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The performance of an eco-friendly adsorbent for methylene blue removal from aqueous solution: Kinetic, isotherm and thermodynamic approaches

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Abstract: The current study aims to determine how well pomegranate peel can remove methylene mlue (MB) from an aqueous solution. For this purpose, kinetic, isotherm and thermodynamic adsorption studies were performed in a batch system. The rate of MB adsorption was rapid and reached the equilibrium at about 60 min. The adsorption capacity reached approximately 42.71 mg g^{-1} at the initial dye concentration of 100 mg L^{-1}. The kinetic modelling of MB adsorption was perofrmed using pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models. The pseudo-second-order model was found to be the most adequate for fitting the kinetic data based on R^2, *RMSE*, *ARE* and χ^2 values. It was also discovered that MB adsorption onto pomegranate peel is not simply rate-limited by intraparticle diffusion. The isotherm approach showed a maximum adsorption capacity of 67.78 mg g^{-1} at 298 K using 2 g L^{-1} of pomegranate peel. The equilibrium modelling was also conducted. The four statistical values highlighted the better fit of the Langmuir model than the Freundlich model. Additionally, the exothermic and spont-aneous nature of the adsorption process was revealed by thermodynamic research. These findings demonstrate the effectiveness of pomegranate peel as an eco-friendly absorbent for MB removal.

Keywords: adsorption; kinetic; pomegranate peel; methylene blue; isotherm, thermodynamic.

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INTRODUCTION

Methylene blue (MB) is one of the most widely utilized synthetic dyes in various industrial sectors.[1] It is known for the promising potential in dyeing cotton, wool, and silk,[2] making it a common choice in the textile industry. However, the release of MB into the environment poses aesthetic issues and dramatic effects on aquatic life,[3] attributed to its visibility, low biodegradability and bioaccumulation through the food chain, posing a danger to human health. The acute exposure to MB can cause tachycardia, cyanosis, jaundice, quadriplegia and tissue necrosis in humans.[4] It also causes eye burns, leading to permanent injury to the eyes of humans and animals.[5] Other adverse effects of MB, such as hypertension, acute kidney failure and hemolytic anemia, have been reported in the literature.[6,7] In this context, various conventional methods have been investigated to remediate water pollution caused by MB. These methods include adsorption,[8–12] classical and advanced chemical oxidation,[13–17] membrane separation[18,19] and coagulation/flocculation.[20–22] Among these approaches, adsorption is an effective and low-cost technique to remove different pollutants from aqueous solutions,[23–26] including MB. The significant advantages of the adsorption process include its effectiveness and economical dye removal, low sludge production and simplicity in execution.[27] Additionally, using agricultural waste as a biosorbent offers a low-cost and eco-friendly approach to a circular economy.[28] Several researchers have demonstrated the potential of various agricultural wastes for MB removal, such as sugarcane bagasse,[29] rice husk,[4] date pits,[30] peanut hull,[31] soursop residues,[29] wheat straw[32] and orange and banana peels.[33]

The pomegranate is a prized fruit, valued for its unquestionable qualities that promote consumption. Global pomegranate production continues to rise owing to the high demand for the fruit and its derivatives, such as juice, syrup and jam. However, the peel, constituting approximately 50 % of the fruit's mass,[34] is often discarded as waste despite its potential uses. The worldwide generation of pomegranate peel was estimated at around 1.9 million tons five years ago.[35] Furthermore, Morocco produces a substantial amount of pomegranate fruit, with an estimated annual production of pomegranate peel reaching 29,000 tons based on the approximately 58,000 tons of fruit harvested annually.[36] In this context, this research aims to enhance the performance of pomegranate peel as an eco-friendly adsorbent for removing MB from an aqueous solution. A preliminary study revealed its potential use for the adsorption of MB.[35] Therefore, the present work focuses on studying the kinetic, isotherm and thermodynamic approaches to gather more information on the mechanism of MB adsorption by pomegranate peel.

