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**Walnut bloom powder as a waste-based sorbent for cationic dyes
removal: equilibrium, kinetic, and thermodynamic studies**

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Draft

Abbreviation: WB: walnut bloom, SEM: scanning electron microscopy, XRD: X-ray diffraction, BET: Brunauer-Emmett-Teller, FTIR: Fourier transform infrared

Abstract

In the present study, for the first time, walnut bloom (WB) powder was used as a natural and economic sorbent for the removal of methylene blue (MB) from an aqueous solution. This new biosorbent was characterized using the following techniques: scanning electron microscopy (SEM), X-ray diffraction (XRD), COHNS, BET (Brunauer-Emmett-Teller) analysis and Fourier transform infrared (FTIR) spectroscopy. MB removal efficiency and its adsorption onto WB powder were tested in a batch system by varying parameters such as initial dye concentration, contact time, pH, temperature, and dosage of biosorbent in which the removal percentages of ~92% was achieved under the optimum conditions. Equilibrium data and adsorption isotherms fitted well with the Langmuir model ($R^2 = 0.999$, $0 < R_L < 1$) with a maximum monolayer adsorption capacity of 46 mg g^{-1} . The chemical kinetics of MB adsorption followed the pseudo-second-order model. Also, the magnitude of thermodynamic functions identified the removal of MB. ΔH° of $-7.32 \text{ kJ mol}^{-1}$ and ΔS° of $-4.32 \text{ kJ mol}^{-1}$ indicated the spontaneity, exothermicity, and favorability of the adsorption process at room temperature.

Keywords: Methylene blue, Removal, Walnut bloom powder

Introduction

3,7-bis(Dimethylamino)-phenothiazine-5-ium chloride or Methylene Blue (MB) is a heterocyclic aromatic compound that is widely used in a range of different fields, especially in the textile industry ¹. Since most of the dyes like MB or their metabolites are toxic and some of them are considered carcinogenic for human health, treating the dye wastewater before releasing it into the groundwater is necessary ². The control of water pollution has become increasingly important in recent years, so the physical and/or chemical and biological processes for color removal such as membrane filtration ³, reverse osmosis ⁴, coagulation/flocculation ⁵, ion exchange ⁶ and Fenton reagents ⁷ are used that are not economically feasible. The adsorption of dye molecules onto a substrate, known as the simple as well as effective and low-cost method, is one of the best treatment methods for MB removals ⁸. The choice of an appropriate adsorbent plays a considerable role in the removal process. The use of different biosorbent prepared from agricultural by-products as an alternative low-cost adsorbent in the removal of MB has been intensively studied in the literature ^{1,9}. The adsorption is an excellent alternative selection needing no additional pretreatment step before application. Results of experiments in the literature review have shown high adsorption capacities of the various affordable adsorbents for MB removal ¹⁰. While some adsorbents such as peanut shell ¹¹, coconut fiber ¹², Alfa grass ¹³, sugarcane bagasse ¹⁴, and pine sawdust ¹⁵ are used without any modification, some others are utilized subsequent to diverse treatments including phosphoric acid treatment ¹⁶, magnetization ¹⁷, ZnCl₂ activation ¹⁸, etc. or pretreatment sorbents by low-cost materials including Rosa damascene ⁸ cellulose and its salts ¹⁹ and oak wood ²⁰.

