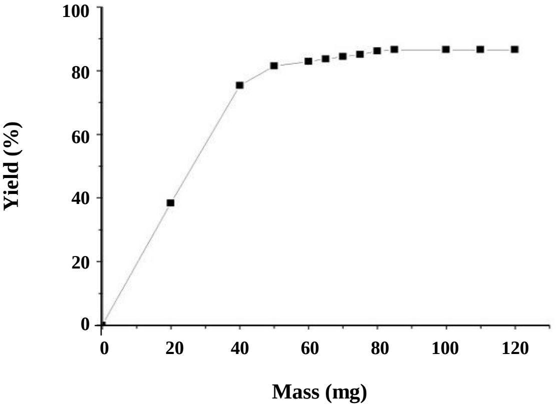

Fig. 7: Effect of mass on adsorption.

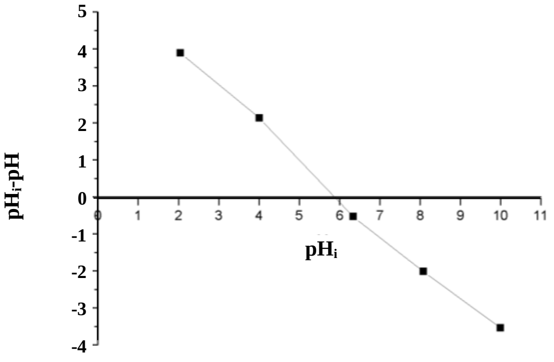

Fig. 8: Point of zero charge (pHpzc).

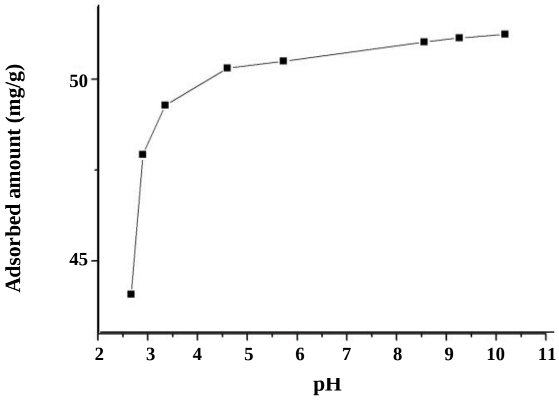

Fig. 9: Effect of pH on MB adsorption by TCS.

the occupation of deep adsorption sites requires the diffusion of the adsorbate within the micropores of the adsorbent. A second, slower phase is thus observed. After this phase, a saturation bearing is observed.

Effect of the mass on dye removal

The mass of adsorbent is one of the parameters that strongly affect the adsorption process. Fig. 7 indicated that with an increase of mass of adsorbent, adsorption efficiency increased. The increase in adsorption efficiency can be explained by the increase in the number of active sites added by (TCS). Fig. 6 shows that a mass of 90 mg of (TCS) is capable to fix a maximum of (MB) of the order of 88%.

Influence of the pH

Adsorption can also be explained on the basis of electrostatic interaction between the ionic dye molecule and the charged biosorbent substrate. At the considered pH range, 3.5 –10.5, the biosorbent was negatively charged for pH values superior to the pHpzc and positively charged for pH values below the pHpzc, ~ 5.8 (Fig. 8).

The low values of the adsorbed amount were measured at slightly acidic pH (Fig. 9). Electrostatic interactions between the biosorbent and the (MB) cation at pH < 5.8 (pHpzc) did not favor adsorption. At pH> pHpzc, the surface of the biomass is negatively charged. The mechanism which might be envisaged for the removal of (MB) was thus the electrostatic interactions between the negative adsorption sites of the biosorbent ($-COO^-$) and the positively charged dye [23].

