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Adsorption of methylene blue dye onto acid-treated tej residue: Kinetic, equilibrium and thermodynamic study

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Dye-containing wastewater is a very toxic and a major threat to the deterioration of water quality and makes it unsuitable for domestic purposes. This drives low cost and eco-friendly adsorbents from environmental waste have been investigated to treat dye-containing wastewater. In the present study, tej residues (TR) have been successfully employed as a natural and non-conventional low-cost adsorbent for the removal of methylene blue (MB) dye from an aqueous solution. Optimization of maximum operating condition has been carried out by batch mode experiment and the result shows maximum removal efficiency of 82.1821 % at *p*H 8.0, adsorbent dosage 0.4g, initial dye concentration 20 ppm, contact time 60 min, and temperature 25°C on the acid-treated surface of tej residue. Adsorption kinetics of the adsorbent has been evaluated by pseudo-first-order, pseudo-second-order and intra-particle diffusion, and it is observed that the pseudo-first-order kinetic model is better fitted with a good correlation coefficient, and the equilibrium data fitted well with the Freundlich isotherm model. The Langmuir isotherm model estimates that the maximum adsorption capacity of the monolayer is found to be 215.053 mg/g. Thermodynamics parameters such as ΔG^0, ΔH^0 and ΔS^0 indicate that the sorption process is feasible and exothermic.

Keywords: Dye removal, Isotherm, Kinetic model, Methylene blue

As industries and the population have grown at an alarming rate, water becomes more vital. This may cause an environmental problem with many types of pollution, including water pollution. Among different pollutants of an aquatic ecosystem, dyes are a large and important group of chemicals[1-4]. Nowadays, dyes are widely used in photo electrochemical cells, textiles, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries[1]. Besides its advantage, it hurts on water bodies by reducing the light penetration of wastewater and adversely affecting aquatic growth and photosynthesis[5]. Moreover, synthetic dyes can harm human health such as heart-beat increase, vomiting, shock, reproductive and central nervous system[6,7]. Hence, it is important to consider their removal or treatments from industrial effluents before discharging into the environment.

There are many physical, chemical and biological treatment methods available for the removal of dyes. Among them, liquid-phase adsorption is an excellent method due to its cost-effectiveness, simplicity of design and ease to operate[7,8]. Moreover, it's been proved to be an effective and attractive process for the removal of non-biodegradable pollutants (including dyes) from wastewater[9]. The utilization of wasted martial or by-products as adsorbents has received special interest from several researchers for different reasons such as high selectivity, low cost, and availability[10]. In recent years, Scholars have studied the production of traditional adsorbents from fruit, vegetable peels and agricultural wastes as cheap and renewable precursors, such as mango peel[11], Pomelo (Citrus grandis) peel[12] , Bamboo charcoal[13], Khat (Catha edulis)[14], Coffee waste[15], Papaya (Carica papaya) leaves[16], overripe Cucumissativus peel[17], Prosopis cineraria[18], tea waste [19], lemon peel[20], banana and orange peels for removal of different dyes in the aqueous solution [21].

Tej is one of the most popular traditional fermented alcoholic drinks in Ethiopia. People enjoy the beverage, particularly when having guests, for recreational and ceremonial purposes. It is easy to prepare, its main components are a medicinal shrub *Rhamnusprinoides* (gesho), honey and water[22,23]. It can be prepared by mixing one part of honey with three parts of water, putting in some stems and branches of gesho, and letting it ferment for 5-6 weeks, and removing the ambula after 2 weeks[23]. In the production of tej, tons of residues (ambula) are produced annually[22,23]. These residues are not used commercially and are not consumed by livestock. More ever, the residue (ambula) can increase environmental pollution. Thus, the production of eco-friendly adsorbents by using this residue could be considered as an alternative for dye removal from industrial effluent. To the best of our knowledge, there are no available reports related to this residue for dye removal from an aqueous solution.

The main objective of this study was to examine the potentiality of tej residue (TR) as a low-cost adsorbent for the removal of Methylene blue (MB) from an aqueous solution in a batch system. The effects of different parameters including solution pH, adsorbent dosage, initial dye concentration, temperature, and contact time were studied. Additionally, the isotherm, kinetic and thermodynamics studies were explored to describe the experimental data.

Experimental Section

Chemicals

The chemicals and reagents used in this study were of analytical grade, including H_2SO_4 (95-97%, Sigma-Aldrich), NaOH (99.8%, Alpha Chemicals, India), Methylene blue (96%, Sigma-Aldrich), HCl (36–38%, Ranchem Industry, and Trading, India).