This study aims to introduce Walnut bloom (WB) as a stable adsorbent to eliminate the contaminant from wastewater, and we used this sorbent for the removal of cationic dyes. The adsorption properties of the proposed biosorbent were evaluated by investigating the adsorption

of MB dye from an aqueous solution. WB, an inexpensive renewable natural resource found in a great amount in nature, remain unused upon production on the ground and after the pollination operation. To the best of our knowledge, no study has been reported until now to evaluate the efficiency of WB waste-based material for dye removal from aqueous solutions, and it was used without any pretreatment. In addition, some of its advantages such as being environment-friendly, locally-available and inexpensive have paved the way toward the use of WB waste-based material for the first time as an effective sorbent for cationic dye removal. Under the optimized condition (natural pH: 6-8, room temperature), WB powder was applied to MB removal by the batch system efficiently, and the removal percentages of ~92% were achieved. Adsorption isotherms fitted well with the Langmuir model with a maximum monolayer adsorption capacity of 46 mg g⁻¹. Kinetic data can be well fitted by the pseudo-second-order model and thermodynamic data indicated that the adsorption was spontaneous, exothermic, and favorable at room temperature.

Experimental

Materials

MB as a model of cationic dye was purchased from Merck (Darmstadt, Germany) and used without further purification. The stock solution of the MB at a concentration of 500 mg L⁻¹ was prepared in distilled water, then the working solutions of dye were prepared by dilution of a stock solution using distilled water. Sodium hydroxide and hydrochloric acid were also provided from Merck Company (Darmstadt, Germany).

Preparation of WB sorbent

WB, generated from local walnut trees (Khosrowshah, Iran), was powdered and washed with sodium hydroxide (0.01 M) and distilled water until the filtrate turned colorless. WB was dried to constant weight in an oven at 60°C and prepared for adsorption tests after sieving to a

particle size of $<500\ \mu\text{m}$. Afterward, the WB powder was stored in polyethylene bottles and used without any physical or chemical treatment.

Instrument

The Fourier transform infrared (FTIR) spectra of WB were obtained with a vector 22 (Bruker, Ettlingen, Germany) FT-IR spectrometer using the KBr tablet in the scanning range of $400\text{--}4000\ \text{cm}^{-1}$ prior and after MB adsorption. The scanning electron microscopy (SEM) images were obtained using scanning electron microscope model Mira 3 Tescan (TESCAN Electron Microscopy Inc., Brno-Czech Republic). X-ray powder diffraction (XRD) measurements were performed by employing a Bruker D8 Advance (Bruker AXS, Karlsruhe, Germany) instrument with a Cu-K α radiation source generated at 40.0 kV and 35.0 mA at room temperature. The specific surface area of WB was analyzed by a BEL instrument (model: BELSORP MINI II, Japan). CHNOS analysis for further characterization was studied by a FlashEA 1112 series, Thermo Finnigan analyser (Costa Rica). DLS (dynamic light scattering) device made by Microtrac (model: Nanotrac wave) with ability of measurement of zeta potential from -222 to 222 mV and determination of particle size range of 12 nm to 22 microns was used to measure the zeta potential and determine the pH_{pzc} . Absorption experiments were carried out by UV-Vis spectrophotometer model T80 at 664 nm. The pH of solutions was measured using a Metrohm 744 pH meter and the sorbent particles were separated from the liquid phase by centrifugation (Beckman model GS6, USA). Also, a stirrer and a Sartorius analytical balance (± 0.0001) were used for solutions' agitation and weighting, respectively.

Batch adsorption experiments

A specific amount of WB as a sorbent among 25 mL of dye solutions with various initial concentrations was added into a 50 mL beaker. The mixture was agitated on stirrer at the rate of 700.0 rpm at constant controlled temperature subsequently. At the end of each

experiment, the adsorption of the obtained supernatant solution was determined by a UV-visible spectrophotometer at λ_{max} of 664 nm to achieve the residual concentration of MB.

The obtained experimental data at various times, temperatures and concentrations were fitted to different models to calculate the kinetics and isotherm parameters of the adsorption process. The removal efficiency ($R\%$), and the amount of adsorbed dye per mass unit of the adsorbent at equilibrium, q_e (mg g^{-1}), were calculated through the following equations (Eqs. 1, 2):

$$(1) \quad R\% = \frac{(C_0 - C_e)}{C_0} \times 100$$

$$(2) \quad q_e = \frac{(C_0 - C_e) \times V}{m} \times 100$$

In these equations, C_0 and C_e are the initial and equilibrium dye concentrations (mg L^{-1}) respectively, m is the adsorbent mass (g) and V is the volume of solution (L).

