Adsorptive removal of methylene blue by tea waste

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ABSTRACT

The potentiality of tea waste for the adsorptive removal of methylene blue, a cationic dye, from aqueous solution was studied. Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, initial methylene blue concentration, adsorbent dosage and pH. The nature of the possible adsorbent and methylene blue interactions was examined by the FTIR technique. The pH_{pzc} of the adsorbent was estimated by titration method and a value of 4.3 ± 0.2 was obtained. An adsorption–desorption study was carried out resulting the mechanism of adsorption was reversible and ion-exchange. Adsorption equilibrium of tea waste reached within 5 h for methylene blue concentrations of 20–50 mg/L. The sorption was analyzed using pseudo-first-order and pseudo-second order kinetic models and the sorption kinetics was found to follow a pseudo-second order kinetic model. The extent of the dye removal increased with increasing initial dye concentration. The equilibrium data in aqueous solutions were well represented by the Langmuir isotherm model. The adsorption capacity of methylene blue onto tea waste was found to be as high as 85.16 mg/g, which is several folds higher than the adsorption capacity of a number of recently studied in the literature potential adsorbents. Tea waste appears as a very prospective adsorbent for the removal of methylene blue from aqueous solution.

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1. Introduction

In industrial water pollution, the color produced by minute amount of organic dyes in water is considered very important because, besides having possible harmful effects, the color in water is aesthetically unpleasant. Colored water can affect plant life, and thus an entire ecosystem can be destroyed by the contamination of various dyes in water. Some dyes are also toxic and even carcinogenic. This dictates the necessity of dye containing water to undergo treatment before disposal to the environment. The conventional methods for color removal are biological oxidation and chemical precipitation [1–3]. But these processes are not always effective and economic where the solute concentrations are very low. Moreover, most of the synthetic organic dyes undergo very slow biodegradation. Currently the sorption technique is proved to be an effective and attractive process for the treatment of dye containing wastewater [4–6]. Also, this method will become inexpensive, if the sorbent material used is of cheaper cost and does not require any expensive additional pretreatment step.

In the present work, methylene blue (MB) is selected as a model compound in order to evaluate the capacity of the adsorbent for the removal of methylene blue from its aqueous solution. Methylene blue is a cationic dye having the structure:
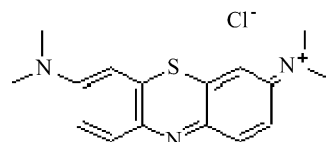
Although MB is seen in some medical uses in large quantities, it can also be widely used in coloring paper, dyeing cottons, wools, coating for paper stocks, etc. Though MB is not strongly hazardous, it can cause some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans [7,8].

The adsorption characteristics of MB on various adsorbents have previously been extensively investigated for many purposes of purification and separation. However, most of the work was on the adsorption behavior of activated carbon [9–14]. Its initial cost and the need for a costly regeneration system make it economically less viable as an adsorbent for wastewater treatment. Cost effectiveness, availability and adsorptive properties, are the main criteria for choosing an adsorbent to remove organic compounds. Taking these criteria into consideration, many researchers have investigated the adsorptive properties of unconventional adsorbents. Kumar et al. [7] studied the adsorption mechanisms of MB

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onto fly ash and demonstrated that fly ash can be used as an adsorbent for the removal of MB from its wastewater and the sorption process is particle diffusion controlled with some predominance of some external mass transfer at the initial stage. Vadivelan et al. [8] studied equilibrium, kinetics, mechanism and process design for the adsorption of MB onto rice husk and found that the kinetics of adsorption were pseudo-second order with regard to external mass transfer at earlier stage and intraparticle diffusion at later stage. Ghosh et al. [15] investigated the adsorption of MB using kaolinite as adsorbent and showed that kaolinite clay could be effective in removing methylene blue in relatively low concentrations from the aqueous medium. Senthilkumaar et al. [16] studied the adsorption of MB onto jute fiber carbon and showed that equilibrium data agreed well with Langmuir isotherm models. Chakrabarti et al. [17] investigated the removal of MB from aqueous solution using glass fibers as adsorbent and showed that the equilibrium dye adsorption followed Langmuir and Freundlich isotherm equation and that the mechanism of adsorption could be explained by using the micro-crack theory of glass structure. Akbal [18] studied the adsorption of basic dyes from aqueous solution onto pumice powder and indicated that pumice powder was effective in removing basic dye such as MB from aqueous solution and that the rate of removal from aqueous solution by pumice powder was pseudo-second order kinetics with good correlation. Gürses et al. [19] investigated the adsorptive removal of MB by clay and observed that the adsorption capacity decreases with increasing temperature and that the adsorption equilibrium was attained in 1 h. Imamura et al. [20] studied adsorption behavior of MB on stainless steel surface and indicated that adsorption data was fitted well to the Langmuir isotherm and both the electrostatic and hydrophobic interaction contribute to the adsorption. Doğan et al. [21] investigated the kinetics and mechanism of removal by adsorption onto perlite and showed that the rate of removal of MB by perlite followed the second order kinetics. Bhattacharyya et al. [22] demonstrated that neem leaf powder was a promising adsorbent for the removal of MB from water and the adsorption followed pseudo-first order kinetics with the interactions largely within the first hour.