Adsorbent preparation

The discarded Tej residue samples were collected from Woldia town, which is locally called Adago (Tigist tej bet), Ethiopia. The samples were firstly washed with distilled water and then dried in air for 3-4 days until they become crisp (Fig. 1 a). The samples were then ground to a fine powder and gently washed with distilled water until the impurities are removed, and then dried in an oven for 24 hours at 60°C to remove the moisture contents completely (Fig. 1b). The activation process was carried out by using 2M of H_2SO_4 solution according to[22-24], with little modification. 15 g of the sample was subjected to soaking by the prepared H_2SO_4 for 24 hr. afterward, the soaked sample was separated by filtration and washed several times with distilled water (Fig. 1C). Further, chemically activated samples were dried at 105 °C for 12 h and kept in a sample holder until used.

Characterization of prepared adsorbent

The physicochemical properties of the adsorbent such as moisture content, ash content, volatile matter, and fixed carbon were determined according to [22-24] with slight modifications.

Moisture content

1.0 g of the adsorbent sample was placed in a clean, dried, and weighed crucible in a preheated oven at 110°C for 2 h. Then, the sample was cooled in desiccators at ambient temperature and its weight was measured again. Hence, the difference between the initial (Mo) and the final mass (M1) of the sample was used to determine the moisture content using equation 1.

$$\text{Moisture content } (MC) = \frac{M_O - M_1}{M_O} x\ 100 \qquad \ldots (1)$$

Ash content

About 1 g of adsorbent sample was placed in a crucible, weighted, and heated in a muffle furnace (Nabertherm B180) under a temperature of 500 °C for 4 h. After that, the crucibles containing the sample were allowed to cool at room temperature and reweighed. The ash content of the sample was calculated as follows.

$$\text{Ash content } (AC) = \frac{\text{Ms}}{\text{Ma}} x\ 100 \qquad \ldots (2)$$

Where Ms and Ma are the mass (g) of ash and mass of the adsorbent respectively

Volatile matter

A gram of the TR sample was placed in pre-dried crucibles and heated in a muffle furnace regulated at 500 °C for 8 min. Then, the crucibles were allowed to cool in desiccators and weighed. Finally, the volatile matter of the adsorbents was calculated using equation 3.

$$\text{Volatile matter } (VM) = \frac{M_1 - M_2}{M_1} x\ 100 \qquad \ldots (3)$$

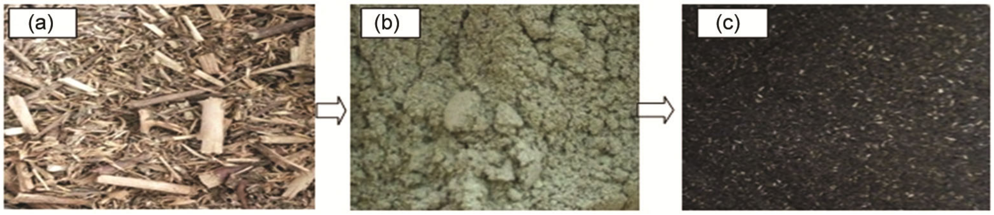

Fig. 1 — Image of raw tej residue (a); Powder form of sample (b) and oven-dried H_2SO_4 treated sample (c)

Where M1 and M2 are initial mass (g) of adsorbent and final mass respectively

Fixed carbon

The TR Fixed carbon content was determined by using equation 4.

$$\text{Fixed carbon content } (FC)\% = 100\,\% - (MC + AC + VM)\,\% \qquad \ldots (4)$$

Fourier Transform Infrared Spectroscopy (FTIR) analysiS

The surface functional groups of the bio-adsorbents were studied by FTIR spectroscopy (JASCO model 4100). The FTIR spectra were recorded between 4500 and 400 cm^{-1}.

Adsorbate preparation

Analytical pure methylene blue (MB) and other reagents used in the present study were taken from Woldia University, chemistry department laboratory. Methylene blue dye is a powdered solid, soluble in water, has a molecular weight: 3l9.9g/mol, maximum absorption wavelength: 665nm, chemical formula: $C_{16}H_{18}ClN_3S$, and its IUPAC name: 3,7-bis (dimethyl amino)-phenothiazin-5-ium chloride. Distilled water was employed for preparing all solutions and reagents. A stock solution of MB was prepared by dissolving 1.0 g in 1L of distilled water, and the solutions for adsorption tests were prepared from the stock solution to the desired concentrations by successive dilutions.

Batch adsorption experiment

The batch adsorption experiments of MB onto the prepared sample were carried out in a series of 100 mL Beakers containing dye concentration (20-60 ppm), adsorbent dosage (0.2-1.0 g), *p*H (2-12), Temperature (25°c-55°c) and contact time (10-80 min). A measured amount of adsorbent (0.4 g) and 25mL of dye sample was taken in 100 mL of the beaker for batch experiment and agitated in a magnetic stirrer on a digital hot plate at 220 rpm. The *p*H of all solutions was adjusted by 1M of HCl and 1M of NaOH. Afterward, all the supernatant solutions were subjected to centrifuge to minimize the effect of the adsorbent sample. At the end of each experiment, the concentrations of MB before and after adsorption were determined by using a Uv-vis spectrometer at a maximum wavelength of 665 nm. The removal efficiency and adsorption capacity (qe) at equilibrium were calculated using Equations 5 & 6.

$$\text{Removal Efficiency } (\%) = \frac{C_O - C_1}{C_O} x\ 100 \qquad \ldots (5)$$

$$q_e\left(\frac{mg}{g}\right) = \frac{(C_O - C_1)V}{m} \qquad \ldots (6)$$

Where, C_o: initial dye concentration (mg/L); C_1: the concentration of MB at equilibrium (mg/L); V: Volume of dye (L); m: mass of the adsorbent (g).