Results and Discussion

Characterization of WB

The SEM images of the WB (Figure 1) show uniform layer size distribution in the range of <500 nm as well as homogeneous porosity and a scaly structure. XRD pattern of WB powder (Figure 2A) shows peaks at 2θ angles of 16 related to the layered planes without a regular crystal structure. Figure 2B and 2C represents the FTIR spectra of WB prior and after MB adsorption. Before MB adsorption, several peaks in the spectrum were observed, corresponding to –OH stretching (at 3421.7 cm^{-1}), C–H stretching (at 2924.91 cm^{-1}), C=O stretching (at 1718.11 cm^{-1}), C=C bending (at 1637.0 cm^{-1}), CH_2 deformation (at 1399.06 cm^{-1}), and –COO symmetric stretching (at 1102.67 cm^{-1}). However, upon MB adsorption, the shifts of bands toward the following wavenumbers were observed: –OH stretching (at 3422.80 cm^{-1}), C–H stretching (at 2922.70 cm^{-1}), CH_2 deformation (at 1384.53 cm^{-1}). The shifts of these bands, as

well as change in peak intensities associated with functional groups of WB, indicated MB adsorption ²¹ onto WB.

The specific surface area of the adsorbent is of particular importance since adsorption occurs at the surface. BET analysis was used to determine the specific surface area of the WB powder, the results of which proved the high specific surface area of the WB ($3.2 \text{ m}^2 \text{ g}^{-1}$ at 120°C for 2h). The higher the specific surface area, the higher the dye removal process. Finally, the chemical composition of the WB was determined by CHNS analysis, and the analysis of the results revealed 3.45% H, 56.55% O, 0% S, 36.95% C, and 3.05% N.

Adsorption studies

The process of adsorption is influenced by some factors including temperature, pH, contact time, and initial concentration of adsorbates. In this section, the adsorption of MB using WB powder was maximized by optimization of different parameters. In this regard, Spectrophotometric measurements were performed to detect the maximum wavelength of MB at 200-900 nm, the results of which showed the maximum absorption of photon energy at 664 nm. Therefore, the determination of experimental parameters influence was measured at 664 nm to minimize errors and to increase the accuracy.

Effect of adsorbent dose

Studies about the effect of adsorbents dose on the removal percentage (%R) of MB (Figure 3) revealed that the adsorption efficiencies improved with the increasing adsorbent dosages due to the availability of more active binding sites on the adsorbents. The maximum dye removal percentages were achieved in the case of using 25 mg of WB as the optimized values.

Effect of pH and pH_{pzc}

One of the most significant factors controlling the adsorption of dye on to adsorbent is the initial pH of the solution, which was adjusted to 2, 4, 6, 8 and 10 at the constant condition

of dye concentration, sorbent dosage, and contact time. When the initial pH of the dye solution rose from 2 to 8, the percentage removal increased from 60% to near 100% depending on the nature of the adsorbent. The results (Figure 3) showed that while the natural pH between 6 to 8 has the maximum removal ability, adsorption of MB on biosorbent tends slightly to decrease above and under this point; therefore, future experiments were followed in natural pH.