EXPERIMENTAL

Adsorbate

Methylene blue, with the molecular formula $C_{16}H_{18}ClN_3S$ (Fig. 1), was supplied by Loba Chemie. It was used without further purification to prepare the stock solution (1000 mg

L^{-1}). The working solutions of MB were subsequently prepared by diluting the stock solution with distilled water.

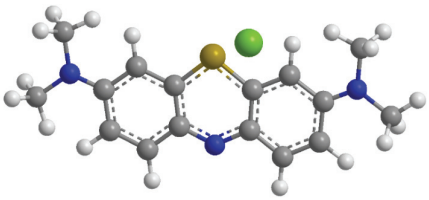

Fig. 1. Chemical structure of methylene blue dye.

Biosorbent preparation

After the separation from pomegranate, the peel is cleaned with distilled water and dried in the sun for about three weeks. The fragments are ground into a powder and washed repeatedly with distilled water until a colourless solution is obtained. The powdered pomegranate peel is then dried at 60 °C for 48 h before being placed in a desiccator, awaiting usage.

ATR-FTIR characterization

The surface functionalities of the produced pomegranate peel powder were identified using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) on a Themosc-ientific Nicolet iS10 FTIR spectrometer. The samples were recorded in transmittance mode.

Adsorption experiments

The adsorption experiments in the present study were conducted in a batch system using the initial pH of the MB solution. For each experiment, 0.1 g of powdered pomegranate peel was added to 50 mL of the MB solution (100 mg L^{-1}) in a 100 mL Erlenmeyer flask. The suspensions were shaken at 300 rpm by an electromagnetic stirrer. The studied concentration was chosen based on the preliminary investigation assessing the effective MB concentration in textile wastewater. The adsorption kinetic approach was carried out from 0 to 300 min at room temperature. The adsorption isotherm approach was performed at 298 K for 120 min by varying the initial dye concentration from 0 to 500 mg L^{-1}. The thermodynamic approach was conducted at varying temperatures from 298 to 328 K for 120 min. At the end of each adsorption experiment, the suspensions were centrifuged at 3800 rpm for 5 min. Then, the residual concentration of MB in the supernatant was determined using a double-beam UV–Vis spectrophotometer at 665 nm. The amount of MB adsorbed per unit mass of adsorbent (q_t) was calculated using the following equation:

$$q_t = \frac{C_0 - C_t}{m} V \tag{1}$$

where C_0 and C_t are, respectively, the initial and time t concentrations of MB in solution, mg L^{-1}, V is the MB solution volume, L, and m is the mass of the powdered pomegranate peel, g.

Kinetic study

The kinetic approach was investigated to determine the order of the adsorption reaction and the mechanism controlling the process. In this regard, four well-known models were used to study the kinetic of MB adsorption onto pomegranate peel: pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich and intraparticle diffusion (IPD), as given in Table I, where q_e / mg g^{-1} and K_1 / min^{-1} represent, respectively, the amount of MB adsorbed at equilibrium and the rate constant of PFO; K_2 / g mg^{-1} min^{-1} represents the rate constant of PSO; α_E / mg g^{-1}

min^{-1} and β_E / g mg^{-1} represent the rates constants of adsorption and desorption of Elovich, respectively; K_{ID} / mg g^{-1} $min^{-1/2}$ represents the IPD rate constant and c the constant related to the thickness of the boundary layer.

