



# Rejected tea as a potential low-cost adsorbent for the removal of methylene blue

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## ABSTRACT

The adsorption of methylene blue (MB) from aqueous solution using a low-cost adsorbent, rejected tea (RT), has been studied by batch adsorption technique. The adsorption experiments were carried out under different conditions of initial concentration (50–500 mg/L), solution pH 3–12, RT dose (0.05–1 g) and temperature (30–50 °C). The equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium adsorption was best described by the Langmuir isotherm model with maximum monolayer adsorption capacities found to be 147, 154 and 156 mg/g at 30, 40 and 50 °C, respectively. Three kinetic models, pseudo-first-order, pseudo-second-order and intraparticle diffusion were employed to describe the adsorption mechanism. The experimental results showed that the pseudo-second-order equation is the best model that describes the adsorption behavior with the coefficient of correlation  $R^2 \geq 0.99$ . The results suggested that RT has high potential to be used as effective adsorbent for MB removal.

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## 1. Introduction

Methylene blue (MB) or tetramethylthionine chloride is one of the basic dyes with the structure of heterocyclic aromatic chemical compound. The cationic dyes were commonly used initially for dyeing of silk, leather, plastics, paper, cotton mordanted with tannin, and also in manufacturing of paints and printing inks [1]. Though MB is not hazardous compared to other dyes, acute exposure to MB will cause increased heart rate, vomiting, and shock [2,3]. Hence, the necessity for the dye containing water to undergo treatment before disposal to the environment. Various conventional methods of color removal from wastewater have been used. These include biological and physical–chemical process. However, these processes are difficult to handle and are not always effective and economical. The adsorption technique appears to offer the best prospects over others and proved itself as one of an effective and attractive process for the treatment of dye containing wastewater [4]. Moreover, this method will become economically attractive, if the sorbent material used is cheap and at affordable production cost.

In fact, activated carbon (AC) is known to be a very effective adsorbent material due to its highly developed porosity, large surface area (that can reach 3000 m<sup>2</sup>/g), variable characteristic sur-

face chemistry, and high degree of surface reactivity [5,6]. These unique characteristics make activated carbon very versatile material, which can remove a wide range of pollutants from various matrices. In addition, it has high adsorption capacity and fast adsorption kinetics [7]. However, its uses is limited because it is expensive, the higher the quality of AC, the greater the cost [5].

In recent years, attention has been shifted towards the materials which are byproducts of wastes from large scale industrial operations and agricultural waste materials. The major advantages of these materials include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of adsorbent and possibility of effluent recovery [8]. Studies reveal that various agricultural waste materials such as grass waste [9], rice hull [10], garlic peel [11], cotton plant waste [12] and broad bean peels [13] have been investigated.

Rejected tea (RT) which is a waste material obtained from tea plantation is proposed as adsorbent for the removal of MB from the aqueous solution. Tea refers to the agricultural products of the leaves, leaf buds and internodes of *Camelia Sinensis*, which has been prepared and cured by various methods. In Malaysia, tea plants are commonly grown in the highland area located at Cameron Highland, Pahang. In the plantation, the harvested tea is only selected from the top leaves of the fresh grown shoots. The harvesting of the tea leaves are done every 15 days, to allow for growth of new leaves. The yield consists of mixed tea harvest and some overgrown woody shoots. This woody overgrown shoots were not treated by tea factory and thus constitute rejected tea. Moreover, during the tea planting procedure, tea producers usually trimmed the tea trees to a height of 1.5–2 m after every 3 years to allow for fresh growth of shoots. These also form part of undesired tea during production

*Abbreviations:* RT, rejected tea; AC, activated carbon; MB, methylene blue; FTIR, Fourier transform infrared; SEM, scanning electron microscope; BET, Brunauer, Emmett, and Teller.

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and a waste in the plantation. An estimate of more than 10,000 tonnes of RT is produced annually. RT accumulates in the agro-industrial yards where it has no significance industrially and are not marketable, but becomes an issue of environmental concerns. Therefore, any attempt to utilize this waste will open a new market for it and will be beneficial.