If the adsorbate becomes ionic, changes in the surface charge of the adsorbent can greatly affect the removal efficiency of the charged compound in the adsorption process. First, the pH_{pzc} point of the adsorbent was determined, which implies that the adsorbent surface charge will be whether positive when the pH of the solution is less than pH_{pzc} and is negative when it is greater than pH_{pzc} , respectively. Moreover, the neutral charge of the adsorbent surface at $\text{pH} = \text{pH}_{\text{pzc}}$ is observed. The WB's pH_{pzc} was obtained at about 1.5. This value describes the surface charge of WB is negative in pH more than pH_{pzc} (1.5) that leads to the more effective MB sorption in natural and basic solutions. Also, the presence of N atoms in the structure of WB helps the more affinity of it to the cationic MB adsorption. In acidic media, the H^+ ions in the solution increase and cover the adsorbent surface in a similar way. With the emergence of electrostatic repulsion between the surface of the adsorbent coated with H^+ ions and the cationic dye, the removal efficiency has decreased. Therefore, the removal percentage increases from $\text{pH}=2$ to $\text{pH}=7$ and decreases in alkaline pH. In alkaline media, due to the possible interaction between dye ions and hydroxide ions, the dye removal efficiency will reduce. Finally, based on the results, the best pH in terms of increased removal efficiency of MB was recognized to be 7.

Effect of contact time

As shown in Figure 3, the removal efficiency elevated from 78% to 91% through the increase of contact time from 10 to 50 min due to available sites of adsorbent, and after reaching equilibrium, removal percent remained constant as a result of rising in surface coverage of

adsorbent. The selected equilibrium time of 50 min for the MB adsorption on the WB, through the obtained experimental results, was used in the next experiments as the optimum contact time.

Effect of initial dye concentration

Removal efficiency is greatly dependent on the initial concentration of adsorbate. 25 mL of solutions with different initial concentrations of adsorbate (varied from 10 mg L⁻¹ to 100 mg L⁻¹) were treated onto the adsorbent to investigate the effect of the initial concentration. According to the results (Figure 3.), rising the initial MB concentration up to 80 mg L⁻¹ led to an increase in MB adsorption probably due to more contact of adsorbent sites with MB. However, the removal efficiency either remained constant or dropped with rising more the adsorbate concentration in the solution. The *qe* amount (mg g⁻¹) and percentage removal rate increased with an increase in the dye concentration. An initial concentration of 80 mg L⁻¹ was chosen for the following experiments because 92% of MB was removed in case of using it as the initial concentration.

Effect of temperature

The effect of temperature on the adsorption isotherms was investigated under isothermal conditions in the temperature range of 10-80°C. The experimental results (Figure 3) indicate that the dye removal extraction drops with a rise in temperature, indicating that the adsorption reaction was exothermic in nature. This study was used for calculating thermodynamic parameters.

Finally, after the optimization of parameters, the reusability of the WB sorbent was studied and the results represented no significant changes in the adsorption capacity of WB through six adsorption/desorption cycles. It is notable that the sorbent was washed with an acidic solution (0.01 N HCl) and water between cycles. However, the adsorption percentage of MB on the WB showed more than a 5 % change in the 7th cycle.

Adsorption isotherms

It is essential to study adsorption isotherms to acquire information about the nature of the MB interaction with adsorbents and to evaluate the applicability and efficiency of any new proposed adsorbent ²². Four important and conventional isotherm models like Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich isotherms are used for adsorption studies. To study the effect of temperature on the adsorption of MB, the adsorption isotherms of MB on WB were measured at constant temperatures.

The Langmuir model assumes that monolayer adsorption on a surface with a finite number of identical sites occurred with no interaction between the adsorbate molecules. In other words, all the sites are energetically equivalent, and no interaction between the adsorbed molecules happens ²³. R_L , separation factor, is a constant describing the adsorption properties of Langmuir isotherms derived from the following equation:

$$(3) \quad R_L = \frac{1}{1 + K_L C_0}$$

The values of R_L describe the shape of isotherm as it is expected irreversible for $R_L=0$, linear for $R_L=1$, favorable $0 < R_L < 1$ and unfavorable interactions of adsorbent-adsorbate pairs for $R_L > 1$ ²⁴. All of the R_L values in this study designates WB as a favorable adsorbent for MB adsorption. The Freundlich model is a semi-empirical equation based on the adsorption on a heterogeneous surface ²⁵. The Tempkin isotherm studies the adsorption heat between adsorbate and adsorbent ²⁶, and The Dubinin-Radushkevich model is often used to determine whether a sorption process is a chemical or a physical one ²⁷. Equations (4)–(7) are mathematical models corresponding to these four sorption isotherms, respectively.