Effect of temperature and initial concentration on the adsorption

Fig. 10 shows a decrease in adsorbed amount with increasing temperature, indicating that the reaction is

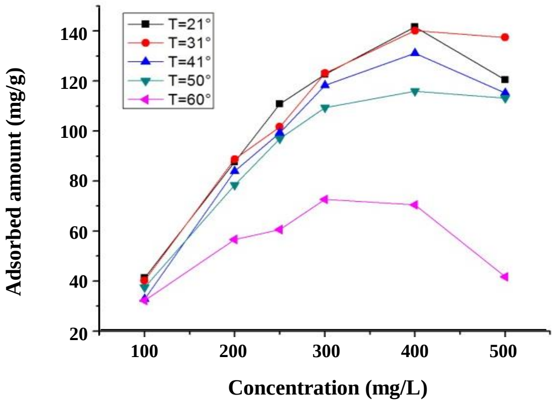

Fig. 10: Effect of temperature and initial concentration on the adsorption.

exothermic and lead under these conditions to physical adsorption [24].

According to bibliographic searches, the adsorption process is highly dependent on the initial concentration of the dye [25]. As shown in Fig. 10, for the temperature 21 °C with increasing initial (MB) concentration from 100 to 500 mg/L, the amount of dye adsorbed by TCS increases sharply from 40 to 136 mg·g^{-1}. It can be ascribed that an increase in adsorbate concentration leads to an increase in mass gradient between the aqueous and solid phases, which acts as a driving force for the transfer of dye molecules from the bulk solution to the particle surface [26].

Equilibrium and kinetic studies

The amount of dye adsorbed at equilibrium onto the tunics of saffron corm was calculated by the following mass balance relationship:

$$Q_{ads} = \frac{(C_0 - C_{eq})}{m} \times V \tag{1}$$

Where *Co* and C_{eq} are the initial and the equilibrium dye concentrations (mg/L), *V* is the volume of solution (L) and *m* is the amount of biomass used[23].

Percent dye removal (%) was calculated using the following equation [23];

$$R(\%) = \frac{(C_0 - C_{eq})}{C_0} \times 100 \tag{2}$$

Equilibrium data, commonly known as adsorption isotherms, describes how adsorbates interact with adsorbents and hence are critical in optimizing the use of adsorbents and provide information on the type and the capacity of the adsorbent.

The Langmuir isotherm model assumes uniform energies of adsorption onto the adsorbent surfaces. Furthermore, the Langmuir equation is based on the assumption of the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent where all adsorption sites are identical. The Langmuir equation is given as follows [27]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

Where K_L (L.mg) is the Langmuir constant and q_m (mg/g) is the maximum amount of adsorbate retained on the support used.

The essential characteristics of the Langmuir isotherm can be expressed in terms of an equilibrium dimensionless parameter (R_L), which is defined by:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

The R_L value indicates the sorption isotherm mode of the process if the process is so unfavorable (R_L>1) or linear (R_L=1), or positive (0<R_L<1) or irreversible (R_L= 0) [16].

The Freundlich isotherm model assumes neither homogeneous site energies nor limited levels of adsorption. The Freundlich model is shown to be compatible with the exponential distribution of active centers, characteristic of heterogeneous surfaces. The linearized form Freundlich equation is (5) [28]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

Where K_F (mg/g) is the Freundlich constant and *1/n* is the intensity of adsorption [28].

The parameters characteristic of each model is summarized in Table 1.

The high value of the regression correlation coefficient of Langmuir adsorption isotherm (R^2=0.94) was obtained, which indicated a good agreement between the experimental values (135mg/g) and isotherm parameters (136.6 mg/g), and also confirmed the adsorption of MB onto tunics of saffron corm followed the Langmuir adsorption isotherm.

To investigate the adsorption kinetic, pseudo-first-order and pseudo-second-order kinetic models have been applied.

Table 1: The characteristic parameters of adsorption models.

Langmuir			
K_L	q_m	R_L	R^2
$3,69.10^{-3}$	136.98	0.35-0.73	0,945
Freundlich			
K_F	1/ n	R^2	
1.7	0.728	0.835	

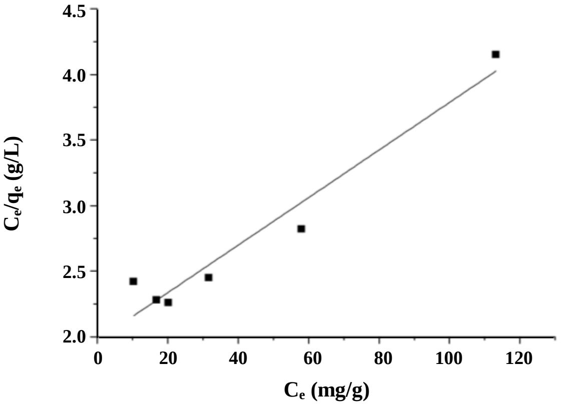

Fig. 11: Langmuir isotherm.