The objective of this work was to evaluate the adsorption potential of rejected tea for methylene blue. The kinetic data and equilibrium data of adsorption studies were processed to understand the mechanism of methylene blue onto the rejected tea.

## 2. Materials and methods

### 2.1. Materials

The rejected tea was collected from tea plantation located at highland area Cameron Highland, Pahang, Malaysia. 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 24 h. The dried RT was then ground and sieved to obtain the particle size in the range 250–355 μm. Finally, the resulting product was stored in air-tight container for further use. No other chemical or physical treatments were applied prior to adsorption experiments.

### 2.2. Chemicals

Stock solution was prepared by dissolving 1.0 g of methylene blue (MB) supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia in 1 L distilled water. The test solutions were prepared by diluting stock solution to the desired concentrations. The maximum wavelength of this dye is 668 nm.

### 2.3. Effect of dosage

The effect of RT dose on the amount of MB adsorbed was obtained by contacting 200 mL of MB solution of initial concentration of 100 mg/L with different amount of RT into a number of 250 mL-stoppered glass Erlenmeyers flasks at temperature of 30 °C and at pH 6–7. The flasks were placed in a thermostated water-bath shaker and agitation was provided at 130 rpm. The dye solutions were then analyzed thereafter at which equilibrium is assumed.

### 2.4. Effect of solution pH

The effect of pH on the removal of MB was analyzed over the pH range 3–12. The pH was adjusted using 0.01 M NaOH and 0.01 M HCl solutions. In this study, 200 mL of dye solution with fixed initial concentration of 100 mg/L was taken in a stoppered conical flask and was agitated with 0.50 g of RT.

### 2.5. Equilibrium studies

Equilibrium studies were carried out by contacting fixed amount of RT (0.50 g) with 200 mL of MB solution of different initial concentrations in 250 mL stopper conical flasks at a temperature of 30 ± 2 °C and pH of 6–7. The procedures were repeated for temperature of 40 and 50 ± 2 °C. The initial and equilibrium concentrations of MB were analyzed using a UV–vis spectrophotometer (Shidmadzu Model UV-1601, Japan) at a wavelength of maximum absorbance (668 nm). The amount of adsorption at equilibrium,  $q_e$  (mg/g), was calculated by

$$q_e = \frac{(C_0 - C_e)V}{W} \times 100 \quad (1)$$

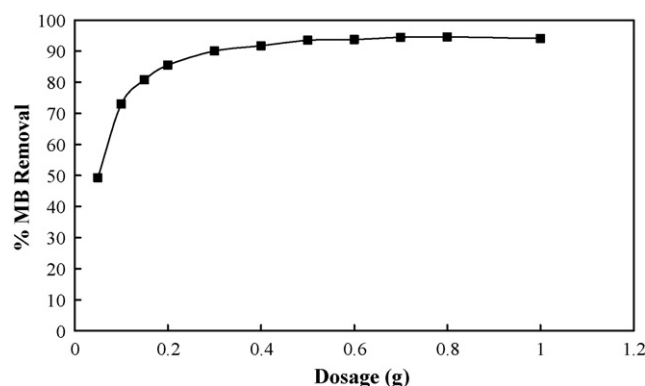


Fig. 1. Effect of adsorbent dosage on the adsorption of MB onto RT.

where  $C_0$  and  $C_e$  (mg/L) are the liquid phase concentrations of MB at initial and equilibrium, respectively.  $V$  (L) is the volume of the solution and  $W$  (g) is the mass of RT used. The percentage removal of dye was calculated as follows:

$$\text{Removal percentage} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

### 2.6. Kinetics studies

Adsorption kinetics experiments were performed by contacting 200 mL MB solution of different initial concentrations ranging from 50 to 500 mg/L with 0.50 g RT in a 250 mL-stoppered conical flask at a temperature of 30 ± 2 °C. At fixed time intervals, the samples were taken from the solution and were analyzed.