$$(4) \quad \frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m}$$

Where C_e is the equilibrium concentration of dye solution (mg L^{-1}), q_e is the equilibrium capacity of dye on the adsorbent (mg g^{-1}), q_m is the maximum monolayer covered adsorption capacity of adsorbent (mg g^{-1}), and k_L is the Langmuir constant related to the adsorption energy.

$$(5) \quad \ln q_e = \ln K_f + \left(\frac{1}{n}\right) \ln c_e$$

Where k_F is Freundlich constant ($\text{mg}^{1-(1/n)} \text{g}^{-1} \text{L}^{1/n}$), n is the extent of deviation from linearity of the adsorption process that is used to determine the type of adsorption mechanism. The obtained value of n ($n > 1$) indicated a favorable and physical adsorption process of MB adsorbate on CFYM adsorbent.

$$(6) \quad q_e = B \ln A + B \ln C_e$$

Where $B = RT/b$ and b are Tempkin isotherm constant (J mol^{-1}), A is the equilibrium binding constant (L mg^{-1}) and B is a constant related to the sorption heat.

$$(7) \quad \ln q_e = \ln q_m - K_{DR} \varepsilon^2$$

Where q_e is the amount of the dye adsorbed per weight unit of the adsorbent (mg g^{-1}), q_m is D-R adsorption capacity, K_{DR} is a constant related to adsorption energy ($\text{mol}^2 \text{J}^{-2}$) and ε is the Polanyi potential obtained by the following equation (Eq. 8):

$$(8) \quad \varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right)$$

Adsorption isotherms of MB on WB as well as the calculated parameters of all investigated isotherms are summarized in Table 1. It is obvious that obtained correlation coefficient (R^2) using the Langmuir isotherm model was the highest among all isotherms that suggest fitting experimental data (Figure 4A) to the Langmuir model and monolayer adsorption of MB dye ions on the adsorbent surface.

Kinetic and thermodynamic studies

The kinetic of MB adsorption on the WB surface was studied for exploring the adsorption mechanism. The various kinds of kinetic models such as pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich were studied for investigating the kinetics of MB adsorption onto WB adsorbent at room temperature.

The following equation is the linearized equation of pseudo first-order kinetic ²⁸.

$$(9) \quad \log (q_e - q_t) = \log (q_e) - \frac{K_1 t}{2.303}$$

Where q_e and q_t are the amounts of adsorbed dye per unit of adsorbent (mg g^{-1}) at the equilibrium time and at a certain time, respectively and k_1 is the adsorption rate coefficient of the pseudo first-order kinetic model (min^{-1}). It is better to mention that the correlation coefficient for this isotherm model was 0.703. Moreover, the notable difference between the experimental q_{exp} value and calculated q_{cal} value indicates that the adsorption kinetic of MB on the WB does not follow the pseudo first-order model.

In the pseudo second-order kinetic model, the rate control step is based on chemisorption ²⁹.

This model is applied using equation 10.

$$(10) \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

An appropriate linear relationship with a correlation coefficient of $R^2=0.999$ between t/q_t and t demonstrates that the adsorption process of MB on the WB could be well explained by the pseudo second-order model (Figure 4B). Furthermore, a very slight difference between the calculated q_{cal} value and experimental q_{exp} value is an indicator of following the pseudo second-order by desired adsorption process.

An evaluated equation of intraparticle diffusion was proposed by Weber-Morris model ³⁰ (Eq.

11):

$$(11) \quad q_t = K_{\text{dift}} t^{0.5} + C$$

In which k_{dif} is the rate constant ($\text{mg g}^{-1} \text{min}^{-0.5}$), and C is the boundary layer thickness (mg g^{-1}).