TABLE I. Adsorption kinetic models

Kinetic model	Non-linear	Linear	Plot	Ref.
PFO	$\frac{dq_t}{dt} = K_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - K_1 t$	$\ln(q_e - q_t)$ *vs.* t	37
PSO	$\frac{dq_t}{dt} = K_2(q_e - q_t)^2$	$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	t / q_t *vs.* t	38
Elovich	$\frac{dq_t}{dt} = \alpha_E \exp(-\beta_E q_t)$	$q_t = \frac{1}{\beta_E}\ln(\alpha_E \beta_E) + \frac{1}{\beta_E}\ln t$	q_t *vs.* $\ln t$	39
IPD	–	$q_t = K_{ID} t^{1/2} + C$	q_t *vs.* $t^{1/2}$	40

Isotherm study

The study of the adsorption isotherm is essential for quantifying and comparing the performance of pomegranate peel in MB removal. In this regard, Langmuir and Freundlich models were employed. The Langmuir isotherm model presupposes that all adsorption sites on the adsorbent are structurally homogeneous, that the adsorption is confined to a monolayer, and also that molecules adsorbed on neighbouring sites do not interact.[41] Accordingly, when an adsorbent reaches an equilibrium saturation point, no further adsorption occurs, indicating a finite capacity for adsorption:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{2}$$

The Langmuir equation may be expressed in its linearized form as follows:

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

where q_{max} / mg g^{-1} denotes the maximum adsorption capacity and K_L / L mg^{-1} represents the Langmuir constant.

The Freundlich adsorption isotherm is an empirical model used to elucidate the multilayer adsorption with the interactions between molecules adsorbed on heterogeneous surfaces featuring non-identical sites and varied adsorption energies. This model is not restricted to the formation of monolayers of adsorbate molecules on the adsorbent.[42] The Eq. (4) illustrates the Freundlich isotherm model:

$$q_e = K_F C_e^{1/n} \tag{4}$$

The linearized form of the Freundlich model can be expressed as follows:

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

where K_F / (mg g^{-1})(L g^{-1})^n is the Freundlich constant and n is the Freundlich exponent.

Analysis of models

The use of error functions is an effective way to assess the fit of a model and its underlying assumptions. This study employed four statistics: coefficient of determination (R^2), root mean square error (*RMSE*), average relative error (*ARE*), and chi-square (χ^2). The optimal model should have a coefficient of determination close to one and the lowest values of *RMSE*, *ARE* and χ^2.

The *RMSE*, *ARE* and χ^2 are calculated using the following expressions:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}(q_{t,\mathrm{cal}} - q_{t,\mathrm{exp}})^2}{N}} \tag{6}$$

$$ARE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{q_{t,\mathrm{exp}} - q_{t,\mathrm{cal}}}{q_{t,\mathrm{exp}}}\right| \tag{7}$$

$$\chi^2 = \sum_{i=1}^{N}\frac{(q_{t,\mathrm{exp}} - q_{t,\mathrm{cal}})^2}{q_{t,\mathrm{cal}}} \tag{8}$$

where N is the number of the experimental data points, $q_{t,\mathrm{exp}}$ / mg g^{-1} is the experimental value, and $q_{t,\mathrm{cal}}$ / mg g^{-1} is the predicted value of q_t with the investigated model.

RESULTS AND DISCUSSION

ATR-FTIR characterization

The ATR-FTIR spectrum of the studied biosorbent is illustrated in Fig. 2. The infrared spectrum of pomegranate peel exhibits bands at 3,368 (hydroxyl group of carboxylic acid or phenol), 2925 and 2853 (C–H stretching vibrations of lignocellulosic components), 1730 (C=O stretching vibration of carboxyl groups), 1615 (aromatic C=C or COO^- stretching vibration of carboxylic acids), 1444 (asymmetric deformation of C–H bond of methyl and methylene groups) and 1327 cm^{-1} (symmetrical deformation of C–H bond of methyl group). The other

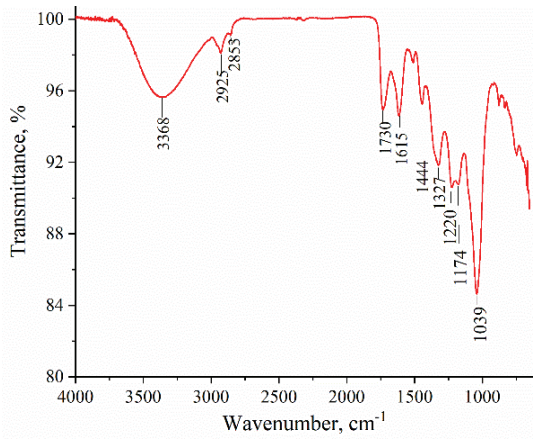

Fig. 2. ATR-FTIR spectrum of pomegranate peel powder.

bands are attributed to the C–O vibration of primary alcohols (C–OH) of cellulose and hemicellulose.

