CELLULOSE CHEMISTRY AND TECHNOLOGY

BIOSORPTION OF METHYLENE BLUE ONTO FOUMANAT TEA WASTE: EQUILIBRIUM AND THERMODYNAMIC STUDIES

A. EBRAHIMIAN and E. SABERIKHAH

Faculty of Fouman, College of Engineering, University of Tehran, P.O. Box 43515-1155, Fouman 43516-66456, Iran

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The sorption of methylene blue (MB) from an aqueous solution by Foumanat tea waste was studied in a batch system. Three widely used isotherms (Langmuir, Freundlich and Temkin) were examined for MB sorption at different temperatures. The four Langmuir linear equations were discussed, and the Langmuir parameters were obtained from them. Langmuir-1 is the most popular linear form and it has the highest coefficient of determination, compared with the other Langmuir linear equation. The maximum saturated monolayer sorption capacity of tea waste for MB was 244 mg/g at 303 K. Various thermodynamic parameters, such as $\Delta G°$, $\Delta H°$, $\Delta S°$ and E_a, were calculated. The findings of this investigation suggested that physical sorption plays a role in controlling sorption. We investigated the adsorption mechanism by FTIR and SEM techniques. FTIR data indicated that MB binding occurred mostly at –OH and C=O groups of tea waste.

Keywords: biosorption, methylene blue, tea waste, isotherm, thermodynamic, adsorption mechanism

INTRODUCTION

Dyeing technology is synonymous to man's existence and the usage of dye products is unavoidable.[1,2] However, dyeing causes major problems when dyes are indiscriminately released into the environment producing pollution to man and his environment due to their slow biodegradability.[1,3] The contamination of water bodies by synthetic dyes has created serious environmental problems worldwide.[4] Nowadays, large amounts of dyeing wastewater containing a certain amount of residual dye and a large number of dyeing auxiliaries are rich in harmful substances, and waters have different colors.[5] The presence of small amount of dyes (less than 1 ppm) is highly visible and undesirable.[6] Hence, the necessity for dye-containing water to undergo treatment before disposal into the environment is highly imperative.[7]

Conventional wastewater treatment methods for removing dyes include physicochemical, chemical and biological methods, such as coagulation and flocculation, adsorption, ozonation, electrochemical techniques, and fungal decolorization.[8,9] But these processes are not always effective and economic where the solute concentrations are very low. Moreover, most of the organic dyes undergo very slow biodegradation. Currently, the sorption technique has been proven to be an effective and attractive process for the treatment of dye-containing wastewater.[10] In recent years, biosorption has been strongly recommended as an economically viable sustainable technology for the treatment of wastewater streams.[11] The importance and usefulness of biosorption in wastewater treatment is well established.[12] Biosorption in environmental engineering is now in the focus and consideration of all nations, owing to its low initial cost, simplicity of design, ease of operation, insensitivity to toxic substances and complete removal of pollutants even from dilute solutions.[11,13,14]

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies give the capacity of the sorbent and describe the sorption isotherm by constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium.[15]

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Two, three and even four-parameter isotherm models are available for modeling adsorption data.[16,17] Two-parameter models are usually preferred because, in spite of their simplicity, they can be easily linearized. Linear regression has been frequently used to evaluate the model parameters. However, transformations of non-linear isotherm equations to linear forms usually result in errors of parameter estimation and distort the fit.[16]

The major interest of this study is to investigate sorption of methylene blue (MB) from aqueous solution using Foumanat tea waste. In order to understand the nature of the sorption, equilibrium isotherms and thermodynamic parameters have been evaluated. Also, we characterized tea waste samples before and after MB adsorption by FTIR and SEM techniques.

EXPERIMENTAL

Biosorbent preparation

The tea waste was collected from the cafeteria of Fouman Faculty of Engineering. The collected materials were washed several times with boiled water and finally with distilled water to remove any adhering dirt. The washed materials were then dried in the oven at 60 °C for 48 h. The dried tea waste was then ground and sieved to a size range of 100-500 µm. Finally, the resulting product was stored in an air-tight container before further use.