Elovich kinetic model was expressed in Eq. 12:

$$(12) \quad q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$$

α ($\text{mg g}^{-1} \text{min}^{-1}$) and β (g mg^{-1}) are rate constants for the Elovich equation and represent the initial adsorption rate and desorption coefficient, respectively.

The calculated kinetic parameters of four models using slope and intercept of these plots were summarized in Table 2. A good linearity plot with the highest correlation coefficient, R^2 , was obtained for the pseudo second-order kinetic model.

Thermodynamic parameters including the change of Gibbs free energy (ΔG° , KJ mol^{-1}), enthalpy (ΔH° , KJ mol^{-1}) and entropy (ΔS° , $\text{KJ mol}^{-1} \text{K}^{-1}$) were employed to evaluate the influence of temperature on the adsorption process were calculated using the following equation ³¹:

$$(13) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$(14) \quad \Delta G^\circ = -RT \ln k_c$$

$$(15) \quad \ln(k_c) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{K}^{-1}$), T is the temperature (K) and k_c (L mol^{-1}) is the thermodynamic equilibrium constant that could be calculated using the following equation (Eq. 16):

$$(16) \quad K_{(c)} = \frac{q_e}{C_e}$$

The ΔH° and ΔS° values can be obtained from slope and intercept of linear Van't Hoff plots of $\ln K_c$ versus $1/T$. Tables 3 summarizes the values of the thermodynamic parameters for MB adsorption on WB particles. The values of ΔG at different temperatures were all negative, indicating the spontaneous nature of the adsorption process. The values of ΔG° became

negative upon rising temperature from 10 to 80 °C as an indication of the favorability of the adsorption of MB onto WB powder at room temperature. Moreover, the negativity of the process enthalpy (ΔH) demonstrated the exothermicity of the adsorption. Finally, the negative values of ΔS° illustrated decreasing of randomness at the adsorbent-solution interface during the adsorption process.

Comparison of proposed adsorbent with the other natural adsorbents

Table 3 lists the natural adsorbents used for the elimination of methylene blue dye. Almost all of these adsorbents are in the same isothermal and kinetic conditions, and the experimental data are consistent with the Langmuir isotherm and quadratic kinetics in most of them. As can be seen, the adsorption capacity of the adsorbent proposed in this study is whether higher than or in some cases close to some adsorbents. Comparing the adsorption capacity of the adsorbent in this research with other natural adsorbents, suitable and ideal adsorption capacity for cationic dye removal can be realized (Table 4).

Conclusions

In this study, the new natural sorbent named WB was introduced as an effective biosorbent for MB removal from aqueous solutions. The methods are offered for successfully higher adsorption capacity towards MB than that of most adsorbents at experimental conditions. Detailed isotherm, kinetics and thermodynamic investigations had confirmed not only the best fitting of the equilibrium data with Langmuir isotherms but the monolayer coverage of the dye ions onto WB surface. In kinetics studies, it was revealed that kinetic of the adsorption process was followed for the pseudo-second-order. Also, the magnitude of thermodynamic functions indicated the spontaneity, exothermicity, and favorability of the adsorption process at room temperature.

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Figure caption

Fig. 1. SEM images of WB powder. The surface images at magnifications of (A) 572 $\times$, (B) 5000 $\times$, (C) 15000 $\times$ and (D) 50000 $\times$.

Fig. 2. XRD pattern of WB (A), FTIR spectra of WB powder, before (B) and after adsorption (C).

Fig. 3. Effects of sorbent weight (A), pH (B), contact time (C), MB concentration (D) and temperature (E) on removal efficiency, conditions: MB solution: 25 mL, stirrer rate= 700.0 rpm and λ_{max} =664 nm.

Fig. 4. Linearized Langmuir isotherm (A), and pseudo-second-order kinetics (B) for the adsorption of MB dye onto WB, conditions: MB solution: 25 mL, stirrer rate= 700.0 rpm and λ_{max} =664 nm.