Result and Discussion

Characterization of adsorbent

Some selected physicochemical characteristics of an adsorbent such as moisture content, volatile matter, ash content, and fixed carbon were determined by using the standard method and presented in Table 1. The result revealed that the adsorbent sample has a very low moisture content (0.981%), which indicates that the adsorbent surface has good quality and the porous nature of the adsorbent is not hindered[25]. The volatile matter was found to be 0.240 %, this is because upon activation process most volatile matter present in the adsorbent evaporates off leaving a material as a gas and liquid product. The low ash content (2.115%) revealed that the inorganic content of the adsorbent surface is insignificant. Similar results were reported by different scholars[14,21,25]. The result showed that the adsorbent has high fixed carbon content, which was 96.664%. Adsorbents with high fixed carbon and low ash content are recommended for adsorption activities[14]. Therefore, the prepared acid-activated sample can be used for this activity.

FTIR analysis of adsorbent

FTIR spectroscopy was used to determine the presence of different functional groups on the surface of the TR adsorbent. The FTIR spectra of TR before and after adsorption with MB are shown in Fig. 2. The broadband around 3436 cm^{-1} could be attributed to the O–H stretching of the hydroxyl group[26]. The band at 2928 cm^{-1} might be due to antisymmetric and symmetric stretching of the C–H bond of methyl and methylene groups[27]. The adsorption peak around 1638 cm^{-1} corresponds to C=O bonds[26]. This indicates that the sample surface contained carbonyl functional groups. The band interval from 2320-2420 cm^{-1} is stretching vibrations of carbon to carbon triple bond of alkynes, while the peaks at 1460 cm^{-1} and 1384 cm^{-1}

Table 1 — Proximate analysis of H_2SO_4 activated tej residue (TR)

Proximate analysis	Mass in percent (%)
Moisture content	0.981
Volatile matter	0.240
Ash content	2.115
Fixed carbon	96.664

indicate the CH_3 and CH_2 vibration[26]. The spectrum of the adsorbent around 1058 cm^{-1} was caused by the stretching vibration of the C-O-C bond[26]. It was noticed that the loading of MB results in a little shift of the band around 1058 cm^{-1} and 2930 cm^{-1}. These shifts showed that the surface functional groups are involved in the adsorption of dyes on TR[27]. In addition to this, the transmittance intensity of TR after adsorptions is slightly less than before adsorption. This is maybe due to the surface of the adsorbent mostly covered by the adsorbed dye molecule.

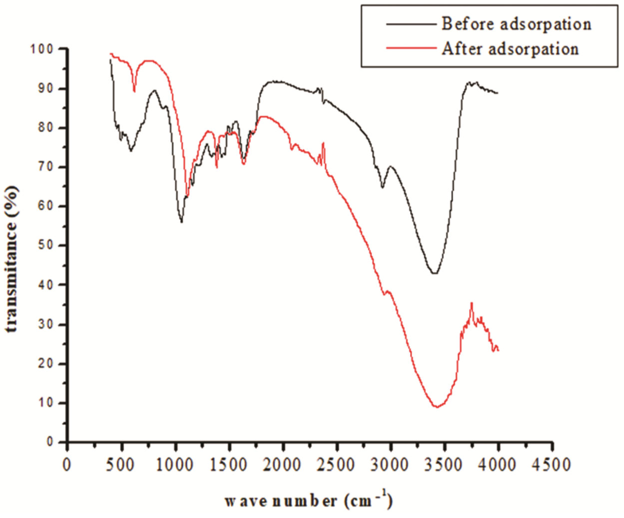

Fig. 2 — FT-IR spectra of tej residue

Optimization of different parameters

Effect of pH

The *p*H of the solution plays a significant role in the whole adsorption process because it can influence the degree of ionization and the surface charge of the adsorbent[28]. The effect of *p*H on the adsorption of MB on TR was studied at pH ranges from 2 to 12 (Fig. 3a). At a lower *p*H value, the concentration of H^+ is high, and the surface charge may develop a positive charge, repulsion interaction between the MB molecules and the adsorbent active surfaces resulting, thus making (H^+) ions compete effectively with dye cations causing a decrease in the amount of dye adsorbed. At higher *p*H values, the concentration of hydrogen ions is low and the surface of TR adopts a negatively surface charge, which leads to increase the adsorption of positively charged ions via attractive electrostatic attraction. Fig. 3 showed that adsorption of MB on TR adsorbent increase with increasing of *p*H until (*p*H=8) and beyond this value the adsorption of MB decreases constantly. Similar trends were reported in the previous work[29]. The optimal *p*H 8 value of the solution was used for the subsequent experiments.