Experimental procedure

Equilibrium isotherms were determined by shaking a fixed mass of tea waste (0.7 g) with 200 mL of MB solutions with different initial concentrations (50, 100, 200, 300, 400 and 500 mg/L) in 250 mL stopperred glass Erlenmeyer's flasks at a temperature of 20 °C and pH of 6-7. The procedure was repeated for temperatures of 30, 40 and 50 °C. Initial pH adjustments were carried out by adding either a 0.01 M hydrochloric acid or 0.01 M sodium hydroxide solution. After shaking the flasks for 120 min, the reaction mixtures were filtered through filter paper, and then the filtrates were analyzed for the remaining MB concentrations with spectrometry at the wavelength of maximum absorbance, 668 nm, using a double beam UV-Vis spectrophotometer (Shimadzu, Model UV 2100, Japan).

Characterization

Fourier transform infrared (FTIR) analysis was applied to determine the surface functional groups, using an FTIR spectroscope (FTIR-2000, Bruker), where the spectra were recorded from 3500 to 500 cm^{-1}. Surface morphology was studied using Scanning electron microscopy (Vegall-Tescan company). Specific surface area based on nitrogen physisorption was measured by Sibata surface area apparatus 1100. The samples were degassed at 250 °C for 2 h prior to the sorption measurement.

RESULTS AND DISCUSSION

Adsorption isotherms

Models have an important role in technology transfer from a laboratory to a pilot plant scale.[13] Sorption equilibriums provide fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation.[18] The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase at equilibrium. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose.[19] An appropriate model can help in understanding the process mechanisms, analyze experimental data, predict answers to operational conditions, and optimize processes.[13,20] Thus, the correlation of equilibrium data using either theoretical or empirical equations is essential for adsorption data interpretation and prediction. Several mathematical models can be used to describe experimental data of adsorption isotherms. Three famous isotherm equations, Langmuir, Freundlich and Temkin, were employed for further interpretation of the obtained biosorption data[13,18,21] of MB onto tea waste.[7,22] However, the Langmuir isotherm can be linearized as four different types (Table 1), and simple linear regression will result in different parameter estimates.[14,23] The more popular linear forms used are Langmuir-1 and Langmuir-2, and the best fit is obtained using Langmuir-1 due to the minimal deviations from the fitted equation resulting in the best error distribution.[23]

Linear regression method

Figure 1 shows the four linear Langmuir equations with the experimental data for the sorption of MB onto tea waste at various temperatures. The values of the Langmuir constants, the saturated monolayer sorption capacity, q_m, and the sorption equilibrium constant, K_L, are presented in Table 2 for the sorption of MB onto tea waste at 293, 303, 313, and 323 K. These values of the coefficient of determinations, R^2, obtained from Langmuir-1 and Langmuir-2, indicate that there is strong positive evidence that the sorption of MB onto tea waste follows the Langmuir isotherm.

Table 1
List of adsorption isotherm models

Isotherm		Linear form	Plot
Langmuir-1	$q_e = q_m K_L C_{e/} 1 \pm K_L C_e$	$C_e/q_e = 1/q_m C_e + 1/K_L q_m$	C_e/q_e vs. C_e
Langmuir-2		$1/q_e = [1/K_L q_m] 1/C_e + 1/q_m$	$1/q_e$ vs. $1/C_e$
Langmuir-3		$q_e = q_m - [1/K_L]\, q_e/C_e$	q_e vs. q_e/C_e
Langmuir-4		$q_e/C_e = K_L q_m - K_L q_e$	q_e/C_e vs. q_e
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + 1/n \log(C_e)$	$\log(q_e)$ v_s $.\log(C_e)$
Temkin	$q_e = RT/B(\ln K_T C_e)$	$q_e = B \ln K_T + B \ln C_e$	q_e vs. $\ln C_e$