In the present study, tea waste (TW) has been used as adsorbent for the removal of MB from its aqueous solution. It is a household waste available in huge amount in Bangladesh. It is an oxygen demanding pollutant. Also it takes a long time for biodegradation. On the other hand, when the tea waste used as adsorbent becomes saturated, it is just incinerated. The waste tea ash obtained by incineration is not a pollutant rather it could be used as an adsorbent. Hence, tea waste is a cost effective adsorbent. In this study, the effects of initial MB concentrations, tea waste mass, pH and contact time on the amount of color removal was investigated. The pH_{pzc} of the adsorbent was determined by titration method. An adsorption–desorption study was also carried out to illustrate the mechanism of adsorption. FTIR analysis was also carried out to examine the possible interaction between adsorbent and methylene blue. Equilibrium isotherm data were fitted to Langmuir and Freundlich equations and constants of isotherm equations were determined. Further, the kinetics involved in the sorption process was evaluated at different initial MB concentrations.

2. Materials and methods

2.1. Materials

The tea waste used in the present investigation as an adsorbent was collected from household. The tea dust discarded after using is called tea waste. The collected materials were then washed with

Table 1
Physical and chemical properties of tea waste used in the experiments

| Chemical characteristics [23]	Percent
Moisture	11.01
Water soluble components	6.04
Insoluble components	80.24
Ash	2.97
Total loss of ignition	94.06
Physical characteristic	Unit
Bulk density	0.228 g/cm^3
Particle size	180–300 μm

tap water and distilled water for several times to remove all the dirt particles. It was then boiled with distilled water to remove caffeine, tannin and other dyes and washed with distilled water till the washing water contains no color. The washed materials were then dried at 95 °C for 16 h. The dried materials were then crushed and sieved and stored in bottles for uses. The chemical and physical characteristics of the tea waste are presented in Table 1. The particle size distribution curve is shown in Fig. 1. The particle size is in the range of 180–300 μm.

2.2. Chemicals

Stock solution was prepared by dissolving 1.0 g of MB (dye content 82%) supplied by Merck, Germany, in 1 L distilled water without further purification. The test solutions were prepared by diluting stock solution to the desired concentrations. The adsorption capacities have been estimated based on the fraction of pure dye material in product. Before mixing the adsorbent the pH of each solution was adjusted to the required value with diluted or concentrated HCl and NaOH.

2.3. Determination of surface charge and pH$_{zpc}$ of the adsorbent

The surface charge (Q) and the pH_{pzc} of the adsorbent in aqueous phase was analyzed with different system pH values by using the titration method described elsewhere [24]. 0.1 g adsorbent was taken in 50 mL 0.1 M KNO$_3$ solution and agitated with magnetic stirrer. Then the pH of the solution was measured after an equilibrium time of 10 min. The titration was carried out with 0.1 M NaOH and 0.1 M HCl, respectively.
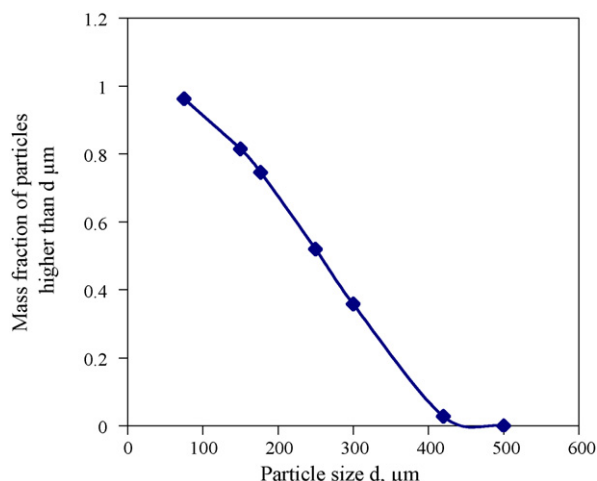
Fig. 1. Particle size distribution curve.

2.4. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy of the adsorbent was done by using an FTIR spectrophotometer (Model: FTIR 2000, Shimadzu, Kyoto, Japan). About 150 mg KBr disks containing approximately 2% of tea waste samples was prepared shortly before recording the FTIR spectra on an FTIR spectrophotometer in the range from 400 to 4000 cm^{-1} with 4 cm^{-1} resolution. The resulting spectra were the average of 30 scans.

2.5. Sorption experiments

The sorption experiments were carried out in 250 mL stopper conical flask containing varying amount of MB solutions and adsorbent dosages. Then the samples were agitated using flash shaker (Stuart Scientific Co. Ltd., Model SF1, UK) at room temperature (27 ± 2 °C). Agitation was made for 6 h, at constant oscillation of 400 osc min^{-1}. The samples were then centrifuged, and the left out concentration in the supernatant solution were analyzed using a UV/VIS spectrometry (Shimadzu Model UV-1601) by monitoring the absorbance changes at a wavelength of maximum absorbance (664 nm).

The effect of pH on the removal of MB was analyzed over the pH range of 2–10. The pH was adjusted using 0.1N NaOH and 0.1 N HCl solutions. In this study, 200 mL of dye solution with concentration of 20 mg/L was taken in a stopper plastic conical flask and was agitated with 0.3 g of tea waste. The pH of the solution changed slightly during sorption. It was presumed that the change in solution pH would cause a change in the structure of MB and consequently, in its adsorption process. The change in the structure of MB would be detected by the variations in the visible spectra of MB. To verify such possibilities, the effect of pH on the visible spectra of MB solution was tested in absence of adsorbents. As the variation in the spectra at given pH might be time-dependent, the visible spectra of MB solution was recorded at the same interval time after the pH was adjusted. It was found that the absorbance of the spectra was stable in the investigated pH range (pH 2–10). Fig. 2 shows the spectra of MB solution at different pH. It is obvious from the figure that there are no appreciable changes in spectra of MB in the investigated pH range.