### 2.7. Characterization of RT

Textural characterization of the prepared RT was carried out by  $N_2$  adsorption at 77 K using Micromeritics ASAP 2020, surface area and porosity analyzer. The Brunauer, Emmett, Teller (BET) surface area and total pore volume of the prepared RT were then determined. Scanning electron microscopy (SEM) analysis was carried out for the RT before and after dye adsorption to study their surface textures. In addition, Fourier transform infrared (FTIR) analysis was applied on the RT to determine the surface functional groups, using FTIR spectroscope (FTIR-2000, PerkinElmer), where the spectra were recorded from 4000 to 400  $cm^{-1}$ .

## 3. Results and discussion

### 3.1. Effect of adsorbent dosage

The effect of dosage on adsorption of MB onto RT is illustrated in Fig. 1. At equilibrium time, the percent removal increased from 49.3% to 93.4% for an increase in RT dose from 0.05 to 0.50 g. It was observed that the percent removal of MB gradually increased with further increase in adsorbent up to 0.50 g and thereafter remained unchanged. The percent removal of MB increased is basically due to the number of active sites and available surface area increase with dosage. The optimum dose was found to be 0.50 g of RT for 200 mL of MB solution.

### 3.2. Effect of solution pH

Fig. 2 shows the effect of pH on the adsorption of MB. The experiments were conducted at 100 mg/L initial MB concentration, 0.50 g RT dose and 30 °C. It was observed that pH gives a significant influence to the adsorption process. MB is cationic dye, which exists in aqueous solution in the form of positively charged ions. As a

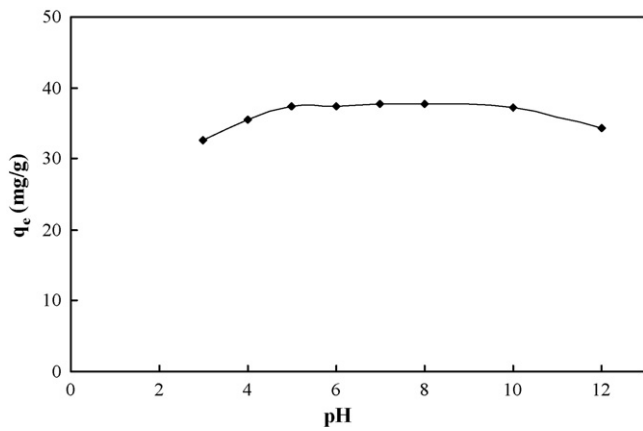


Fig. 2. Effect of solution pH on the adsorption of MB on RT.

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. As shown in Fig. 2, the equilibrium adsorption capacity was minimum at pH 3 (32.6 mg/g), this increased up to 4 and remained nearly constant (37 mg/g) over the initial pH ranges of 4–8. This phenomenon occurred due to the presence of excess  $H^+$  ions in the adsorbate and the negatively charged surface adsorbent. Lower adsorption of MB at acidic pH is due to the presence of excess  $H^+$  ions competing with the cation groups on the dye for adsorption sites. At higher solution pH, the RT possibly negatively charged and enhance the positively charged dye cations through electrostatic forces of attraction. A similar result was reported for the adsorption of MB onto wood shavings [14].

### 3.3. Effect of initial concentration and contact time on (MB) adsorption

Fig. 3 shows the effect of the initial dye concentration (50–500 mg/L) on the adsorption of MB. It was observed that amount of MB adsorbed was rapid for the first 40 min and thereafter it proceeded at a slower rate and finally reached saturation. The equilibrium adsorption increases from 18.6 to 134 mg/g, with increase in the initial MB concentration from 50 to 500 mg/L. It was also found that the equilibrium removal of MB decreased from 90.4% to 62.3% as the initial MB concentration increased from 50 to 500 mg/L. The findings are because as the initial concentration

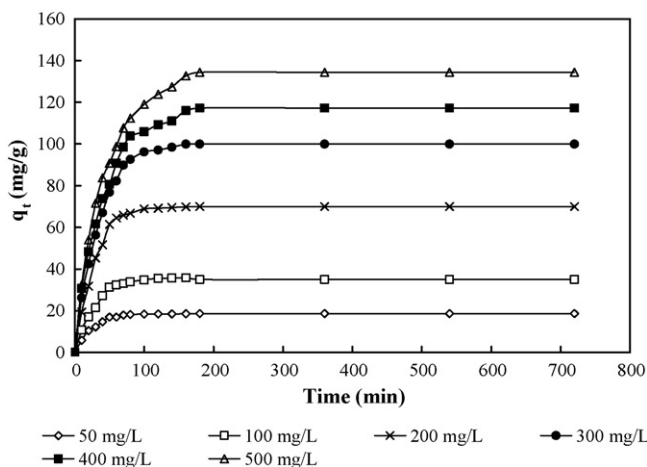


Fig. 3. Effect of contact time and initial concentration on the adsorption of MB on RT.