Table 2
Isotherm parameters obtained using the linear regression method

	Langmuir-1 isotherm		
Temperature (K)	q_m (mg/g)	K_L (L/mg)	R^2
293	200	0.034	0.999
303	244	0.027	0.999
313	213	0.026	0.999
323	196	0.022	0.997
	Langmuir-2 isotherm		
Temperature (K)	q_m (mg/g)	K_L(L/mg)	R^2
293	175.44	0.041	0.997
303	250	0.021	0.998
313	208.33	0.027	0.996
323	156.25	0.038	0.993
	Langmuir-3 isotherm		
Temperature (K)	q_m (mg/g)	K_L(L/mg)	R^2
293	197.39	0.034	0.989
303	245.21	0.022	0.997
313	215.64	0.026	0.990
323	185.60	0.030	0.968
	Langmuir-4 isotherm		
Temperature (K)	q_m (mg/g)	K_L (L/mg)	R^2
293	199.63	0.034	0.988
303	243.91	0.022	0.997
313	214.79	0.026	0.990
323	188.13	0.029	0.969
	Freundlich		
Temperature (K)	n	K_F (mg/g)(L/mg)$^{1/n}$	R^2
293	1.53	10.1	0.991
303	1.50	10.2	0.990
313	1.52	10.14	0.991
323	1.55	10.02	0.995
	Temkin		
Temperature (K)	B	K_T (L/mg)	R^2
293	38.03	0.52	0.994
303	37.88	0.49	0.994
313	37.22	0. 58	0.998
323	36.74	0.52	0.962

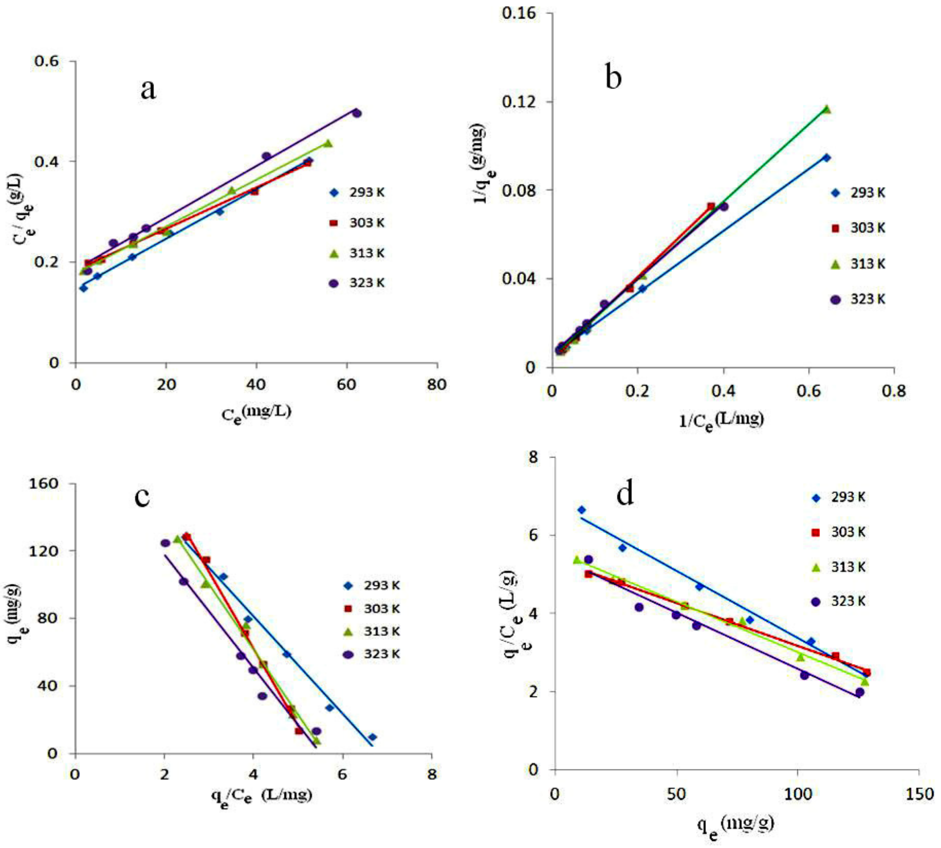

Figure 1: Langmuir isotherms obtained using the linear method for the sorption of MB onto tea waste at various temperatures: a) Langmuir-1, b) Langmuir-2, c) Langmuir-3 and d) Langmuir-4

The applicability of the Freundlich and Temkin sorption isotherms was also analyzed, using the same set of experimental data (Figures 2 and 3). If only the linear form of Langmuir-1 is used for comparison, Langmuir-1 fits the experimental data better than the Freundlich isotherm due to the higher value of the coefficient of determinations (Table 2). In contrast, when using the linear form of the other Langmuir equations, the Freundlich isotherm fits the experimental data better than the Langmuir isotherm in most cases, especially in the case of Langmuir-3 and Langmuir-4. The Freundlich and Temkin isotherm constants and the coefficients of determination are shown in Table 2. The magnitude of the Freundlich constant n gives a measure of favorability of biosorption. Values of n >1 represent a favorable biosorption process.[24] For the present study, the value of n also presents the same trend at all the temperatures indicating a favorable nature of biosorption of MB by tea waste. Langmuir-1 and Freundlich isotherms were the best fitting models for our experiment results (Table 2).