Effect of Adsorbent dosage

To get full information about the interaction between adsorbate and adsorption sites, it is important to get the adsorbent dose. The effect

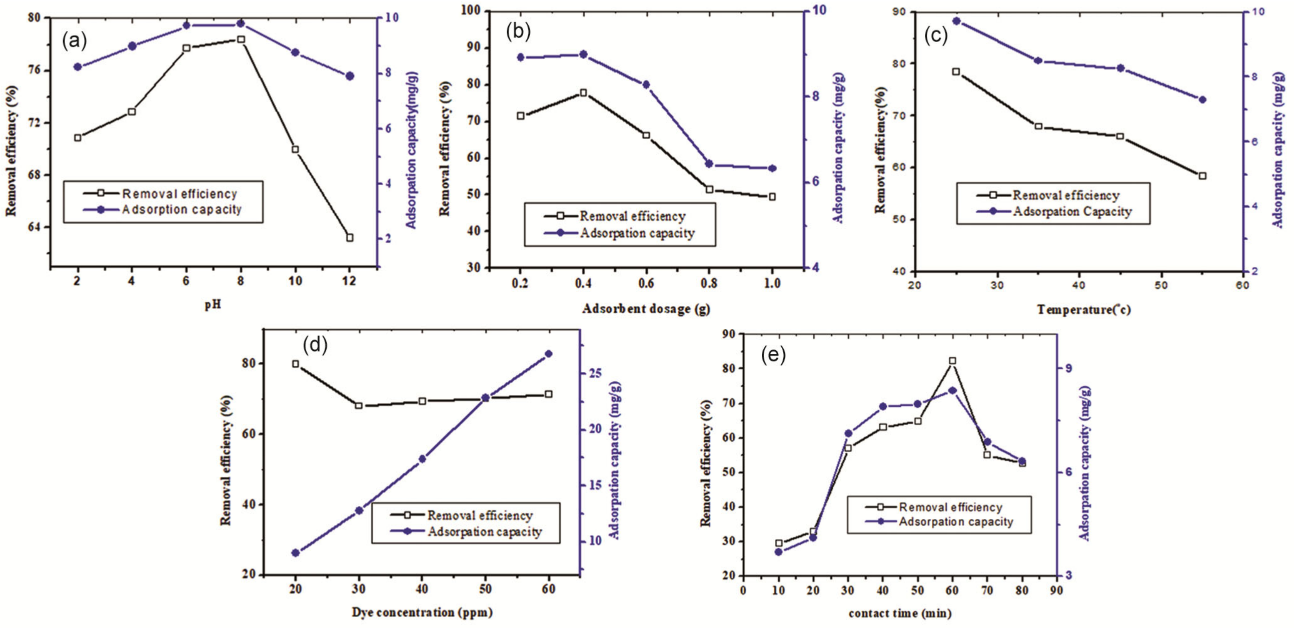

Fig. 3 — (a) Effects of solution pH on uptake of MB by chemical activated TR; (b) Effect of adsorbent dosage; (c) Effect of temperature; (d)Effect of MB dye concentration and (e) Effects of contact time

of TR dosage on the removal efficiency and adsorption capacity was carried out by varying the adsorbent dosage from 0.2-1.0g. Fig. 3(b) showed that the adsorption capacity for MB dye gradually decreased with increasing adsorbent dosage. This is due to the occupation of the active site of the adsorption by MB dye and its saturation condition was achieved at low doses of TR[30]. However, with the increase in adsorbent dosage, a growing number of adsorption sites could not adsorb the dyes effectively while the amount of adsorbate remains constant. This observation is due to the increasing adsorbent dosage may increase the number of active sites to uptake more adsorbate[31]. However, as the amount of the adsorbent increased above 0.4 g, the numbers of existing adsorption areas were higher than the effective number of MB dyes. This may cause agglomeration of adsorbent, which leads to reduce removal efficiency of BM dye.

Effect of Temperature

The effect of temperature on the adsorption process of MB in the range of 25°C-55°C was investigated. As presented in Fig. 3(c), the adsorption capacity was found to be decreased with increasing temperature, which indicates that the process is exothermic[32]. In addition to this, as the temperature increased, the rate of diffusion of dye was enhanced and diffused out of the boundary layer of the active site of the adsorbent, which results in a reduction in the removal efficiency of MB dye. Therefore, the maximum adsorption of MB dye using TR was obtained at 25^{o}c. So, the favourable adsorption process is obtained at a low temperature.