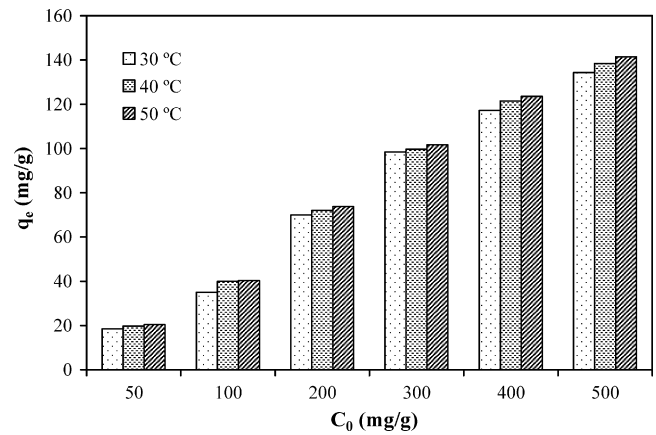


Fig. 4. Effect of temperature on the equilibrium adsorption capacity of RT at different initial concentrations.

Table 1

Isotherm parameters for removal of MB by RT at different temperatures.

Isotherm	Parameters	Temperature (°C)		
		30	40	50
Langmuir	$q_{max}$ (mg/g)	147	154	156
	$K_L$	0.047	0.049	0.060
	$R^2$	0.99	0.99	0.99
Freundlich	$K_F$ (mg/g(L/mg) $^{1/n}$ )	3.15	3.41	3.69
	$n$	2.19	2.29	2.45
	$R^2$	0.98	0.93	0.94

increases, the mass transfer driving force becomes larger, hence resulting in higher MB adsorption. It is also shown in Fig. 3 that the contact time needed for MB solutions with initial concentrations of 50–200 mg/L to reach equilibrium was 120 min. The initial concentration provides an important driving force to overcome all mass transfer resistances of the MB between the aqueous and solid phase. While for MB solutions with initial concentrations of 300–500 mg/L, equilibrium time of 180 min was required. However, the experimental data were measured at 720 min to be sure that full equilibrium was attained.

### 3.4. Effect of temperature

The effect of temperature on the adsorption rate of MB on RT was investigated at three different temperatures (30, 40, and 50 °C) using initial concentration of 50–500 mg/L (Fig. 4).

The major effect of temperature is influence by the diffusion rate of adsorbate molecules and internal pores of the adsorbent particle. It is observed that the equilibrium adsorption uptake increases with increased temperature at all concentrations studied. An increase of temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and within the internal pores of the adsorbent particle, due to decrease in the viscosity of the solution [15]. From the result, an increase in temperature from 30 to 50 °C increased the RT monolayer adsorption capacities from 147 to 156 mg/g (Table 1). This phenomenon indicates that the adsorption process is endothermic in nature. This may be due to the mobility of molecules which increases generally with a rise in temperature, thereby facilitating the formation of surface monolayers [16].

### 3.5. Adsorption isotherm

The most common models used to represent the data of adsorption from solution are Langmuir [17] and Freundlich [18] isotherms.

**Table 2**  
Comparison of monolayer equilibrium capacity for methylene blue onto other different adsorbents.

Adsorbent	Adsorbent capacity (mg/g)	References
Rejected tea	147	This work
Rice husk	40.6	[3]
Peanut hull treated with sulfuric acid	124	[19]
Cherry sawdust	39.8	[20]
Walnut sawdust	59.2	[20]
Orange peel	18.6	[21]
Jute processing waste	16.6	[22]
Chemically activated desert plant	130	[23]
Date pits	80.3	[24]
Guava (Psidium Guajava) leaf powder	185	[25]
Bamboo dust-based activated carbon	143	[26]

In this work, both models were used to describe the relationship between the amount of MB adsorbed and its equilibrium concentration. The applicability of the isotherm models to the adsorption study was judged by the correlation coefficient,  $R^2$  value of each plot. The higher the  $R^2$  value, the better the fit.