A desorption study was carried out by agitating 200 mL solution of methylene blue of 50 mg/L with 0.2 g adsorbent. During adsorption the pH of the solution was increased gradually from 2.5 to 10 and during desorption the pH of the solution was decreased grad-
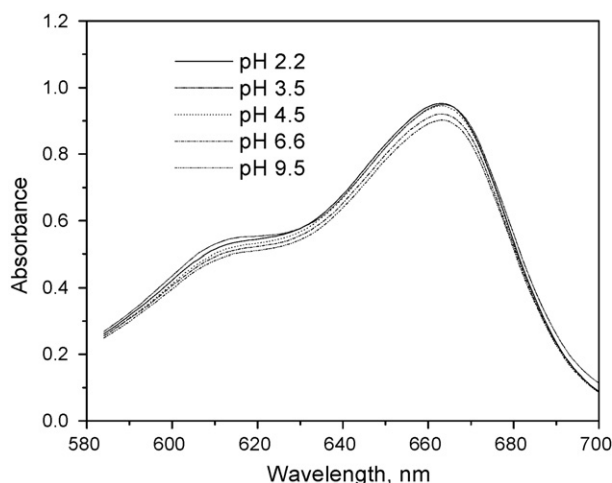
ually from 10 to 2.5. The concentrated HCl and NaOH were used to change the pH so that the change in volume of the solution is negligible.

The effect of tea waste mass on the amount of removal of MB solution was obtained by contacting 200 mL of MB solution of initial dye concentration of 50 mg/L with different weighed amount (0.2, 0.3, 0.4, 0.5 and 0.6 g) of tea waste in stopper conical flask. All the experiments were carried out at an optimum pH of 8.

Equilibrium studies were carried out by contacting 0.3 g of tea waste with 200 mL of MB solution of different initial concentrations (10, 20, 30, 40 and 50 mg/L) in 250 mL stopper conical flasks at a temperature of 27 ± 2 °C and pH of 8. The shaking time of 6 h was sufficiently high for the attainment of adsorption equilibrium. After the equilibrium had reached, the concentrations in the samples were analyzed as before.

Sorption kinetics experiments were carried out by contacting 200 mL MB solution of different initial concentrations ranging from 20 to 50 mg/L with 0.2 g tea waste in a 250 mL stoppered conical flask at a temperature of 27 ± 2 °C and pH of 8. Samples were pipetted out at different time intervals. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed as before.

3. Theory and calculation

3.1. Adsorption isotherms

The analysis and design of the sorption process requires the relevant adsorption equilibria to better understand the adsorption process. Sorption equilibrium provides fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. In the present investigation the equilibrium data were analyzed using the Freundlich and Langmuir isotherm expression given by the following equations, respectively,

$$\text{Freundlich}: \quad q_e = K_f C_e^{1/n} \tag{1}$$

$$\text{Langmuir}: \quad q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \tag{2}$$

where K_f and n are Freundlich constants related to sorption capacity and sorption intensity of adsorbents. The value of n falling in the range of 1–10 indicates the favorable sorption. q_e is the adsorption density at equilibrium of MB, C_e is the equilibrium concentration of the dye in solution, q_0 is the monolayer adsorption capacity and K_L is the Langmuir constant related to the free energy of adsorption. The linearized forms of Freundlich and Langmuir equations can be written as follows:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L}\frac{1}{C_e} \tag{4}$$

3.2. Adsorption kinetics

Kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step. In the present work, the kinetic data obtained from batch studies have been analyzed by using pseudo-first order and pseudo-second order models.

The first order equation of Lagergren [25] is generally expressed as follows:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{5}$$

Fig. 2. Effect of pH on visible spectra of MB solution. MB concentration: 10 mg/L.

where q_e and q are the adsorption density (mg/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first order sorption (min^{-1}).

The integrated form of Eq. (5) becomes

$$-\ln\left(\frac{1-q}{q_e}\right) = k_1 t \tag{6}$$

A plot of $-\ln(1 - q/q_e)$ against t should give a linear relationship passing through the origin with the slop k_1.

The pseudo-second order kinetic rate equation is expressed as follows [26]:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{7}$$

where k_2 is the rate constant of pseudo-second order sorption (g/mg. min)). The integrated form of Eq. (7) becomes

$$\frac{t}{q} = \frac{1}{k_2 q_e{}^2} + \frac{t}{q_e} \tag{8}$$

If the second order kinetic equation is applicable, the plot of t/q against t of Eq. (8) should give a linear relationship. The q_e and k_2 can be determined from the slope and intercept of the plot.

3.3. Definition of removal

The removal R is defined as follows:

$$R = 1 - \frac{C_e}{C_0} \tag{9}$$

where C_0 is the initial concentration of solution.

4. Results and discussions

4.1. Determination of surface charge and pH$_{zpc}$ of the adsorbent

The surface charge Q of the adsorbent was calculated from the experimental titration data according to the following equation [24]:

$$Q = \frac{1}{w}(C_A - C_B - [H^+] - [OH^-]) \tag{10}$$

where, w is the dry weight of adsorbent in aqueous system (g/L); C_A is the concentration of added acid in aqueous system (mol/L); C_B is the concentration of added base in aqueous system (mol/L); $[H^+]$ is the concentration of H$^+$ (mol/L); $[OH^-]$ is the concentration
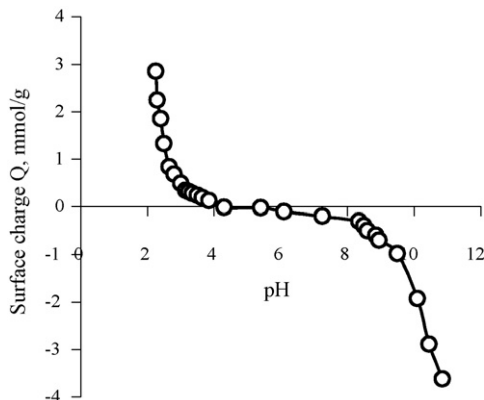
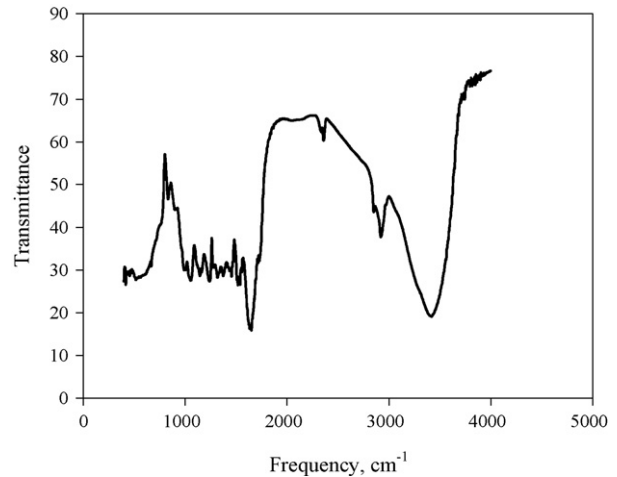**Fig. 3.** Surface charge of adsorbent as a function of pH.

Fig. 4. FTIR spectra of tea waste.

of OH$^-$ (mol/L). Then the pH value at the point of zero charge was determined by plotting Q versus pH.

Fig. 3 shows the surface charge of the adsorbent as a function of pH. From Fig. 3 it is obvious that the surface charge of the adsorbent at pH 4.3 ± 0.2 is zero. Hence, the pH$_{pzc}$ of the tea waste adsorbent is 4.3 ± 0.2.

4.2. Fourier transform infrared spectroscopy analysis

The FTIR spectra of tea waste are shown in Fig. 4, and the FTIR spectroscopic characteristics are shown in Table 2. The functional groups on tea waste and the corresponding infrared absorption frequencies are shown in Table 2. As shown in Fig. 4 and Table 2, the spectra display a number of absorption peaks, indicating the complex nature of tea waste. The troughs due to the bonded OH groups are observed in the range of 3340–3380 cm^{-1} [27]. The FTIR spectroscopic analysis indicated broad bands at 3420 cm^{-1}, representing bonded –OH groups. The bands observed at about 2920–2850 cm^{-1} could be assigned to the aliphatic C–H group [28,29]. At wave number 1733 cm^{-1} a shoulder is observed which may be due to the carbonyl stretch of carboxyl. The trough at 1640–1660 cm^{-1} represents the C=O stretching mode conjugated with the NH$_2$ (amide 1 band) [28]. In some studies, this spectrum represents a chelated form of the carbonyl on the carboxyl group [29,30]. In other studies this peak was described as the region of both ionized-non-coordinated and ionized-coordinated COO$^-$ group [31,32]. The peaks observed at 1543 and 1520 cm^{-1} correspond to the secondary amine group [33]. Symmetric bending of CH$_3$ is observed to shift to 1456 cm^{-1} [33]. The peaks observed at 1240 and 1143 cm^{-1} could be assigned to

Table 2
The FTIR spectral characteristics of tea waste

IR peaks	Frequencies (cm^{-1})	Assignment
1	3420	Bounded –OH
2	2925	Aliphatic C–H group
3	2858	Aliphatic C–H group
4	1733	Carbonyl stretch of unionized carboxylate
5	1648	C=O stretching
6	1543	Secondary amine group
7	1520	Secondary amine group
8	1456	Symmetric bending of CH$_3$
9	1240	–SO$_3$ stretching
10	1143	C–O stretching of ether groups
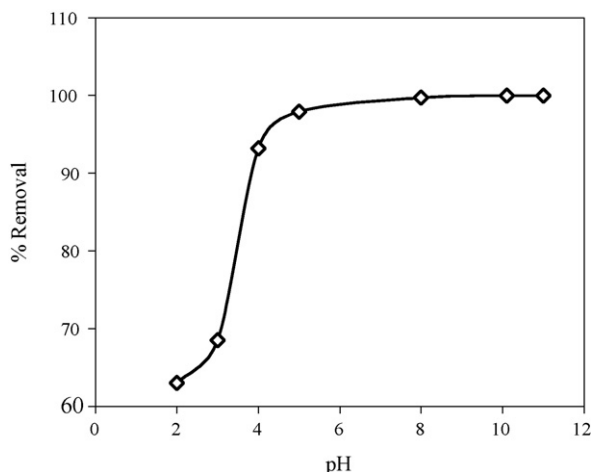
Fig. 5. Effect of initial pH on the removal of MB onto tea waste.

Fig. 6. Adsorption–desorption curve of MB onto tea waste. Solution concentration = 50 mg/L, adsorbent dose = 1 g/L.

–SO$_3$ stretching and C–O stretching of ether groups, respectively [33,34].

4.3. Effect of pH

MB is a cationic dye, which exists in aqueous solution in form of positively charged ions. As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH [35]. Fig. 5 shows the effect of pH on the percent removal of MB. As shown in the figure, an abrupt increase in the removal was observed in the pH range of 3–5. The adsorption, however, remained almost constant within the range of pH 5–10. The pH$_{pzc}$ value (the pH at the point of zero charge) of the tea waste is found to be 4.3 ± 0.2 (Fig. 3). At pH < pH$_{pzc}$, tea waste surface may get positively charged due to the adsorption of H$^+$. Amine groups (Fig. 4 and Table 2) become protonated at pH below pH$_{pzc}$ according to Eq. (11). At lower pH, a possible protonation of the carboxyl groups might also occur. Thus a force of repulsion occurs between the dye cations and the adsorbent surface. In addition, at lower pH the concentrations of H$^+$ being high, they compete with the positively charged MB cations for vacant adsorption sites. Thus, at low pH, the adsorption is very low. The reverse situation occurs at pH > pH$_{pzc}$. At pH > pH$_{pzc}$, the surface of tea waste may get negatively charged due to adsorption of OH$^-$, and the carboxyl groups (Fig. 4 and Table 2) of the tea waste may get deprotonated producing negatively charged adsorption sites Eqs. (12) and (13). Thus at high pH, the adsorption process is highly favored through the electrostatic forces of attraction.