Effect of Dye concentration

The effect of dye concentrations on the adsorption of BM dye by the prepared adsorbent was carried out at different concentrations (20- 60 ppm) with a shaking speed of about 220 rpm. As shown in Fig. 3(d), the removal efficiency of MB decreased with increasing dye concentration. The experimental result revealed that the maximum removal efficiency was obtained at a low concentration (20 ppm), beyond this concentration the removal efficiency was found to be decreased, and no more change was observed as BM dye concentration increased further. It can be explained by the fact that as the concentration of dye in the solution increases, the number of active sites on the surface of the adsorbent is decrease because the adsorbent dose is fixed, and therefore the removal efficiency decreases[33]. The adsorption capacity (qe) was increased as the concentration of dye increased. This is due to the increase in interaction between dye molecules and adsorbent surfaces with increasing dye concentration[34]. Similar findings were reported in different kinds of literature[33, 34]

Effect of Contact Time

To examine the required time for maximum performance of an adsorbent process, the experiment was carried out from 10 to 80 min contact time at optimum values of adsorbent dose 0.4 g, pH 6, initial concentration of dye 20 ppm, and at room temperature. It can be observed from Fig. 3(e) that the removal efficiency increases rapidly with an increase in contact time up to 60 min and beyond this contact time both the adsorption capacity and removal efficiency were decreased. The rapid increase in adsorption around the initial stage is due to the availability of an excess number of active sites on the surface of the adsorbent on which MB molecules get adsorbed through boundary layer adsorption[35]. In the later stage, when all the sites are occupied with dye molecules, the remaining dye molecules form aggregates at a higher contact time and reduce the adsorption capacity of the adsorbent. Therefore, the minimum time required for maximum performance of the adsorbent and to reach equilibrium was 60 min, with an adsorption capacity of 8.3668 mg/g.

Kinetic modeling

The study of chemical kinetics includes careful monitoring of the experimental conditions which influence the rate of a chemical reaction and helps to attain equilibrium in a reasonable length of time. In this study, various kinetic models, namely pseudo-first-order (equation 7), pseudo-second-order (equation 8), and intra-particle diffusion (equation 9) have been used for their validity with the experimental adsorption data for MB dye onto acid-treated sample prepared from tej residue wastes.

$$\log(qe - qt) = logqe - k_1 t \qquad \text{... (7)}$$

$$\frac{t}{qt} = \frac{1}{K_2 qe^2} + \frac{t}{qe} \qquad \text{... (8)}$$

$$qt = K_{diff} t^{1/2} + C \qquad \text{... (9)}$$

where q_e (mg/g) is the amount adsorbed at equilibrium time; q_t (mg/g) is the amount adsorbed at a time, t (min); k_1 is the pseudo-first-order rate constant; K_2 is the pseudo-second-order rate constant; k diff (mg/g min1/2) is the intra-particle diffusion rate constant, and C is the intercept that indicates the boundary layer thickness. The kinetic rate constant, k, and q_e for each model can be calculated by plotting graph log (q_e–q_t) versus t for pseudo-first-order, t/q_t versus t for pseudo-second-order models, and q_t versus $t^{1/2}$ for intra-particle diffusion models and the graphs presented as follow.

The calculated value of k, q_e, and correlation coefficient (R^2) for each kinetics model was presented in Table 2. As seen in Table 2, the calculated amount of adsorbed dye obtained through the pseudo-first-order model was close to the experimental value than the pseudo-second-order and intra-particle diffusion model. Furthermore, Fig. 4(a) showed that the correlation coefficient of pseudo-first-order (R^2= 0.96674) was found to be greater than that of pseudo-first-order Fig. 4(b) and intra-particle diffusion model Fig. 5(c), this indicates that the adsorption experiment of removal of MB dye by using TR follows pseudo-second-order model kinetics[2].

To examine the mechanism of the adsorption process and rate-limiting step, the experimental results are usually tested using the intra-particle diffusion model. From equation 9, a plot of qt as a function of the square root of time ($t^{0.5}$), produces a straight line that passes through the origin. Fig. 5 (d) showed that the line does not pass through the origin, thus confirming that the intra- particle diffusion model represents the only rate-limiting step, although it shows a slower rate than the surface adsorption step[30, 32].

Sorption Isotherms

In the present study, two isotherm equations, namely Langmuir and Freundlich were used for the analysis of the isotherm data[32]. The equation for Langmuir isotherm is represented as follows [35]:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad \text{... (10)}$$

where C_e is the equilibrium concentration of MB (mg/L), q_e is the quantity of MB dye adsorbed at equilibrium (mg/g), q_{max} is the maximum amount of MB sorbet (mg/g), and b is the adsorption constant (L/mg). A plot of 1/C_e versus 1/q_e gives a linear plot, and qmax and b can be obtained from the intercept and slope of the plot, respectively.