Langmuir isotherm [17] assumes monolayer adsorption onto a homogeneous surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. In order to establish the maximum sorption capacity, the Langmuir equation of the following form was applied

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{1}{q_{max}}C_e \quad (3)$$

where  $q_e$  is the amount adsorbed at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/L), and  $q_{max}$  (mg/g) and  $K_L$  are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of  $C_e/q_e$  versus  $C_e$  (Figure not shown).

The linear form of the Freundlich isotherm [18] model is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface and is expressed by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $K_F$  and  $1/n$  are Freundlich constants related to adsorbent adsorption capacity and adsorption intensity, respectively. The values of  $K_F$  and  $1/n$  can be obtained from the intercept and slope, respectively from the linear plot of experimental data of  $\log q_e$  versus  $\log C_e$  (Figure not shown). All calculated isotherm constants by both models are listed in Table 1. It can be seen from the  $R^2$  values, which are a measure of goodness-of-fit, that the Langmuir exhibited better fit at all temperatures compared to the Freundlich model. The fact that this occurred may be due to homogeneous distribution of active sites onto RT surface. The potential of RT can be evaluated by comparing the monolayer adsorption capacity of MB onto various adsorbents as shown in Table 2. The performance of the RT is clearly seen to be considerably effective for this purpose.

### 3.6. Adsorption kinetics studies

The transient behavior of the dye adsorption process was analyzed by using the pseudo-first [27] and pseudo-second-order [28] kinetic models. The pseudo-first-order equation is expressed in the form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (5)$$

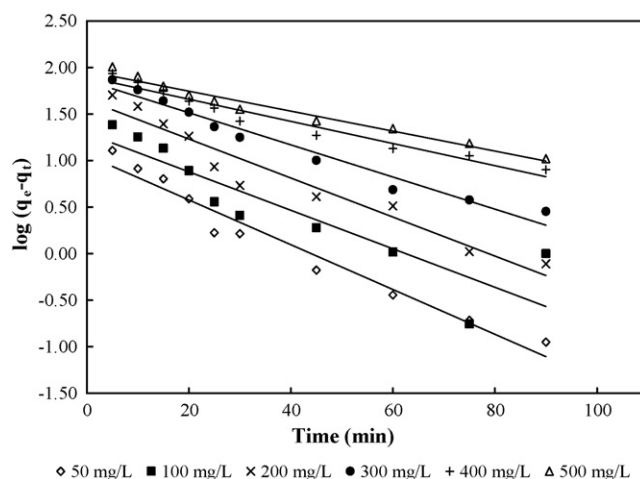


Fig. 5. Pseudo-first-order kinetics for adsorption of MB onto RT at 30 °C.

where  $k_1$  is the rate constant of pseudo-first-order equation and  $q_e$  denotes the amount of adsorption at equilibrium. Plotting  $\log(q_e - q_t)$  against  $t$  permits calculation of  $k_1$  (Fig. 5). The rate constants,  $k_1$ , evaluated from these plots with the correlation coefficients obtained are listed in Table 3.

The pseudo-second-order kinetic equation can be represented by the following equation

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \quad (6)$$

where  $k_2$  is the rate constant of the pseudo-second-order equation. Plotting  $t/q_t$  against  $t$  (Fig. 6), gives a straight line where  $k_2$  can be calculated. The  $R^2$  listed for the pseudo-first-order kinetic model were between 0.96 and 0.97. The  $R^2$  values for pseudo-second-order model were  $\geq 0.99$ , which is higher than the  $R^2$  values obtained for the pseudo-first-order model and closer to unity. Therefore, the adsorption kinetics could well be satisfactorily more favorably described by pseudo-second-order kinetic model for MB adsorption onto RT. Similar phenomena have been observed in sorption of MB onto mansonina (Mansonina altissima) wood sawdust [29].