$$\begin{matrix} R & & R \\ | & & | \\ \text{TW-NH} & + H^+ = & \text{TW-NH}_2{}^+ \end{matrix} \qquad (11)$$

$$\text{TW–COOH} = \text{TW–COO}^- + H^+ \qquad (12)$$

$$\text{TW–COOH} + OH^- = \text{TW–COO}^- + H_2O \qquad (13)$$
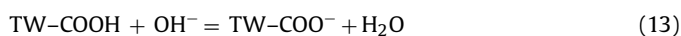
4.4. Desorption study

Desorption studies as a function of pH were conducted to explore the possibility of recovery of adsorbent and adsorbate. The adsorption–desorption was studied for a MB solution with a concentration of 50 mg/L. At first the adsorption was observed by increasi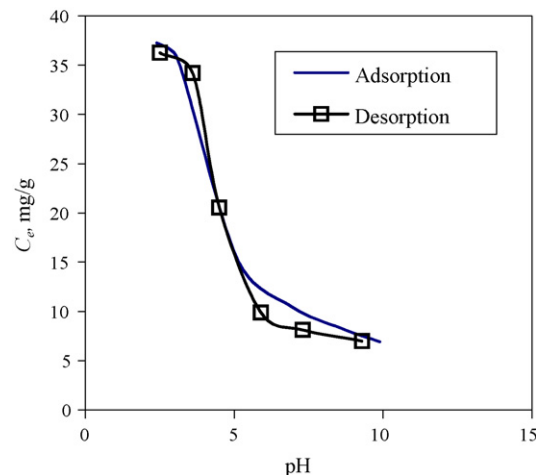ng the pH from 2.5 to 10 (Fig. 6). The desorption was then carried out by decreasing the pH. Equilibrium concentration of MB in solution at pH 10 was 6.98 mg/L. The concentration in solution increased from 6.98 to 36.25 mg/L with the decrease in pH from 10 to 2.5 (Fig. 6). At lower pH, the protons replace the cationic MB dye molecules and the protonated surface of the adsorbent became positively charged. Due to this positive charged surface, the repulsion force between the adsorbent surface and dye molecule increased resulting decreased in adsorption. The increase in MB concentration in solution with decrease in pH indicates that the most of dye uptake was carried out by ion-exchange mechanism and the process is reversible.

4.5. Effect of adsorbent dosage

Fig. 7 shows the effect of adsorbent dosage on the removal of MB. The percentage removal of MB increased with the increase in adsorbent dosage. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase dosage of the adsorbent. But the adsorption density of MB decreased with increase in adsorbent dosage.
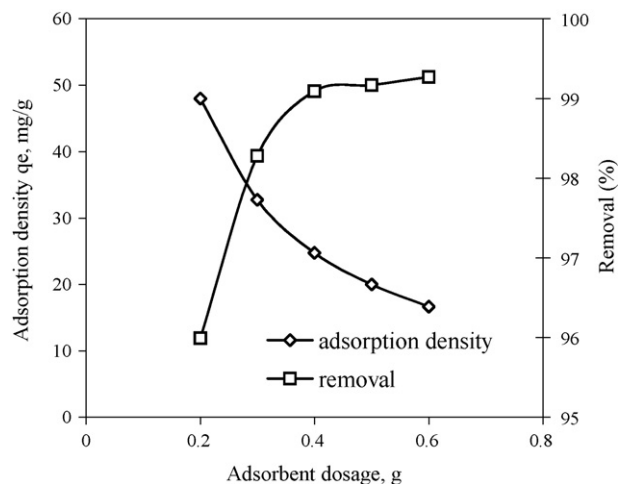

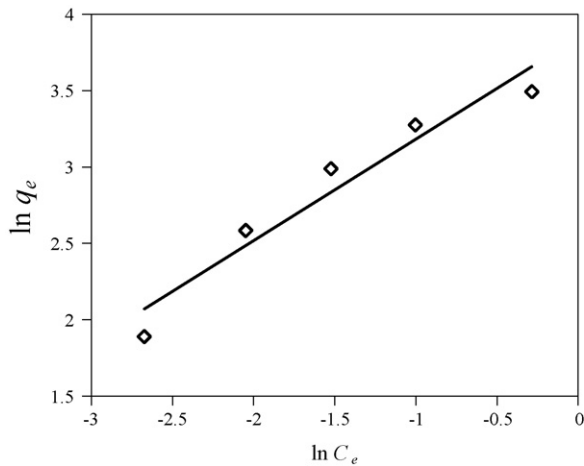Fig. 7. Effect of adsorbent dosage on the adsorption of MB onto tea waste.

Fig. 8. Freundlich plot for MB sorption onto tea waste.