The Freundlich isotherm is the other empirical model which is commonly used to describe adsorption data and considers that the adsorption occurs on a heterogeneous surface with an increase of the concentration[31,34]. The linear expression of the Freundlich isotherm model can be illustrated in equation 11 below.

$$logq_e = logk_f + \frac{logC_e}{n} \qquad \text{... (11)}$$

where qe represents the equilibrium amount of MB dye adsorbed by the adsorbent, (mg/g), K_f represents the Freundlich constant that shows adsorption capacity (mg/L), n represents the intensity of the

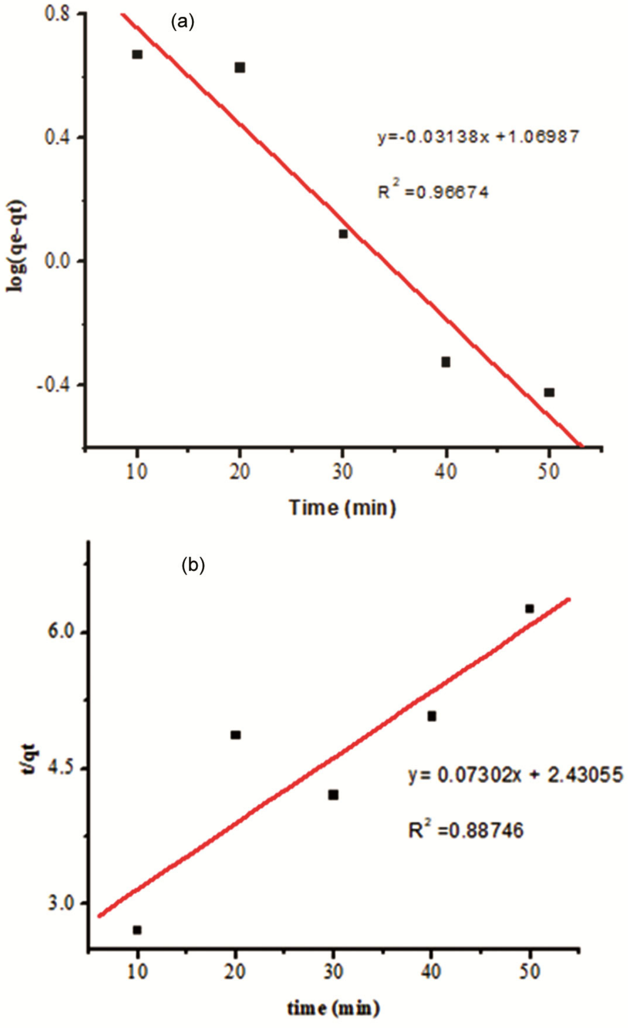

Fig. 4 — (a) Pseudo-first-order and (b) Pseudo-second-order

Table 2 — kinetics parameters

Kinetics model	Qe (Experimental)	Qe(calculated)	R^2	K
Pseudo-first-order	8.3668	11.7454	0.96674	-0.03138
Pseudo-second-order	8.3668	13.3904	0.88746	0.014285
Intra-particle diffusion	8.3668	1.28513	0.94215	-0.65039