The effect of the isotherm shape can be used to predict whether a sorption system is favorable or unfavorable. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless factor, R_L, which describes the type of pattern and is defined as R_L in Eq. (1):

$$R_L = 1/(1+K_L C_0) \qquad (1)$$

where R_L is a dimensionless separation factor, C_0 is the highest initial dye concentration and K_L is the Langmuir constant that indicates the nature of adsorption (Table 2).

The values of R_L indicate the type of isotherm: irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).[25] In this work, the values of R_L for sorption of MB onto tea waste were 0.055, 0.069, 0.077 and 0.083 at temperatures of 293, 303, 313 and 323 K, respectively. These values indicated that the adsorption behavior of tea waste was favorable for the MB ($R_L < 1$).

Non-linear regression method

In this work, the Langmuir-1, Freundlich and Temkin models were evaluated by the average relative error (ARE) function (Eq. (2)),[26] which measures the differences of the amount of dye uptake by the adsorbent, predicted by the models, and the actual q measured experimentally.

$$\text{Average relative error}=100\%/p \sum[\,|q_{cal}-q_{exp}|/q_{exp}] \quad (2)$$

where q_{cal} is each value of q predicted by the fitted model and q_{exp} is each value of q measured experimentally, and p is the number of experiments performed.

The data of the fitted models are presented in Table 3. Figure 4 shows the adsorption isotherms and experimental data at various temperatures. As can be seen, the best isotherm model that fits the experimental data with a lower error was the Langmuir-1 (at 293 and 313 K) and Freundlich (at 303 and 323 K) isotherm models. The average relative error measures how close is the q fitted by the model to the actual q measured experimentally.[26]

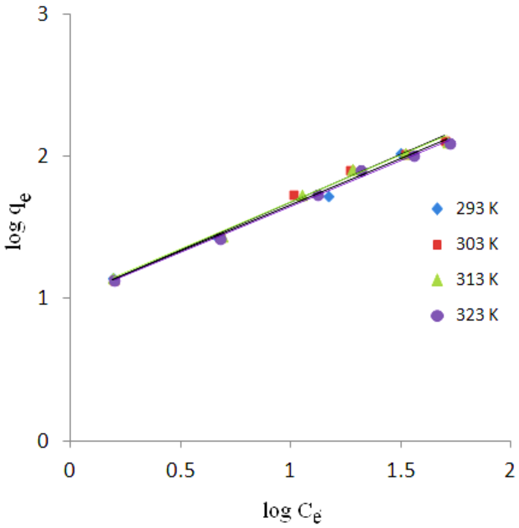

Figure 2: Freundlich isotherm obtained using the linear method for the sorption of MB onto tea waste at various temperatures

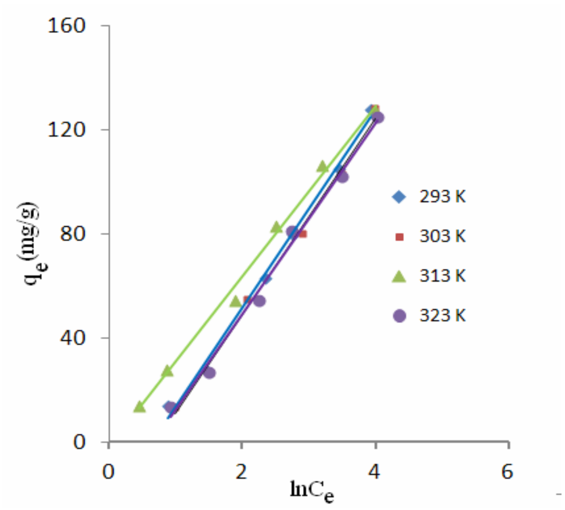

Figure 3: Temkin isotherm obtained using the linear method for the sorption of MB onto tea waste at various temperatures