Table 3
Adsorption capacity of different adsorbents for MB adsorption

Adsorbents	Sorption capacity q_0 (mg/g)	Ref.
Fly ash	5.57	[7]
Rice husk	40.59	[8]
Glass fibers	2.24	[17]
Clay	6.3	[19]
Neem leaf powder	8.76	[22]
Coir pith	120.43	[36]
Fly ash	75.52	[37]
Banana peel	20.8	[38]
Orange peel	18.6	[38]
Peanut hull	68.03	[39]
Clay	300	[40]
Diatomite	156.6	[41]
Silica	11.21	[42]
Activated sludge biomass	256.41	[43]
Spirodela polyrrhiza biomass	144.93	[44]
Dead fungus *Aspergillus niger*	18.54	[45]
Raw date pits	80.3	[46]
Fe(III)/Cr(III) hydroxide	22.8	[47]
Cotton waste	277	[48]
Tea waste	85.16	This study

4.6. Adsorption isotherms

Figs. 8 and 9 show the adsorption equilibrium data fitted to Freundlich Eq. (3) and Langmuir Eq. (4) isotherm expressions, respectively. It is evident from Figs. 8 and 9 that the equilibrium data were better represented by the Langmuir isotherm equation than done by the Freundlich equation. The calculated Freundlich constants, K_f and n, are 46.81 and 1.506, respectively. The best fit of equilibrium data in the Langmuir isotherm expression predicts the monolayer coverage of MB onto tea waste particles. High K_L (1.266) value shows that sorption rate is much higher than that of desorption. The adsorption capacity of tea waste for MB and those of some other low cost adsorbents collected from literature are presented in Table 3. It is obvious from Table 3 that tea waste has several folds higher adsorption capacity (85.16 mg/g) than the others.

4.7. Adsorption kinetics

Fig. 10 shows the extent of dye adsorption as a function of time and initial concentrations. The amount of MB adsorbed per unit mass of tea waste increased with increase in MB concentration. The unit adsorption of MB increased from 9.9 to 24.76 mg/g as the MB concentration increased from 20 to 50 mg/L. Equilibrium was established at 300 min for all the initial concentrations studied. The surface of tea waste may contain a large number of active sites and the solute (MB) uptake can be related to the active sites on equi-

librium time. Also up to 90–95% of the total amount of dye uptake was found to occur in the first rapid phase (30 min) and thereafter the sorption rate was found to decrease. The higher sorption rate at the initial period (first 30 min) may be due to an increased number of vacant sites available at the initial stage, as a result there exist increased concentration gradients between adsorbate in solution and adsorbate in adsorbent surface. This increased in concentration gradients tends to increase in dye sorption at the initial stages. As time proceeds this concentration is reduced due to the accumulation of dye particles in the vacant sites leading to a decrease in the sorption rate at the larger stages from 30 to 300 min.

Figs. 11 and 12 show the pseudo-first order Eq. (6) and pseudo-second order Eq. (8) plots for different initial dye concentration ranging from 20 to 50 mg/L. The linear lines of Fig. 11 should have passed through the origin. Therefore, it was evident from Fig. 11 that the adsorption of MB did not follow the first order kinetic model. The pseudo-second order rate constant k_2 and the adsorption density q_e at equilibrium are given in Table 4. It is obvious from Table 4 that the pseudo-second order rate constants decreased with increasing initial concentrations. The fitted $q_{e,fitted}$ values were very close to the experimental $q_{e,exp}$ values. In the view of these results, it can be said that the pseudo-second order kinetic model provided a good correlation for the adsorption of MB onto tea waste in contrast to the pseudo-first order model.
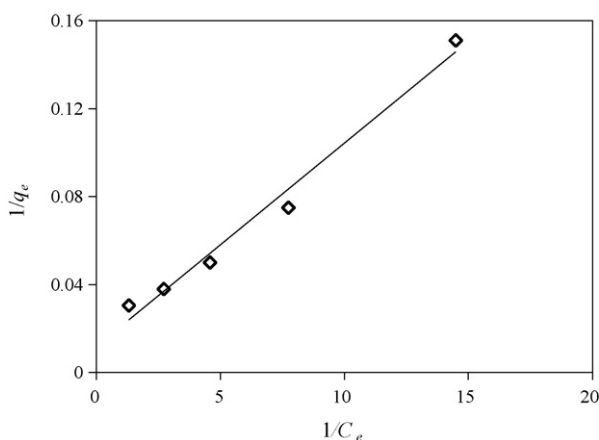

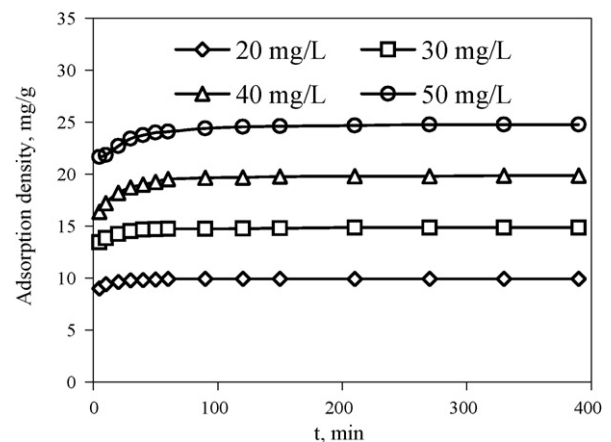**Fig. 9.** Langmuir plot for MB adsorption onto tea waste.

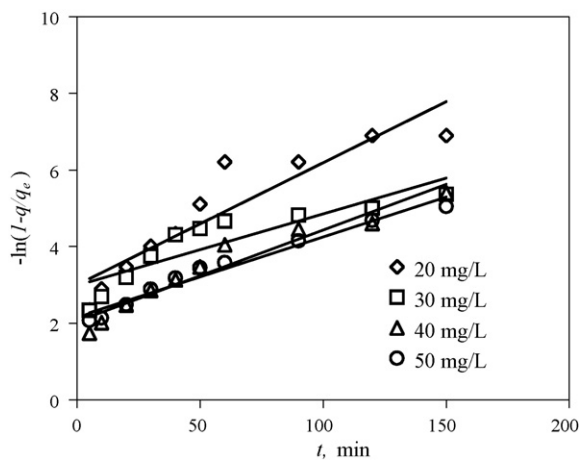**Fig. 10.** Effect of initial concentration and contact time on adsorption of MB onto tea waste.

