Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23598

146 (2019) 385–392
April

Coconut tree bark as a potential low-cost adsorbent for the removal of methylene blue from wastewater

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Received 23 June 2018; Accepted 11 December 2018

ABSTRACT

The existing issue was undertaken to evaluate the potentiality of coconut tree bark (CTB) to remove methylene blue (MB) dye from aqueous solutions. Effects of a variety of process parameters such as pH (3–12), initial dye concentration (25–200 ppm), contact time (10–250 min) and adsorbent dosages (0.5–4.0 g/L) were studied and optimized for the CTB–MB system. Langmuir isotherm model was studied and the results were compared with that of Temkin model and found that Langmuir model fits the data best. Adsorption kinetics of the system was carried out and the experimental data were best-fitted with pseudo-second-order kinetic model. The mechanism of MB dye adsorption was studied by intra-particle diffusion model, which points out that the adsorption process has boundary layer effect and mass transfer analysis of the CTB–MB system indicated better transportation of adsorbate from liquid phase to solid phase. Fourier transform infrared results demonstrated possible functional groups that were responsible for adsorption of MB dye on CTB surface. These results revealed the suitability of the locally available CTB as bio-adsorbent for the removal of MB dye from the wastewater.

Keywords: Adsorption; Coconut tree bark; Methylene blue; Kinetics; Isotherm; Diffusion; Mass transfer

1. Introduction

Wastewater treatment has become a major concern due to the uncontrolled release of organic or inorganic pollutants from a variety of industries into river which creates a serious problem in both of the aquatic environment and human life. Many industries such as textile, leather, paper, plastic, tannery, cosmetics, rubber and paint make use of dyes to color their products that are the sources of dye-bearing effluents [1]. It is estimated that more than 100,000 commercially accessible dyes within excess of 700,000 ton dyestuff produced in a year [2]. Methylene blue (MB) is a basic dye which is applied as a dyeing agent for leather, calico, cotton and tannins, as well as it is used as a biological staining agent [3]. Severe exposure of MB dye can cause diseases such as eye and gastrointestinal problem, vomiting, diarrhea, cyanosis, jaundice and tissue necrosis. In addition, it may result in convulsions, dyspnea and methaemoglobinaemia [4,5]. So, this dye contained in industrial effluent should be treated before disposal into the environment. Generally, dyes are poorly biodegradable which generates the key problem in the treatment of dye containing wastewater [6]. There are several methods existing for the removal of dyes from the wastewater. These methods involve the biotreatment [7–9], flocculation–coagulation [10], photocatalytic degradation [11], Fenton chemical oxidation [12,13], cation exchange membranes [14], electrochemical degradation [15], etc. but these methods are very costly and sometimes cause problems in operation. Among the above methods, adsorption is one of the most effective techniques for the wastewater treatment because of high performance, low

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cost, simple design, formation of no destructive by-products during operation [16]. Moreover, this technique is applied for the treatment of different types of water pollutants such as heavy metals [17–20], uncolored organic pollutants [21] and hazardous dyes [22–27]. Commercially activated carbon is used to take out dye particles from wastewater by adsorption but high cost has motivated to seek out alternative industrial, agricultural and biomass wastes as low-cost adsorbent. From this perspective, due to the availability of coconut tree bark (CTB), native Bangladesh, as bio-adsorbent was utilized in this research work to separate MB dye from wastewater. In addition, a few of non-conventional cost-effective adsorbents such as cashew nut shell [28], raw and modified pine cone [29], pine leaves [30], pine cone biomass [6], wood apple shell [31], rice husk [32], orange peels [33], banana peel [33], castor seed shell [34], coconut shell charcoal [35], *Artocarpus camansi* Blanco (Breadnut) core [36], breadnut peel [37], *Casuarina equisetifolia* needle [38], fishbone charcoal [39], etc., have been employed for the removal of MB dye from aqueous solution.

In the present work, the key objective is to investigate the potentiality of CTB as bio-adsorbent to remove MB dye from the wastewater. The effect of variety of operating parameters such as pH, initial MB dye concentration, adsorbent dosages and contact time on adsorption of MB dye onto CTB surface has been explored. Under various optimal conditions, the equilibrium isotherm data were analyzed by using Langmuir isotherm and Temkin models. To investigate the mechanism of adsorption, kinetics and mass transfer analyses were performed.

2. Materials and methods

2.1. Materials

CTB was collected locally. NaOH, HCl and MB dye were purchased from Merck, Germany, and 0.1 M NaOH and 0.1 M HCl were prepared in the laboratory. Stock solution of MB dye was prepared by dissolving 319.85 g/mol MB dye in double-distilled water and then different concentrated (25, 50, 100, 150 and 200 ppm) solutions were prepared by dilution of the stock solution.