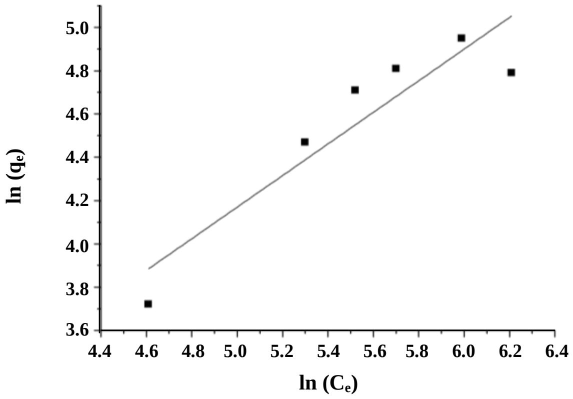

Fig. 12: Freundlich adsorption isotherm.

The linear equation for the pseudo-first-order of the kinetic model is expressed as [29]:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303} t \tag{6}$$

Where K_1 (min^{-1}) is the rate constant of the pseudo-first adsorption, q_e and q_t (mg/g) is the adsorption capacities at equilibrium and at time t (min), respectively. The rate constants k_1, q_e and correlation coefficients R^2 were calculated using the slope and intercept of plots of log (q_e–q_t) versus t (Fig. 13).

The pseudo-second-order rate expression is linearly expressed as [29]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

Where q_e and q_t (mg/g) are the adsorption capacity at equilibrium and time t, K_2(g/mg.min) is the rate constant of the pseudo-second-order adsorption. The rate constants K^2, q_e and correlation coefficients R^2 were calculated from the linear plots of t/q_t versus t (Fig. 14).

The calculated value (50 mg/g) of q_e obtained from Eq.(7) complied well with the experimental value (49mg/g) and also R^2(Table2) value was significant in this case, which showed that adsorption kinetics followed a pseudo-second-order kinetic model.

Thermodynamic studies

The thermodynamic parameters: standard Gibbs free energy change ΔG, standard enthalpy change ΔH (kJ/mol)and standard entropy change ΔS (J/mol.K), were calculated to evaluate the feasibility and nature of the adsorption process. The standard Gibbs free energy change ΔG (kJ/mol) of the adsorption reaction can be determined from the following equation[30]:

$$\Delta G = -RT \ln K_d \tag{8}$$

Where *T* is the absolute temperature, *R* is the universal gas constant, and K_d is the thermodynamic equilibrium constant. The K_d value was calculated using the following equation[30]*:*

$$K_d = \frac{C_a}{C_e} \tag{9}$$

Where C_a (mg/L) and C_e (mg/L) are the equilibrium concentrations of MB on the adsorbent and in the solution[30].

The relation between ΔG, ΔH, and ΔS can be expressed by the following equations [30]:

Table 2: Kinetic parameters.

Pseudo-first-order model			
q_e ex	q_e cal	K_1	R^2
49.69	8.15	0.042	0.970
Pseudo second order model			
q_e ex	q_e cal	K_2	R^2
49.69	50	0.015	0.999

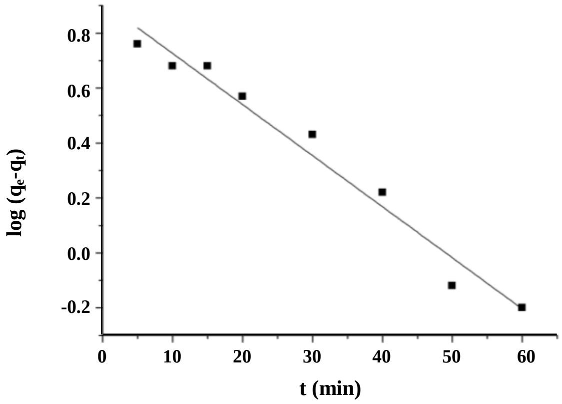

Fig. 13: Pseudo-first-order model.