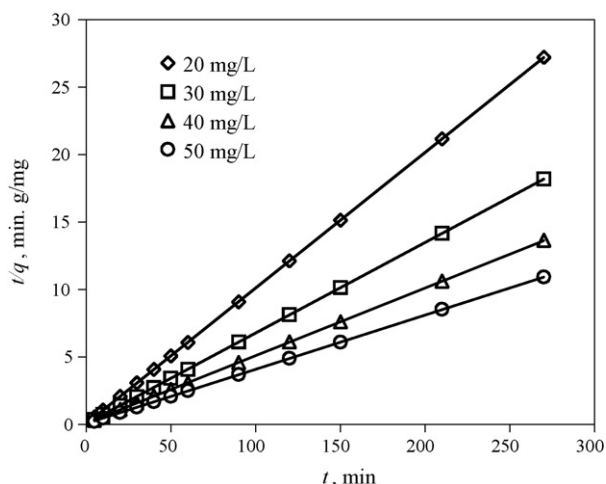**Fig. 11.** Pseudo-first order kinetics for the adsorption of MB onto tea waste.

Fig. 12. Second order kinetics for adsorption of MB onto tea waste.

Table 4
Pseudo-second order kinetic constants for the adsorption of MB onto tea waste

C_0 (mg/L)	$q_{e,exp}$ (mg/g)	$q_{e,fitted}$ (mg/g)	k_2 (g/mg min)
20	9.92	9.93	0.212
30	14.85	14.88	0.0872
40	19.85	19.93	0.0304
50	24.76	24.87	0.0239

5. Conclusion

1) The tea waste can be used as an adsorbent for the removal of MB from its aqueous solutions.
2) The amount of dye adsorbed was found to vary with initial solution pH, initial dye concentrations, contact time, and adsorbent dose.
3) The adsorption–desorption study showed that the adsorption was reversible and followed the ion-exchange mechanism.
4) The amount of dye uptake (mg/g) was found to increase with increase in initial solution concentration and found to decrease with increase in adsorbent dosage.
5) The equilibrium data fitted very well in a Langmuir isotherm equation, confirming the monolayer sorption capacity of MB onto tea waste with a monolayer sorption capacity of 85.16 mg/g.
6) The kinetics of MB adsorption onto tea waste was examined using the pseudo-first and pseudo-second order kinetics mod-els. The adsorption kinetic followed the pseudo-second order kinetic model.

References

[1] K.R. Ramakrishna, T. Viraraghavan, Dye removal using low cost adsorbents, Water Sci. Technol. 36 (1997) 189–196.
[2] C. O'Neill, F.R. Hawkes, D.L. Hawkes, N.D. Lourenco, H.M. Pin-heiro, W. Dele, Colour in textile effluents—sources, measurement, discharge consents and simulation: a review, J. Chem. Technol. Biotechnol. 74 (1999) 1009–1018.
[3] I.M. Banat, P. Nigam, D. Singh, R. Marchant, Microbial decolourization of textile dyes containing effluents: a review, Bioresour. Technol. 58 (1996) 217–227.
[4] T. Sauer, G. Cesconeto Neto, H.J. Jose, R.F.P.M. Mureira, Kinetics of photocatalytic degradation of reactive dyes in a TiO$_2$ slurry reactor, J. Photochem. Photobiol. A 149 (2002) 147–154.
[5] G.M. Walker, L. Hansen, J.A. Hanna, S.J. Allen, Kinetics of reactive dye adsorption onto dolomitic sorbents, Water Res. 37 (2003) 2081–2089.
[6] A.K. Jain, V.K. Gupta, A. Bhatnagar, A. Suhas, A comparative study of adsorbents prepared from industrial wastes for removal of dyes, Sep. Sci. Technol. 38 (2) (2003) 463–481.
[7] K.V. Kumar, V. Ramamurthi, S. Sivanesan, Modeling the mechanism involved during the sorption of methylene blue onto fly ash, J. Colloid Interf. Sci. 284 (2005) 14–21.
[8] V. Vadivelan, K.V. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice hush, J. Colloid Interf. Sci. 286 (2005) 90–100.
[9] S. Wang, Z.H. Zhu, A. Coomes, F. Haghseresht, G.Q. Lu, The physical and surface chemical characteristics of activated carbons and the sorption of methylene blue from wastewater, J. Colloid Interf. Sci. 284 (2005) 440–446.
[10] K.V. Kumar, S. Sivanesan, Equilibrium data, isotherm parameters and process design for partial and complete isotherm of methylene blue onto activated carbon, J. Hazard. Mater. B134 (2006) 237–244.
[11] K.V. Kumar, Linear and non-linear regression analysis for the sorption kinetics of methylene blue onto activated carbon, J. Hazard. Mater. B137 (2006) 1538–1544.
[12] J.H. Potgieter, An experimental study of the adsorption behaviour of methylene blue on activated carbon, Colloids Surf. 50 (1990) 39–399.
[13] S.S. Barton, The adsorption of methylene blue by activated carbon, Carbon 25 (3) (1987) 3432–4350.
[14] J. Avom, J.K. Mbadcam, C. Noubactep, P. Germain, Adsorption of methylene blue from an aqueous solution onto activated carbon from palm-tree cobs, Carbon 35 (1997) 365–369.
[15] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (2002) 295–300.
[16] S. Senthilkumaar, P.R. Varadarajan, K. Porkodi, C.V. Subbhuraam, Adsorption of methylene blue onto jute fiber carbon: kinetics and equilibrium studies, J. Colloid Interf. Sci. 284 (2005) 78–82.
[17] S. Chakrabarti, B.K. Dutta, On the adsorption and diffusion of methylene blue in glass fibers, J. Colloid Interf. Sci. 286 (2005) 807–811.
[18] F. Akbal, Adsorption of basic dyes from aqueous solution onto pumice powder, J. Colloid Interf. Sci. 286 (2005) 455–458.
[19] A. Gürses, S. Karaca, Ç. Doğar, R. Bayrak, M. Açıkyıldız, M. Yalçın, Determination of adsorptive properties of clay/water system: methylene blue sorption, J. Colloid Interf. Sci. 269 (2004) 310–314.
[20] K. Imamura, E. Ikeda, T. Nagayasu, T. Sakiyama, K. Nakinishi, Adsorption behavior of methylene blue and its congeners on a stainless steel surface, J. Colloid Interf. Sci. 245 (2002) 50–57.
[21] M. Doğan, M. Alkan, A. Türkyilmaz, Y. Özdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, J. Hazard. Mater. B109 (2004) 141–148.
[22] K.G. Bhattacharyya, A. Sharma, Kinetics and thermodynamics of methylene blue adsorption on Neem (*Azadirachta indica*) leaf powder, Dyes Pigments 65 (2005) 51–59.
[23] S. Çay, A. Uyanık, A. Özaşık, Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste, Sep. Purif. Technol. 38 (2004) 273–280.
[24] E. Kiefer, L. Sigg, P. Schosseler, Chemical and spectroscopic characterization of algae surfaces, Environ. Sci. Technol. 31 (1997) 759–764.
[25] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenkapsakademiens, Handl. 24 (1898) 1–39.
[26] Y.S. Ho, G. Mckay, Pseudo-second order model for sorption process, Process Biochem. 34 (1999) 451–465.
[27] D. Vien-Lin, N.B. Colthup, W.G. Fateley, J.C. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, San Diego, USA, 1991.
[28] A. Kapoor, T. Viraraghavan, Heavy metal biosorption sites in *Aspergillus niger*, Bioresour. Technol. 61 (1997) 221–227.
[29] Y.S. Yun, D. Park, J.M. Park, B. Volesky, Biosorption of trivalent chromium on the brown seaweed biomass, Environ. Sci. Technol. 35 (2001) 4353–4358.
[30] J.L.G. Torresdey, K. Dokken, K.J. Tiemann, J.G. Parsons, J. Ramos, N.E. Pingitore, G. Gamez, Infrared and X-ray absorption spectroscopic studies on the mech-