Table 3
Average relative error (ARE) for the non-linear regression method

Model	Temperature (K)	ARE
Langmuir-1	293	2.01
	303	15.33
	313	6.74
	323	13.81
Freundlich	293	10.68
	303	4.5
	313	11.45
	323	5.43
Temkin	293	39.1
	303	20.27
	313	45.64
	323	27.75

Table 4

Thermodynamic parameters for the adsorption of MB on to tea waste

		Langmuir-1 isotherm			
Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol K)	E_a (kJ/mol)	S*
293	-2.482	-11.51	-30.88	-5.50	0.933
303	-2.234				
313	-1.863				
323	-1.579				

*S**: sticking probability

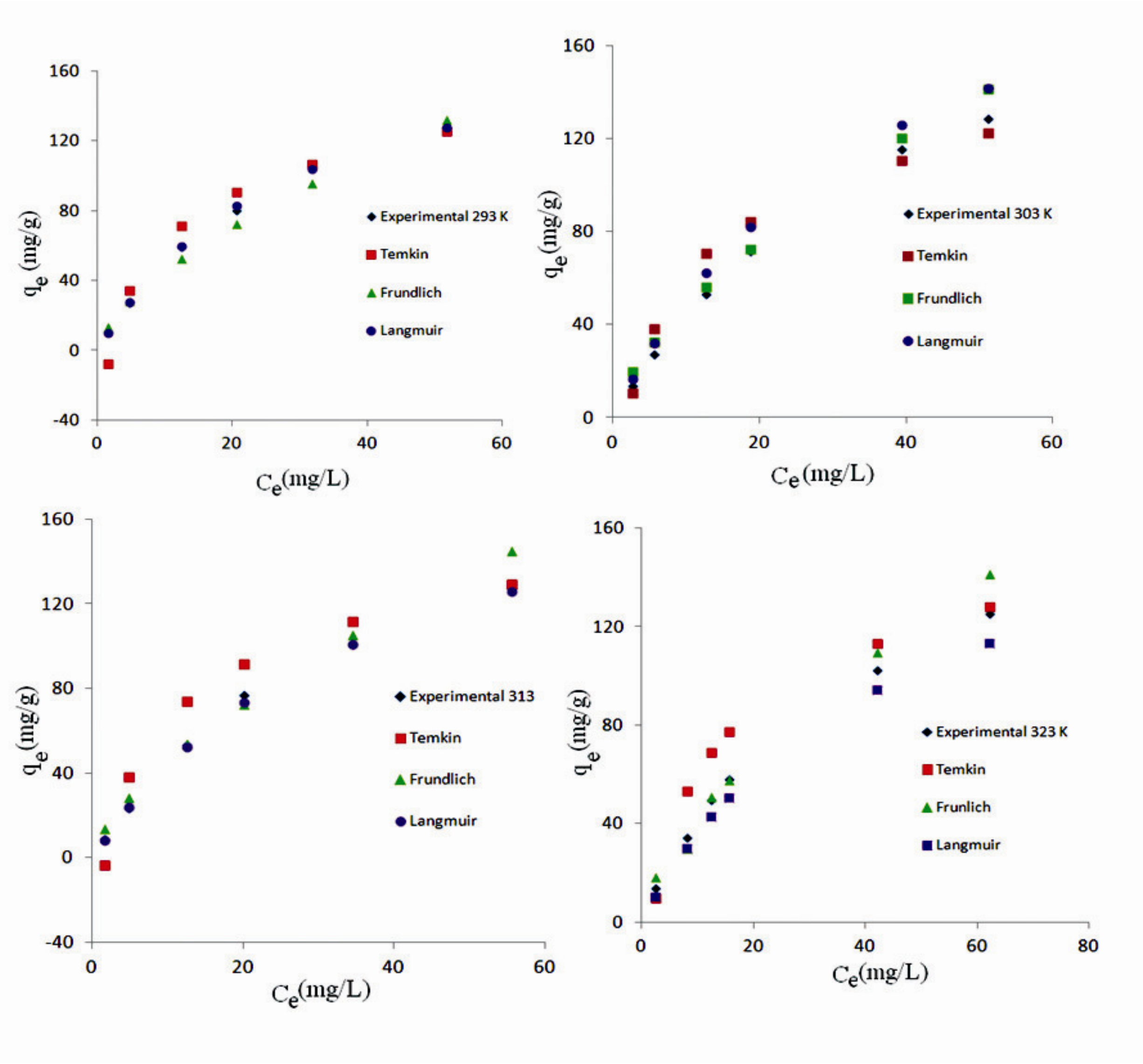

Figure 4: Isotherm obtained using the non-linear method for the sorption of MB onto tea waste at various temperatures