Adsorption kinetics

The kinetic study of MB adsorption onto pomegranate peel was conducted over a range of contact times from 5 to 300 min. The results depicted in Fig. 3 clearly illustrate a two-stage adsorption process. Initially, there was a rapid increase in MB adsorption, reaching 33.94 mg g^{-1} within just 10 min. Subsequently, the rate of MB adsorption slowed down, gradually reaching its maximum around 60 min, with no significant changes observed thereafter. This behaviour can be attributed to numerous vacant sites on the pomegranate peel surface during the initial stage, which were rapidly occupied by MB molecules until saturation was achieved.

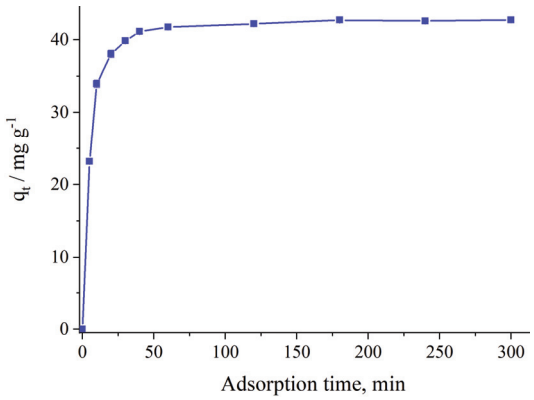

Fig. 3. MB adsorption kinetic onto pomegranate peel.

Additionally, to understand better the adsorption ability of the produced biosorbent, the adsorption kinetic of rhodamine B (RhB) dye onto pomegranate peel was previously investigated. The rate of RhB adsorption was rapid, reaching the equilibrium at approximately 120 min, with an adsorption capacity of around 30.47 mg g^{-1}.[27] However, it's noteworthy that this value is lower than that observed for MB adsorption, which reached 42.71 mg g^{-1}, indicating a higher affinity of pomegranate peel for MB dye.

Kinetic modeling

Four kinetic models were fitted to the obtained kinetic data: PFO, PSO, Elovich and IPD (Fig. 4). The kinetic parameters and the associated statistical analysis of each model are presented in Table II. The suitability of the PSO model to fit the MB adsorption onto pomegranate peel can be inferred from a simple review of the Table II. Indeed, this model presents the highest coefficient of determination (R^2 = 1) and the lowest values of *RMSE*, *ARE* and χ^2. Additionally, the fit ade-

quacy of the PSO model for MB adsorption has been revealed by other researchers as well.[43]