anism of chromium(III) binding to alfalfa biomass, Microchem. J. 71 (2002) 157–166.

[31] R.E. Sievers, J.C. Bailar, Some metal chelates of ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, and triethylenetetraaminehexaacetic acid, Inorg. Chem. 1 (1962) 174–182.

[32] L.R. Drake, S. Lin, G.D. Rayson, P.J. Jackson, Chemical modification and metal binding studies of *Datura innoxia*, Environ. Sci. Technol. 30 (1996) 110–114.

[33] E. Malkoc, Y. Nuhoglu, Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed column, J. Hazard. Mater. B135 (2006) 328–336.

[34] E. Malkoc, Y. Nuhoglu, Fixed bed studies for the sorption of chromium(VI) onto tea factory waste, Chem. Eng. Sci. 61 (2006) 4363–4372.

[35] K.R. Ramakrishna, T. Viraraghavan, Use of slag for dye removal, Waste Manage. 17 (1997) 483–488.

[36] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, Waste Manage. 21 (2001) 381–387.

[37] P. Janos, H. Buchtova, M. Ryznarova, Sorption of dyes from aqueous solution onto fly ash, Water Res. 37 (2003) 4938–4944.

[38] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. B92 (2002) 263–274.

[39] R. Gong, M. Li, C. Yang, Y. Sun, J. Chen, Removal of cationic dyes from aqueous solution by adsorption on peanut hull, J. Hazard. Mater. B121 (2005) 247–250.

[40] M. Bagane, S. Guiza, Removal of a dye from textile effluents by adsorption, Ann. Chim. Sci. Mater. 25 (2000) 615–626.

[41] M.A. Al-Ghouti, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth, J. Environ. Manage. 69 (2003) 229–238.

[42] C.D. Woolard, J. Strong, C.R. Erasmus, Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams, Appl. Geochem. 17 (2002) 1159–1164.

[43] O. Gulnaz, A. Kaya, F. Matyar, B. Arikan, Sorption of basic dyes from aqueous solution by activated sludge, J. Hazard. Mater. B108 (2004) 183–188.

[44] P. Waranusantigul, P. Pokethitiyook, M. Kruatrachue, E.S. Upatham, Kinetics of basic dye (methylene blue) biosorption by giant duckweed (Spirodela polyrrhiza), Environ. Pollut. 125 (2003) 385–392.

[45] Y. Fu, T. Viraraghavan, Removal of a dye from an aqueous solution by fungus *Aspergillus niger*, Water Qual. Res. J. Can. 35 (2000) 95–111.

[46] F. Banat, S. Al-Asheh, L. Al-Makhadmeh, Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters, Process Biochem. 39 (2003) 193–202.

[47] C. Namasivayam, S. Sumithra, Removal of direct red 12B and methylene blue from water by adsorption onto Fe(III)/Cr(III) hydroxide, an industrial solid waste, J. Environ. Manage. 74 (2005) 207–215.

[48] G. McKay, J.F. Porter, G.R. Prasad, The removal of dye colours from aqueous solutions by adsorption on low-cost materials, Water Air Soil Pollut. 114 (1999) 423–438.