In order to quantitatively compare the applicability of the model in fitting the data, a normalized standard deviation,  $\Delta q$ , was calcu-

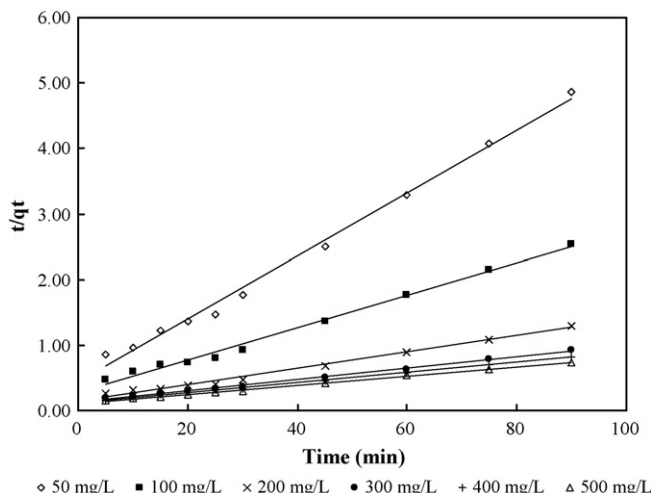


Fig. 6. Pseudo-second-order kinetics for adsorption of MB onto RT at 30 °C.

**Table 3**  
Kinetic parameters for the removal of MB by RT at 30 °C.

$C_0$ (mg/L)	Pseudo-first-order				Pseudo-second-order			
	$q_e$ (mg/g)	$k_1$ (1/min)	$R^2$	$\Delta q$ (%)	$q_e$ (mg/g)	$k_2$	$R^2$	$\Delta q$ (%)
50	18.6	0.006	0.96	14.5	20.8	0.005	0.99	4.4
100	34.9	0.004	0.94	13.6	40.5	0.002	0.99	5.9
200	69.9	0.005	0.94	13.7	80	0.001	0.99	5.4
300	99.9	0.004	0.97	10.4	116	0.001	0.99	6.2
400	117	0.027	0.96	12.4	128	0.001	0.99	3.5
500	134	0.003	0.97	12.1	145	0.001	0.99	2.9

lated from the following equation

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum [(q_{t,\text{exp}} - q_{t,\text{cal}})/q_{t,\text{exp}}]^2}{n-1}} \quad (7)$$

where the  $q_{t,\text{exp}}$  and  $q_{t,\text{cal}}$  refer to the experimental and calculated values and  $n$  is the number of data points. The lower the values of  $\Delta q\%$  indicates the better fit. The calculated  $q_{e,\text{cal}}$  values obtained from the pseudo-first-order kinetic model did not give reasonable values (10.4–14.5%). Thus the experimental results did not follow the pseudo-first-order kinetic model. However, for pseudo-second-order kinetic, the calculated  $q_{e,\text{cal}}$  values agreed with experimental  $q_{e,\text{exp}}$  values, giving relatively small deviation of 2.9–6.2%. Therefore, the results obtained prove that the kinetics of MB adsorption on RT followed pseudo-second-order model, suggesting that chemisorption might be the rate-limiting step that controlled the adsorption process.

Intraparticle diffusion mechanism was studied to investigate the diffusion mechanism of adsorption process. Weber and Moris plot [30] ( $q_t$  versus  $t^{0.5}$ ) Eq. (8), was used to investigate intraparticle diffusion mechanism. According to this theory:

$$q_t = k_{id}t^{1/2} + C \quad (8)$$

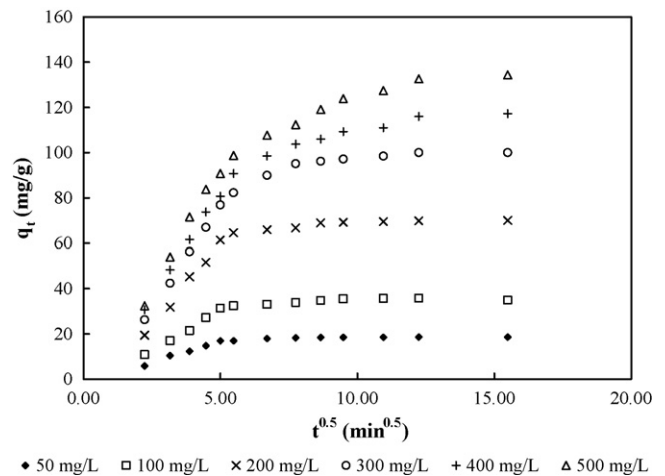
where  $k_{id}$  (mg/g min<sup>1/2</sup>), the rate parameter of stage  $i$ , is obtained from the slope of the straight line of  $q_t$  versus  $t^{1/2}$ . Fig. 7 shows the pore diffusion plot of MB adsorption on RT at 30 °C. It was observed that the adsorption process tends to be followed by two and three linear portions which were not linear over the whole time. If intraparticle diffusion occurs, then  $q_t$  versus  $t^{1/2}$  will be linear and if the plot passes through the origin, then the rate-limiting process is only due to the intraparticle diffusion. Otherwise, some other mechanism along with intraparticle diffusion is also involved [31]. Such finding is similar to that made in previous works on adsorption [32].

### 3.7. FTIR of RT

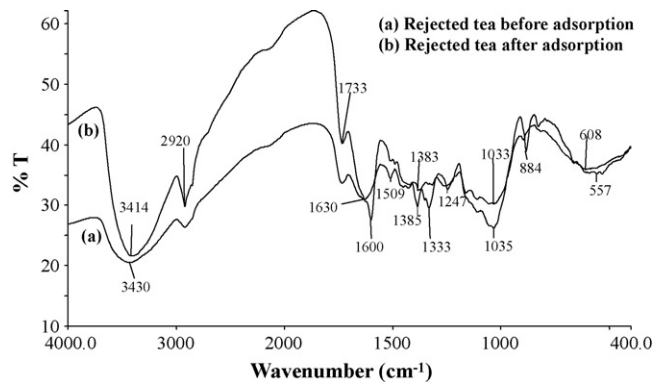
The FTIR spectroscopic characteristics from the FTIR spectra in Fig. 8 are shown in Table 4. The FTIR spectra obtained revealed that

**Table 4**  
FTIR spectral characteristics of RT before and after adsorption.

IR peak	Frequency (cm <sup>-1</sup> )			Assignment
	Before adsorption	After adsorption	Differences	
1	3430	3414	-16	Bonded —OH groups
2	—	2920	—	Aliphatic C—H groups
3	—	1733	—	C=O stretching
4	1630	1600	-30	C=O stretching
5	1509	—	—	Aromatic nitro compound
6	1383	1385	+2	Symmetric bending of CH <sub>3</sub>
7	—	1333	—	Aromatic nitro compound
8	—	1247	—	S=O stretching
9	1033	1035	+2	C—O stretching
10	—	884	—	C—C stretching
11	608	557	-51	—C—C— group