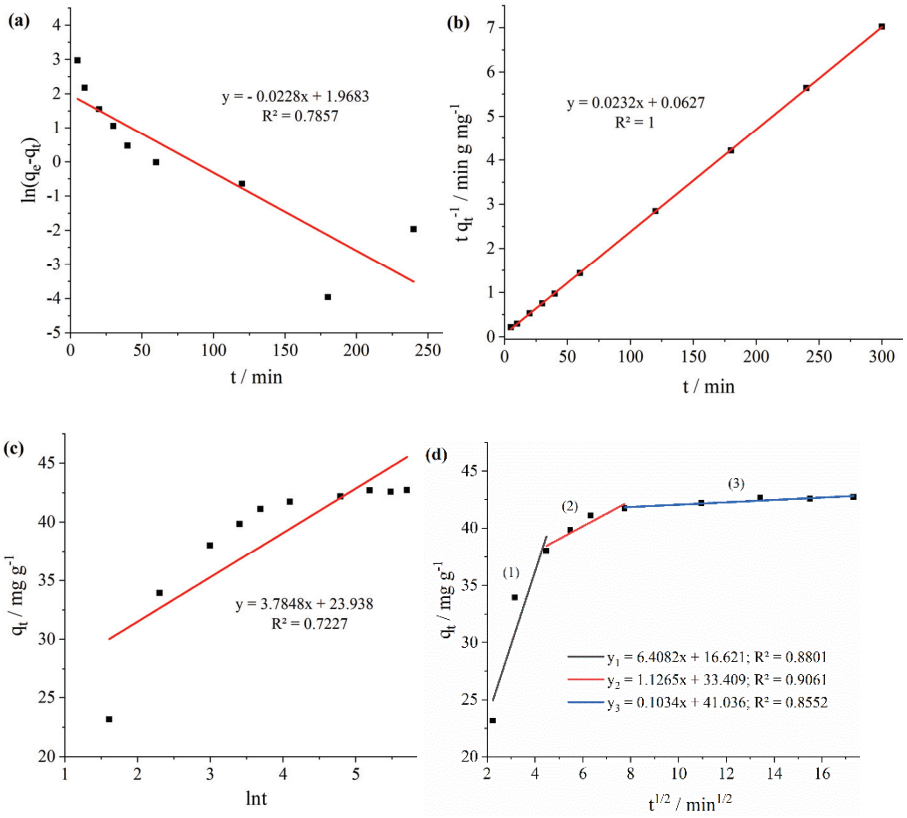

Fig. 4. a) PFO, b) PSO, c) Elovich and d) IPD linear plots for MB adsorption onto pomegranate peel at 298 K.

TABLE II. Kinetic parameters for the adsorption of MB onto pomegranate peel

Kinetic model	Kinetic parameters at 298 K		Statistical analysis			
			R^2	*RMSE*	*ARE* / %	χ^2
PFO	$q_{e,cal}$ / mg g^{-1}	K_1 / min^{-1}	0.7857	34.43	88.75	3.51×10^3
	7.16	0.02				
PSO	$q_{e,cal}$ / mg g^{-1}	K_2 / g mg^{-1} min^{-1}	1	1.56	2.52	0.86
	43.14	0.009				
Elovich	α_E / mg g^{-1} min^{-1}	β_E / g mg^{-1}	0.7227	3.07	7.55	2.78
	2.11 10^3	0.26				
IPD (2)	K_{ID} / mg g^{-1} min$^{-1/2}$	c	0.9061	6.26	13.37	9.10
	1.13	33.41				

Furthermore, Fig. 4d illustrates the tri-linearity observed in the IPD plot, which doesn't pass through the origin. This suggests that the intraparticle diffusion is not the only rate-limiting step, and the MB adsorption process is controlled by three mechanisms. Indeed, the first linear section with a sharp slope represents the bulk diffusion at the adsorbent's external surface (instantaneous adsorption). The second section depicts the intraparticle diffusion (gradual adsorption), and the last one, the plateau portion, represents the equilibrium.[44] The intercept of the second section provides information on the thickness of the boundary layer (Table II). A higher intercept indicates a thicker boundary layer, amplifying its effect.[45,46] Other researchers have reported similar findings regarding the adsorption of MB onto tea residues and diatomite.[47,48]

Models validation

Fig. 5a depicts the accuracy of the PSO model in describing the MB adsorption kinetic data. This observation is further supported by Fig. 5b, which provides a graphical comparison of the experimental and the predicted equilibrium adsorption capacities for each model. The figure highlights the predictive quality of the PSO model in representing MB adsorption onto pomegranate peel, as evidenced by its closest predicted value ($q_{e,cal}$ = 42.76 mg g^{-1}) to the experimental value ($q_{e,exp}$ = 42.71 mg g^{-1}).