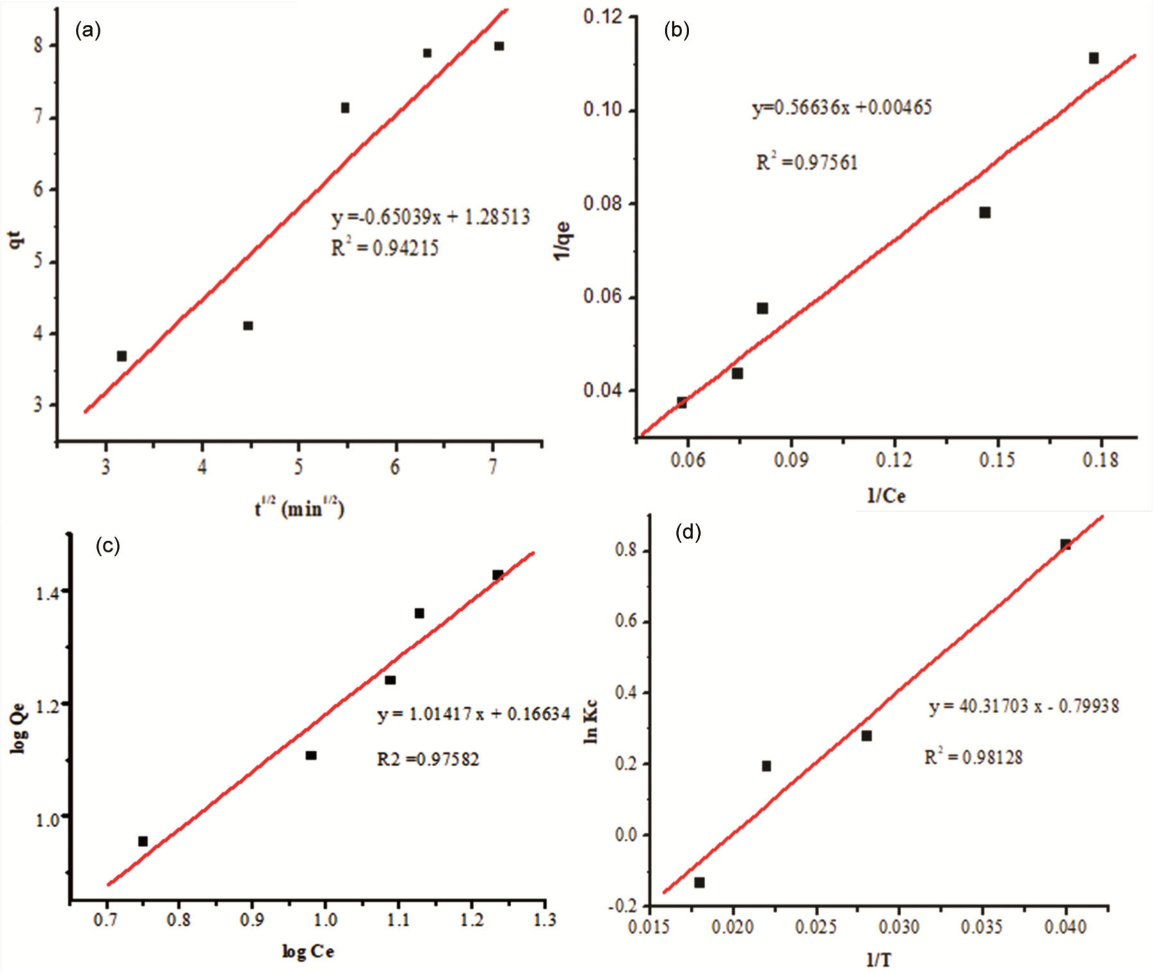

Fig. 5 — (a)Intra-particle diffusion; (b) Langmuir plot for the sorption of MB onto TR; (c) Freundlich plot for the sorption of MB onto TR and (d) Van'tHoff plot

Table 3 — Isotherm parameters

Isotherm	R^2	Isotherm parameters
Langmuir	0.97561	qm =215.053 b=0.00821
Freundlich	0.97582	Kf =1.4667 n= 0.9860

Table 4 — Dimensionless constant separation factor (RL) value at different initial concentration

Adsorbent	RL values				
	20(mg/l)	30(mg/l)	40(mg/l)	50 (mg/l)	60(mg/l)
TR	0.8589	0.8023	0.7527	0.7089	0.6699

adsorption constant, and C_e represents the equilibrium concentration of MB dye solution (mg/L)[25]. The parameters of Freundlich isotherms can be obtained from a linear plot of log q_e versus log C_e. K_f can be calculated from the intercept of the linear plot and n can be obtained from the slope of the equation and if its value is greater than one (n>1) the adsorption system would be favored[26].

All parameters of these two isotherms were calculated from linear equations and presented in Tables 3 and 4. By comparing the correlation coefficients (Fig. 5(b) and Fig. 5(c), it can be concluded that Freundlich (R^2=0.97582) isotherm provides a fitted model for the sorption system than the Langmuir model (R^2 =0.97561), which is based on multilayer sorption onto a surface containing a finite number of identical sorption sites, and it can be assumed the adsorbent surface is heterogeneous[1]. The presented values in Table 3 showed that the maximum adsorption capacity of MB was found to be 215.053 mg/g from the Langmuir isotherm model equation. The comparison of this value (Table 6) with other previous work shows that TR adsorbent was good potential in the aspect of MB removal.

In addition to this, the feasibility of the adsorption system at different initial dye concentrations (20, 30, 40, 50, and, 60 mg/L) was examined by using a dimensionless constant separation factor (RL) and the value RL for each initial dye concentration can be determined by using equation 12.

$$R_L = \frac{1}{1+bC_O} \quad \text{... (12)}$$

where RL represents the separation factor, b represents the Langmuir constant (L/mg), and CO represents the initial concentration of MB dye (mg/L)[25]. RL > 1 implies an unfavourable monolayer adsorption process and RL=1 indicates a linear process. The process is favourable when 0 < RL < 1 and irreversible when RL= 0[26]. As shown in Table 4 the calculated value of RL for each initial dye concentration lies in the range of 0- 1, which confirmed the favourable adsorption of MB dye over the adsorbent [27, 28].

Thermodynamics study

The thermodynamic parameters including change in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were calculated by using the following van't Hoff equations[4]. In this study, the adsorption experiments were performed in the range of 25 to 55^{o}c to examine the effect of temperature.

$$\Delta G° = -RT\ln(Kc) \quad \text{... (13)}$$

$$\text{Ln}Kc = \frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \quad \text{... (14)}$$

where, Kc represents the Langmuir equilibrium constant (L. mol^{-}); R indicates the gas constant (8.314 × J $mol.K^{-1}$), and T is the temperature (K). The values of $\triangle H^0$ and $\triangle S^0$ were calculated from the slope and intercept of the plots of ln (Kc) versus 1/T[25].