Adsorption thermodynamics

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously.[23] Gibb's free energy change, Δ*G*°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if Δ*G*° is a negative value. The thermodynamic parameters of Δ*G*°, enthalpy change, Δ*H*°, and entropy change, Δ*S*°, for the adsorption processes are calculated using the following equations:[24]

$$\Delta G^\circ = - RT \ln K_D \quad (3)$$

K_D, is given by the following equation:

$$K_D = q_e/C_e \quad (4)$$

where K_D is the distribution coefficient[24] and:

$$\ln K_D = -\Delta H^0/R\ (1/T) + \Delta S^0/R \quad (5)$$

where R is a universal gas constant (8.314 J/mol K) and T is the absolute temperature in K. The plot of $\ln K_D$ versus 1/T was found to be linear.

The values of ΔH° and ΔS° were determined, respectively, from the slope and intercept of the plot. The thermodynamic parameter, ΔG°, is shown in Table 4. ΔH° and ΔS° for the sorption process were calculated to be -11.51 kJ/mol and -30.88 J/mol K, respectively. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for MB to sorb onto tea waste. The value of ΔH° was negative, indicating that the sorption reaction is exothermic. The negative value of ΔS° reflects the affinity of the tea waste for MB and suggests some structural changes in MB and tea waste interaction. In addition, the negative value of change in entropy ΔS° reflects the decreased randomness at the solid/solution interface during the adsorption of MB on tea waste. This is a direct consequence of: (i) opening up of tea waste structure, (ii) enhancing the mobility and extent of penetration within the tea waste, and (iii) overcoming the activation energy barrier and enhancing the rate of intraparticle diffusion.[13,27]

The activation energy (E_a) was obtained from the slope of plot ln (1-θ) against 1/T, where the surface coverage (θ) was calculated from the relation in Eq. (6).[28]

$$\theta = 1 - C/C_0 \quad (6)$$

where C_0 and C are the initial and residual concentration of MB in solution, respectively (mg/L).

In order to further support the assertion that physical adsorption is the predominant mechanism, the value of sticking probability (S^*) was estimated from the experimental data. It was calculated using a modified Arrhenius type equation related to surface coverage, as expressed in Eq. (7).[29]

$$S^* = (1-\theta)\, e^{-(E_a/RT)} \quad (7)$$

The parameter S^* indicates the measure of the potential of an adsorbate to remain on the adsorbent indefinitely. It can be expressed as in Table 4. The effect of temperature on the sticking probability was evaluated throughout the temperature range from 293 to 323 K, by calculating the surface coverage at various temperatures. The apparent activation energy (E_a) and the sticking probability (S^*) are estimated from the plot with a reasonably good fit for MB on the tea waste. The E_a values calculated from the slope of the plot were found to be -5.5 kJ/mol. The negative values of E_a indicate that lower solution temperatures favor MB removal by adsorption onto tea waste and the adsorption process is exothermic in nature. Relatively low values of E_a suggest that MB adsorption is a diffusion controlled process. The results shown in Table 4 indicate that the probability of MB to stick onto the tea waste surface is very high, as $0 < S^* < 1$ for MB (Table 5). These values confirm that the sorption process is physisorption.[29]

Proposed adsorption mechanism

The major challenge in an adsorption study is to clarify the adsorption mechanism. However, before understanding the adsorption mechanism, it is necessary to consider two points: firstly, the structure of the adsorbate; and secondly, the adsorbent surface properties. It must be pointed out that MB is a cationic dye having amine groups in its structure. In aqueous solutions, MB dissociates into MB^+ and Cl^- ions. BET, FTIR and SEM were used for adsorbent characterization before and after MB sorption.