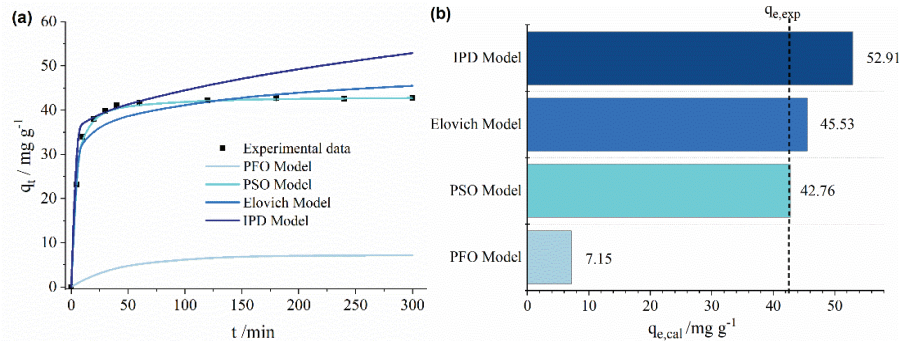

Fig. 5. Kinetic models validation with experimental data.

Adsorption isotherm and modeling

The equilibrium mechanisms between MB and the pomegranate peel surface were studied through Langmuir and Freundlich models. The adsorption isotherm was simulated at 298 K (Fig. 6), and the associated parameters were determined and grouped with statistical analysis in Table III. The linear fitting plots of the Langmuir and Freundlich models are represented in Fig. 6. The Langmuir model provided a better fit to the experimental data, with a coefficient of determination closer to one (R^2 = 0.9998) and lower *RMSE*, *ARE* and χ^2 values compared to the

Freundlich model (Table III). This adequacy indicates the monolayer adsorption of MB onto pomegranate peel.

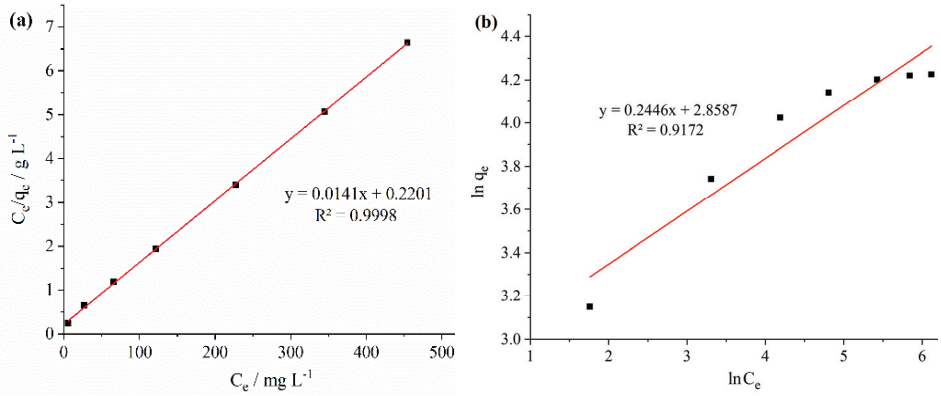

Fig. 6. a) Langmuir and b) Freundlich linear isotherm plots for MB adsorption onto pomegranate peel at 298 K.

TABLE III. Equilibrium parameters for MB adsorption onto pomegranate peel at 298 K

Isotherm model	Isotherm parameters at 298 K		Statistical analysis			
			R^2	*RMSE*	*ARE* / %	χ^2
Langmuir	q_{max} / mg g^{-1}	K_L / L g^{-1}	0.9998	2.00	4.05	1.10
	70.96	0.06				
Freundlich	n	K_F / (mg g^{-1})(L g^{-1})^n	0.9172	5.72	9.69	4.01
	4.09	17.44				

The Langmuir model's adequacy is further supported by Fig. 7, which displays the experimental and predicted isotherms of MB adsorption onto pomegranate peel. A simple examination of the figure confirms the Langmuir model's predictive quality. Indeed, the Langmuir maximum adsorption capacity (70.96 mg g^{-1}) is close to the maximum experimental adsorption capacity (67.78 mg g^{-1}).