**Fig. 7.** Intraparticle diffusion plots for removal of MB at different initial dye concentrations.



**Fig. 8.** FTIR of RT adsorbent: (a) before dye sorption and (b) after dye adsorption.

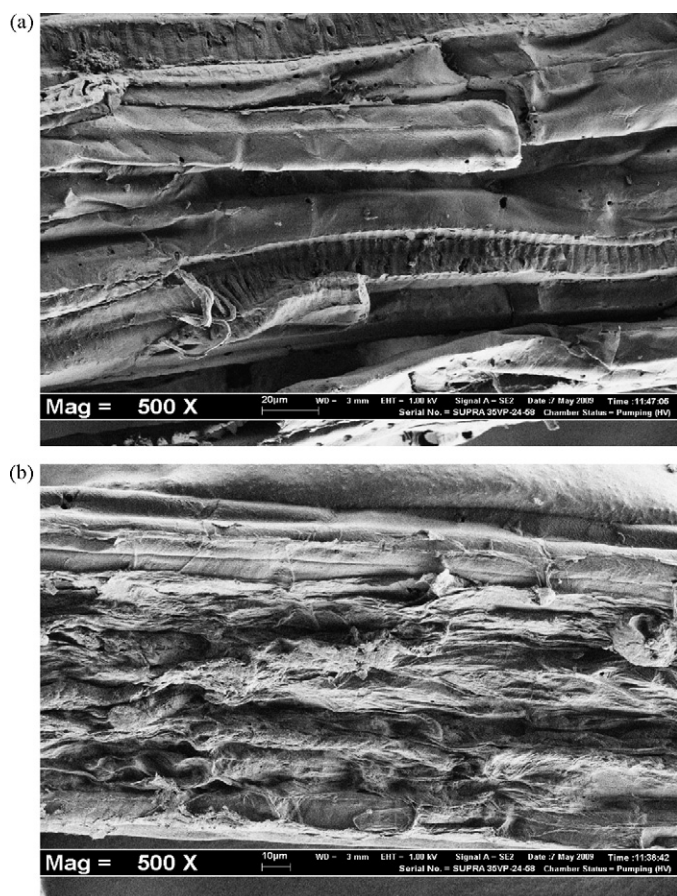


Fig. 9. SEM micrograph of RT particle (magnification: 500 $\times$ ): (a) before dye sorption and (b) after dye adsorption.

there were various functional groups detected on the surface of RT sample before and after adsorption. There are some peaks that were shifted, disappeared and new peaks were also detected. As seen in Table 4, three significant bands decrease of the functional groups on the RT were detected at the bands of 3430, 1630 and 608 which indicated the bonded  $\text{—OH}$  groups,  $\text{C=O}$  stretching, aromatic nitro compound and  $\text{—C—C—}$  group. These three significant bands in the spectrum indicate the possible involvement of that functional group on the surface of RT in MB adsorption process.

### 3.8. SEM and BET surface area of RT

Fig. 9 shows the SEM micrographs of RT samples before and after dye adsorption. Fig. 9a shows that the RT possesses a rough surface morphology with some pores. The surface of MB-loaded adsorbent (Fig. 9b), however, shows that the surface of RT is covered with dye molecules. It was found that the BET surface area, total pore volume and average pore diameter of the RT were  $4.2 \text{ m}^2/\text{g}$ ,  $0.0045 \text{ cm}^3/\text{g}$  and  $43 \text{ \AA}$ , respectively.

## 4. Conclusion

Rejected tea (RT) has been proven to be an effective low-cost adsorbent for the removal of MB via adsorption from aqueous solution. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The adsorption equilibrium was best described by the Langmuir isotherm model with maximum monolayer adsorption capacities found to be 147, 154 and 156 mg/g at 30, 40 and 50  $^\circ\text{C}$ , respectively. Kinetics of the adsorption over RT was also observed and it was found that the process proceeds via

pseudo-second-order kinetics. Intraparticle diffusion model was applied to interpret the adsorption mechanism. A comparison of the adsorption capacity of RT with different adsorbents previously used for the adsorption of MB reveals that rejected tea is remarkably effective for this purpose.

## Nomenclature

$C_0$	initial liquid phase concentration (mg/L)
$C_e$	equilibrium liquid phase concentration (mg/L)
$k_1$	rate constant of pseudo-first-order adsorption ( $\text{min}^{-1}$ )
$k_2$	rate constant of pseudo-second-order adsorption ( $\text{g/g min}$ )
$k_{id}$	intraparticle diffusion rate constant ( $\text{mg/g min}^{1/2}$ )
$K_F$	Freundlich isotherm constant related to adsorption capacity [ $(\text{mg/g})(\text{L/mg})^{1/n}$ ]
$K_L$	Langmuir isotherm constant (L/mg)
$n$	Freundlich isotherm constant related to adsorption intensity
$q_e$	equilibrium solid phase adsorbate concentration (mg/g)
$q_t$	amount of adsorption at time $t$ (mg/g)
$q_{\text{max}}$	maximum adsorption capacity (mg/g)
$R^2$	correlation coefficient
$V$	volume of solution (L)
$W$	mass of adsorbent (g)

## Subscripts

exp	experimental
cal	calculated

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