Table 5
Potential sticking probability relationship between sorbate and sorbent[29]

Values of S*	Potential sticking probability
$S^* > 1$	Adsorbate unsticking to adsorbent – no sorption
$S^* = 1$	Linear sticking relationship between adsorbate and adsorbent- possible mixture of physisorption and chemisorption mechanism
$S^* = 0$	Indefinite sticking of adsorbate to adsorbent chemisorption mechanism predominant
$0 < S^* < 1$	Favourable sticking of adsorbate to adsorbent- physisorption mechanism predominant

S^*: sticking probability

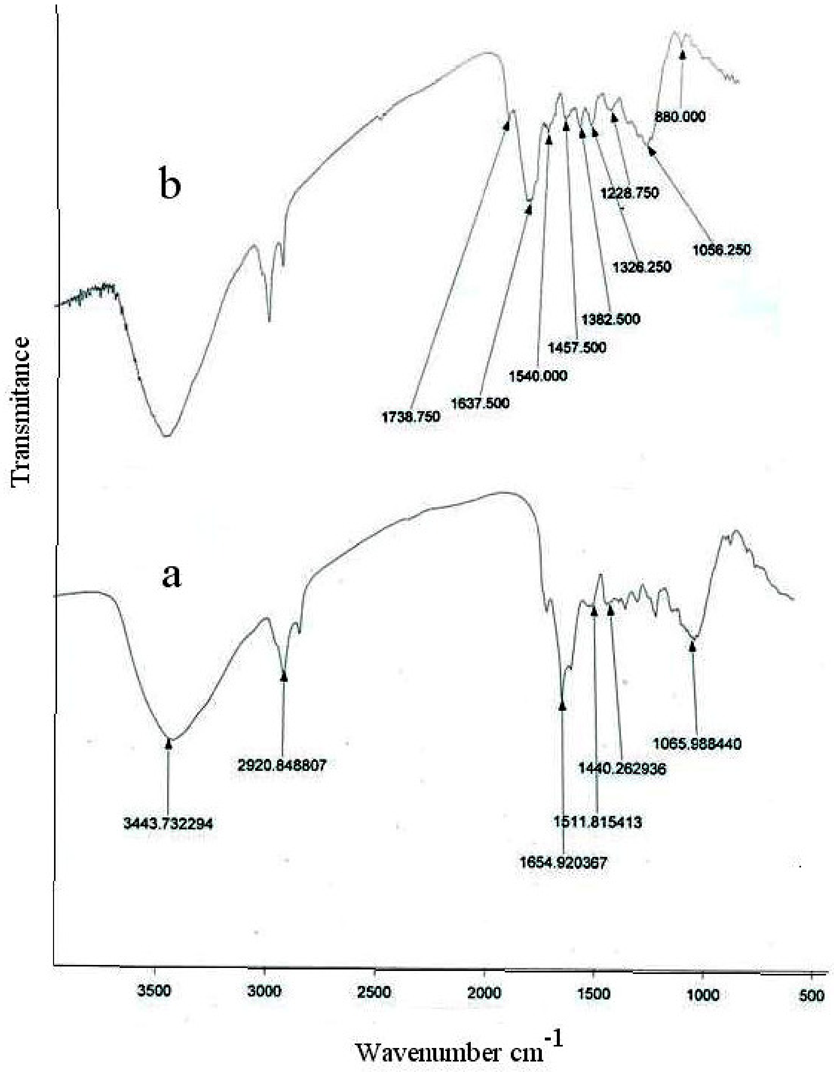

Figure 5: FTIR spectra of tea waste a) before and b) after MB adsorption

The FTIR spectra of tea waste before and after MB adsorption are shown in Figure 5. In the FTIR spectrum of tea waste before adsorption (Figure 5a), the broad and intense absorption peaks at around 3443 cm^{-1} correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols and carboxylic acids, as in pectin, cellulose and lignin, thus, showing the presence of "free" hydroxyl groups on the adsorbent surface.[30] The peak at 2921 cm^{-1} is attributed to the symmetric and asymmetric C–H stretching vibration of aliphatic acids.[30] The peak at 1655 cm^{-1} is due to asymmetric stretching vibrations of C=O and the peak observed at 1512 cm^{-1} can be assigned to an aromatic compound group. The other prominent peaks are due to NH_2, C=O and –C–C– (1440, 1066 and 875 cm^{-1}, respectively) groups. Some distinct changes are noted between the spectra before and after MB adsorption onto tea waste. In the case