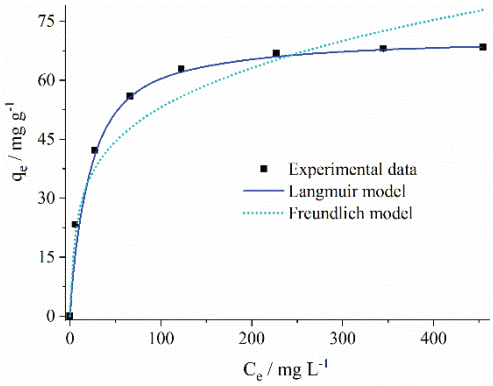

Fig. 7. MB adsorption isotherm onto pomegranate peel.

Moreover, it is advisable to compare the adsorption capacity of pomegranate peel with that of other biomass reported in previous research. Table IV demonstrates that pomegranate peel has a higher adsorption capacity than other biomass, suggesting it could be used as an inexpensive and environmentally friendly adsorbent for the removal of MB.

TABLE IV. Comparison of maximum adsorption capacities of various biomass for MB dye

Biomass	q_{max} / mg g^{-1}	Reference
Rice husk	40.59	4
Soursop residues	55.40	29
Sugarcane bagasse	17.43	29
Date pits	80.29	30
Wheat straw	60.66	32
Orange peel	18.60	33
Banana peel	20.80	33
Orange albedo	77.79	49
Potato peel	97.08	50
Avocado peel	62.11	51
Hamimelon peel	58.60	51
Dragon fruit peel	62.58	51
Tucuma cake	17.24	52
Pomelo peel	81.71	53
Pomegranate peel	67.78	This work

Thermodynamic study

The thermodynamic study plays an essential role in understanding the adsorption process of MB onto pomegranate peel. In this respect, the thermodynamic parameters of MB adsorption, namely the free energy change, $\Delta G°$ / kJ mol^{-1}, the enthalpy change, $\Delta H°$ / kJ mol^{-1}, and the entropy change, $\Delta S°$ / J mol^{-1}·K^{-1} were determined using the following equations:

$$\Delta G^\circ = -RT \ln K_d ; K_d = \frac{q_e}{C_e} \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

$$\ln K_d = \left(\frac{\Delta S^\circ}{R}\right) - \left(\frac{\Delta H^\circ}{R}\right)\frac{1}{T} \tag{11}$$

were K_d is the distribution coefficient for adsorption, C_e / mg L^{-1} is the equilibrium concentration of MB, q_e / mg g^{-1} is the amount of MB adsorbed at equilibrium, T / K is the absolute temperature and R is the gas constant (8.314 J mol^{-1} K^{-1}).

The slope and intercept of the ln K_d *vs.* T^{-1} plot, shown in Fig. 8, were used to calculate the values for $\Delta H°$ and $\Delta S°$. The obtained results are presented in Table V.

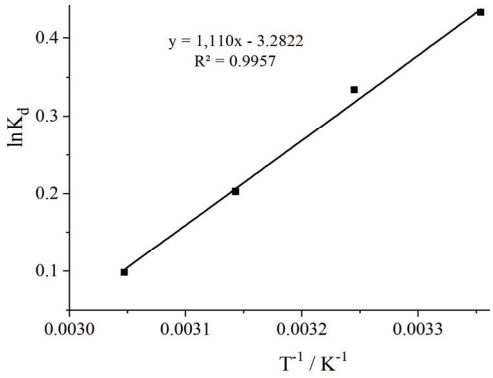

Fig. 8. The plot of ln K_d *vs.* T^{-1} for the MB adsorption onto pomegranate peel.