Figures

Figure 1

Figure 3

Figure 4

Tables

Table 1. Adsorption isotherms parameters of MB on the WB powder at different temperatures

Model	Equation	Parameters			
		$q_m(\text{mg g}^{-1})$	$k_L(\text{L mg}^{-1})$	R^2	
Langmuir	$1/q_e = 1/(k_a q_m c_e) + 1/q_m$	34.13	0.827	0.9986	
Freundlich	$\ln q_e = \ln k_F + (1/n) \ln c_e$	n	$K_f(\text{L mg}^{-1})$	R^2	
		-5.33	60.77	0.9800	
Tempkin	$q_e = B \ln(A) + B \ln(C_e)$	B	$A(\text{L mg}^{-1})$	R^2	
		-7.78	-1617.7	0.9849	
Dubinin-Radushkevich	$\ln q_e = \ln q'_m - k_{DR} \varepsilon^2$	$q'_m(\text{mg g}^{-1})$	$K_{DR}(\text{mol}^2 \text{J}^{-2})$	$E(\text{kJ mol}^{-1})$	R^2
		20.11	9E-8	3.53	0.9126

Table 2. Kinetic parameters for the adsorption of MB onto WB Powder

Model	Parameters	
Pseudo-first-order $\log(q_e - q_t) = \log q_e - k_1 t / 2.303$	$q_{e, \text{exp}}$ (mg g ⁻¹)	45.211
	q_e (mg g ⁻¹)	3.52
	K_1 (min ⁻¹)	0.18
	R^2	0.7033
Pseudo-second-order $t / q_t = 1 / k_2 q_e^2 + t / q_e$	q_e (mg g ⁻¹)	45.87
	K_2 (mg L ⁻¹ min ⁻¹)	0.019
	R^2	0.9999
Intraparticle diffusion $q_t = k_{\text{dif}} t^{0.5} + C$	C	38.819
	K_{dif} (mg g ⁻¹ min ^{-0.5})	0.717
	R^2	0.6714
Elovich $q_t = 1 / \beta \ln(\alpha \beta) + 1 / \beta \ln(t)$	(mg g ⁻¹ min ⁻¹) α	4.0×10 ⁶
	(g mg ⁻¹) β	0.411
	R^2	0.82

Table 3. Thermodynamic parameters for the adsorption of MB on WB

$\Delta S^\circ (\text{J mol}^{-1} \text{K}^{-1})$	$\Delta H^\circ (\text{kJ mol}^{-1})$	$\Delta G^\circ (\text{J mol}^{-1})$	Temperature (K)
-4.32	-7.32	-6060.24	282
		-6053.24	293
		-6047.47	303
		-6024.68	308
		-5960.24	323
		-5752.78	353

Table 4. Comparison of MB maximum adsorption capacity onto different natural adsorbents

Sorbent/weight/solution volume	q (mg g ⁻¹)	Kinetic	Isotherm	Ref.
Banana leaf/300mg/200 mL	109.89	Pseudo-second-order	Langmuir	32
Sugar extracted spent rice biomass/0.25–0.5 g/100 mL	8.13		Langmuir	33
Bush Cane Bark Powder/ 1000mg/100 mL	23.49		Langmuir	34
Silkworm exuviae/50mg/25 mL	25.530		Freundlich	35
Iranian natural clays/400 mg/1000mL	123.5		Langmuir	36
Saudi Red Clay/300 mg/50 mL	50.25		Langmuir	37
Raw beech sawdust/4g/1000mL	9.78		Langmuir	38
Hazelnut shell/ 1g/2000 mL	38.22		Langmuir	39
Rice husk ash/80 mg/1000mL	18.14		Langmuir	40
Cellolignin/100 mg/25 mL	76. 33		Langmuir	41
WB/25 mg/25 mL	46.6		Langmuir	This work