of the spectrum obtained after MB adsorption, there is a remarkable shift in the positions of –OH, C=O and –C–C– group peaks, which indicates MB binding mostly at –OH and C=O groups. The changes in the FTIR spectra confirm the complexation of MB with functional groups present in the adsorbents.[24,31,32] Figure 6 shows our proposed model for MB adsorption onto tea waste.

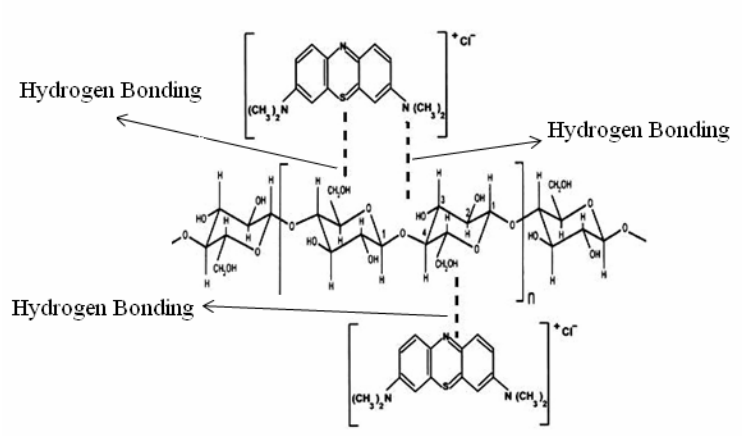

Figure 6: Adsorption mechanism of MB onto tea waste

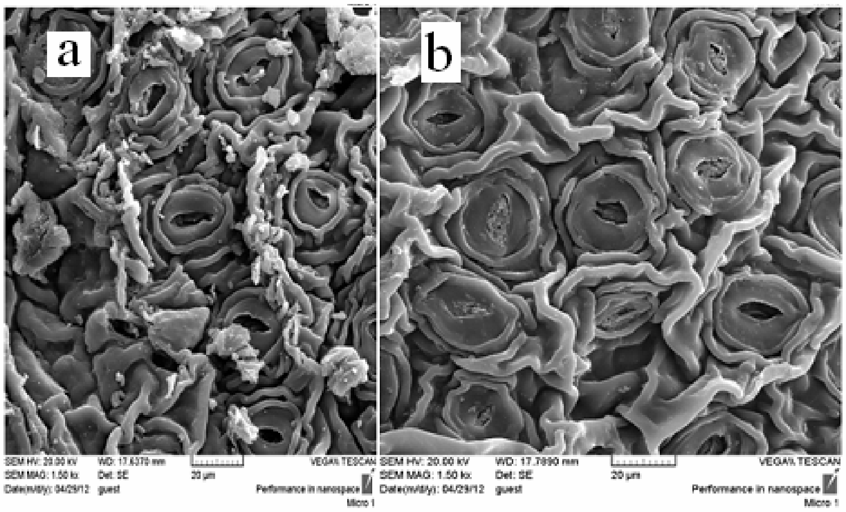

Figure 7: SEM micrographs of tea waste a) before and b) after MB adsorption

Figure 7 shows the SEM micrographs of tea waste samples before and after MB adsorption. Figure 7a shows that the tea waste possesses a flower-like surface morphology with some pores. The surface of MB-loaded adsorbent (Figure 7b), however, shows that the pores of tea waste are covered with MB molecules. The BET surface area and pore volume were measured to be of 21 m^2/g and 0.008 cm^3/g, respectively, for tea waste before MB adsorption.

CONCLUSION

In conclusion, the results clearly establish that the sorption of MB onto tea waste was favored at lower solution temperatures. The activation energy further supports lower solution temperatures and an excellent sticking of MB. The sorption process is spontaneous and exothermic and the mechanism is physisorption. The equilibrium data agree with the Langmuir-1 isotherm. The FTIR data indicate that MB binding occurred mostly at –OH and C=O groups of the tea waste.

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