TABLE V. Thermodynamic parameters

T / K	$\Delta G°$ / kJ mol^{-1}	$\Delta H°$ / kJ mol^{-1}	$\Delta S°$ /J mol^{-1}·K^{-1}
298	–1.07	–9.23	–27.29
308	–0.86		
318	–0.54		
328	–0.27		

The negative values of $\Delta G°$ for the various temperatures examined, as shown in Table V, demonstrate the spontaneity of MB adsorption. The negative value of $\Delta H°$ supports the exothermic nature of the adsorption process and suggests that no energy needs to be added in order to transfer MB from the aqueous phase to the solid. Moreover, the negative value of $\Delta S°$ suggests a reduction in randomness at the adsorbent/adsorbate interface during the adsorption process, without any significant change in the adsorbent structure.[54] Similar findings were also reported by Miraboutalebi *et al.*[55] for the adsorption of MB onto corn silks.

CONCLUSION

The findings indicate that pomegranate peel possesses a strong MB adsorption capacity. The MB adsorption occurred rapidly, reaching the equilibrium around 60 min, with an adsorption capacity close to 42.71 mg g^{-1} at an initial dye concentration of 100 mg L^{-1}. The results from the kinetic approach suggest that MB adsorption onto pomegranate peel perfectly follows pseudo-second-order kinetic and that the intraparticle diffusion is not the only rate-limiting step in the adsorption process. Additionally, a maximum adsorption capacity of 67.78 mg g^{-1} was observed with the isotherm approach, and the equilibrium data showed good compliance with the Langmuir model. The exothermicity and spontaneity of the adsorption process were indicated by the negative values of $\Delta G°$ and $\Delta H°$, res-

pectively. In terms of $\Delta S°$, the negative value suggested an increase in disorder at the adsorbent/adsorbate interface during the adsorption process. Moreover, the pomegranate peel exhibited a comparatively higher adsorption capacity for MB compared to other biomass. These findings highlight the potential of pomegranate peel as an environmentally friendly absorbent for effluent containing MB.

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И З В О Д

ПЕРФОРМАНСЕ ЕКОЛОШКИ ПРИХВАТЉИВОГ АДСОРБЕНТА ЗА УКЛАЊАЊЕ МЕТИЛЕНСКОГ ПЛАВОГ ИЗ ВОДЕНОГ РАСТВОРА: КИНЕТИЧКИ, ИЗОТЕРМНИ И ТЕРМОДИНАМИЧКИ ПРИСТУПИ

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Представљена студија има за циљ да утврди колико добро кора нара може уклонити метиленско плаво (MB) из воденог раствора. У ту сврху су спроведене кинетичке, изотермне и термодинамичке студије адсорпције у шаржном систему. Брзина адсорпције MB је била брза и достигла је равнотежу за око 60 min. Достигнути капацитет адсорпције је близу 42,71 mg g^{-1} при почетној концентрацији боје од 100 mg l^{-1}. Кинетичко моделовање адсорпције MB је спроведено коришћењем модела псеудо-првог, псеудо-другог реда, Еловичевог модела и модела дифузије унутар честица. Утврђено је да је модел псеудо-другог реда најадекватнији за уклањање кинетичких података на основу вредности R^2 (коефицијент детерминације), $RMSE$ (квадратна средња грешка), ARE (просечна релативна грешка) и χ^2 (хи-квадрат). Такође је откривено да адсорпција MB на кори нара није једноставно ограничена брзином дифузије унутар честица. Изотермни приступ је показао максимални капацитет адсорпције од 67,78 mg l^{-1} на 298 K коришћењем 2 g l^{-1} коре нара. Такође је спроведено моделовање равнотеже. Четири статистичке вредности су истакле да се Лангмуров модел најбоље уклапа у односу на Фројндлихов модел. Додатно, егзотермна и спонтана природа процеса адсорпције је откривена термодинамичким истраживањем. Приказани резултати показују ефикасност коре нара као еколошки прихватљивог апсорбента за уклањање MB.

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