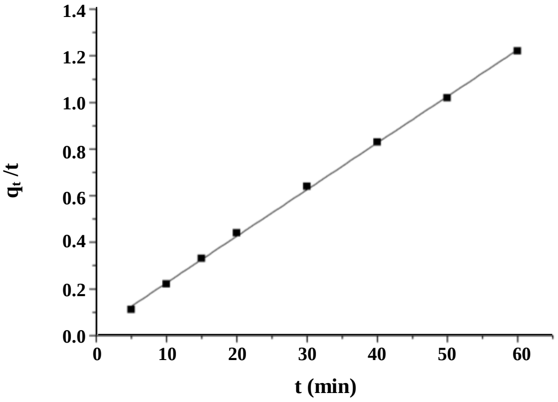

Fig. 14: Pseudo-second-order model.

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (11)$$

The values of *ΔH* and *ΔS* were calculated from the slope and intercept of the plot of ln (K_d) versus 1/T, (Fig. 15),and the thermodynamic adsorption parameters are summarized in Table 3.

The negative values of the all estimated ΔG indicate the adsorption process is spontaneous and thermodynamically favorable. The obtained results between -20 and 0 kJ/mol suggests that the related adsorption reaction proceeds through the physisorption mechanism[30].

The positive value of ΔS indicates the affinity of biosorbent to methylene blue is increased randomly at the adsorbent-adsorbate interface during adsorption. The negative value of ΔH reflects that adsorption is an exothermic process[29].

Comparison of the MB adsorption capacity of various adsorbents reported in the literature

The maximum adsorption capacity (q_m) for the removal of (MB) onto Tunics of the saffron corm as well as the other adsorbents reported in the literature are listed in Table4.

Comparing the result obtained for (qm) with those of other adsorbents reported, it is very clear that this new biomass is an effective adsorbent for the removal of (MB) aqueous solutions. Thus, it may be a potential alternative for removing dyes from industrial and other effluents.

CONCLUSIONS

This study shows that the adsorption of the methylene blue dye onto the studied biomaterial was highly dependent on contact time, initial dye concentration, adsorbent dose, and temperature.

The study also showed that:

- The Langmuir isotherm model better adapted to the experimental data with high correlation coefficients ($R^2 = 0.94$).
- The adsorption was favorable, spontaneous, exothermic and followed a pseudo-second-order kinetics for all the concentrations studied ($R^2 = 0.99$).
- The removal percentage of methylene blue from the colored waters is greater than 96%.

Table 3: Thermodynamic parameters.

T (K)	ΔG	ΔH	ΔS	R^2
293	-4.31	-0.837	11.88	0.95
303	-4.44			
313	-4.56			
323	-4.66			
333	-4.79			

Table 4: Comparison of maximum monolayer biosorption capacity of (MB) by some biosorbents.

Biosorbent	q_m [mg.g^{-1}]	Reference
Zizyphus lotus	44.3	[31]
PinusDurangensis	102	[28]
Tea Waste	32.25	[5]
Dehydrated Maize Tassels	3.08	[32]
Tunics of the corm of the saffron	136.98	This study

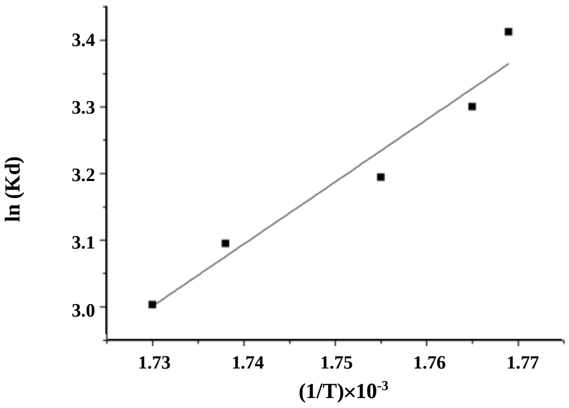

Fig. 15: ln (K_d) variation with 1 / T.

Therefore, it can be concluded that saffron corm tunics can be used as a cost-effective alternative environmentally friendly alternative material for the removal of dyes from polluted wastewater without laborious pretreatment

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