Table 5 displays that ΔG° values are negative except at 55°C temperature, which inform about the spontaneity and viability of the adsorption process of MB dye on TR[25]. Furthermore, small values of ΔG^0 were obtained at lower temperature, at this condition the high amount of MB was adsorbed over TR. The calculated value of Enthalpy change (ΔH) was found to be –33.52kJ/mol. This result suggests that the adsorption process is exothermic. Furthermore, the value of ΔH being less than 40 kJ/mol conforms to the process is not Chemisorptions[33]. The negative values of ΔS° revealed that the MB dye molecules become less ordered in solution and stay on the adsorbent surface without changing the internal structure of the adsorbent throughout the process.

Proposed adsorption mechanism

The probable adsorption mechanism of MB dyes on the surface of TR is provided in Fig. 6. The possible adsorption mechanism of MB can be explained by considering the electrostatic interaction between the negatively charged surface of TR and positively charge MB dye. This electrostatic interaction can be explained with the help of surface functional groups of TR adsorbent and the *p*H dependency of the adsorption of MB onto TR. FTIR analysis confirmed the presence of hydroxyl groups and carboxyl groups on the surface of TR. The ionization of these groups, which depends on solution *p*H, results in an electrical charge on the surface of the TR adsorbent[25]. The hydroxyl groups and carboxyl groups present on the surface of TR can gain or lose a proton, resulting in a surface charge that varies with changing *p*H.

Table 5 — Thermodynamic parameters for the adsorption of MB on TR

ΔH^0 [K J mol^{-1}]	ΔS^0 [J mol^{-1} K^{-1}]	ΔG^0 [KJ mol^{-1}]			
-335.2	-66.46	25 °c	35°c	45°c	55°c
		-2023.41	-715.97	-511.85	365.23

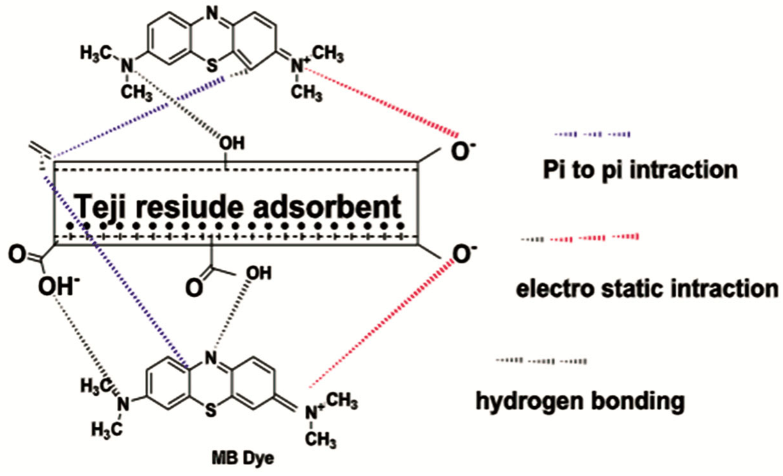

Fig. 6 — Proposed adsorption mechanism of MB on TR adsorbents

Table 6 — Adsorption comparison of different adsorbents in MB in the literature

Adsorbent	q_e(mg/g)	Reference
Ginkgo biloba leaves	48.07	26
Composite granules	36	31
Mango leaf powder	156	7
Kendu (*diospyrosmelanoxylonroxb*)	144.9	17
Coffee husk	416.68	2
Orange peel	218.52	28
Magnetized Papaya Seeds	120.48	16
Mango peel	277.8	11
Cw- ACA	138.88	22
Sawdust of lemon	52.4	32
Bamboo charcoal	49.5	13
Tej residue	215.053	This study

As shown in Fig. 6, the electrostatic interaction was not the only mechanism for MB removal, there are also hydrogen bonding interactions and π–π interactions between the adsorbent and adsorbate. This type of interaction was also observed in MB dye removal using Mango leaf powder as an adsorbent[7,8]. The comparison of the previous study on the adsorption of MB dye by different adsorbents with the current finding is presented in Table 6.

Conclusion

The ability of TR to remove MB from aqueous solution was investigated under different experimental conditions in batch mode. Adsorption experiments were carried out as a function of solution pH, initial dye concentrations, contact time, adsorbent dosage, and temperature. The equilibrium data revealed that the Adsorption isotherm was well fitted in Freundlich isotherm model. Moreover, the kinetics study revealed that the adsorption process follows a pseudo-first-order kinetic model. Since TR used in this work was freely, abundantly, and locally available, it can be expected as a promising adsorbent for the removal of dyes from aqueous solutions.

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