2.2. Preparation of adsorbent

The collected CTB was washed with distilled water to remove the dirt and mud. Then the washed sample was sun dried and again washed with 5% HCl to remove soluble impurities. The sample was further cleaned with distilled water and dried in a dryer for 2 h at 105°C to leave out moisture from the sample and then the dried CTB sample was crushed in a micro plant grinding machine to convert into fine powder which was used as adsorbent for the whole experiment.

2.3. Adsorbent characterization

pH of the solutions was analyzed by pH meter over the pH range 3–12. The absorbance of solutions was measured by an UV-1650 spectrophotometer (Shimadzu Co., Japan) at wavelength 664 nm. Fourier transform infrared (FT–IR) analysis was done to determine the functional groups of CTB surface. FT–IR spectra of the biosorbent were recorded before and after MB bonding in the range of 4,000–500 cm^{-1}. Specific surface area based on N_2 physisorption was assessed using Brunauer–Emmett–Teller (BET) analysis (ASAP 2010, Micromeritics, Universiti Malaysia Pahang (UMP), Malaysia).

2.4. Adsorption experiments

Adsorption studies were performed by batch technique to investigate the effect of various parameters on adsorption of MB dye onto CTB surface. For adsorption studies, a series of 250 mL conical flasks were used to keep 100 mL of adsorbate solution of variable concentrations (25, 50, 100, 150 and 200 ppm) and a desired pH was maintained for each sample. A known amount of adsorbent (0.5, 1, 1.5, 2, 2.5, 3 and 4 g) was added into each flask at different moment at different conditions and shaken continuously at a constant oscillation of 211 osc/min for 5 h. Then the samples of various concentrations were filtered and analyzed. The CTB–MB system was optimized and optimized conditions were found to be as follows: initial dye concentration 100 ppm, dose 1.5 g/L, pH 10, contact time 150 min. Each experiment was repetitive under indistinguishable conditions and the average values were taken and to compute the percentage removal of MB from aqueous solution, following equation was used:

$$\text{MB removal } (\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

where C_0 is the initial concentration (mg/L) and C_t is the concentration at time t. The quantity of adsorption at equilibrium, q_e (mg/g) was calculated by the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 and C_e are the liquid-phase concentrations (mg/L) of MB at initial and at equilibrium, correspondingly. V is the volume (L) of the solution and m is the mass (g) of dry adsorbent.

2.5. Adsorption kinetics

2.5.1. Pseudo-first-order and pseudo-second-order kinetic models

To study the mechanism of MB adsorption onto CTB surface, the adsorption kinetics was analyzed using pseudo-first-order Lagergren equation (Eq. (3)) and pseudo-second-order rate equation (Eq. (4)) expressed as follows [40,41]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where q_t is the amount of dye adsorbed at time t ($mg.g^{-1}$), q_e is the adsorption capacity at equilibrium ($mg.g^{-1}$),

k_1 is pseudo-first-order rate constant (min^{-1}) and k_2 is pseudo-second-order rate constant (g mg^{-1} min^{-1}).

2.5.2. Intraparticle diffusion model

Diffusion coefficient for intra-particle movement of CTB adsorbent has been calculated at initial dye concentration and pH by employing rate Eq. (5) according to Weber–Morris model [42]:

$$q_t = K_{id} t^{0.5} + I \tag{5}$$

where K_{id} is the intra-particle diffusion constant (mg/g $min^{0.5}$).

2.6. Adsorption equilibrium isotherm

2.6.1. Langmuir adsorption isotherm model

Langmuir isotherm model was developed to investigate how adsorptions occur on homogeneous surface and it is valid for monolayer adsorption onto adsorbent surface [43]. In linear form, this equation is represented as Eq. (6):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{6}$$

where C_e is the concentration of adsorbate at equilibrium (mg/L), q_e is the amount of dye adsorbed at equilibrium (mg/g), q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir isotherm constant (L/mg).

2.6.2. Temkin adsorption isotherm model

Temkin and Pyzhev [44] clarify the interaction between adsorbing species and adsorbent amid adsorption isotherms and this equation can be expressed in linear form as follows:

$$q_e = B \ln K_T + B \ln C_e \tag{7}$$

where K_T is the Temkin equilibrium binding constant (L/mg) and $B = RT/b$ is related to heat of adsorption (J/mol).

2.7. Mass transfer analysis

Mass transfer analysis for adsorption of MB on the CTB surface was carried out by using the following equation expressed in [45]:

$$\ln\left(\frac{C_t}{C_o} - \frac{1}{1+MK_{bq}}\right) = \ln\left(\frac{MK_{bq}}{1+MK_{bq}}\right) - \left(\frac{1+MK_{bq}}{MK_{bq}}\right)\beta S_s t \tag{8}$$

where M is the mass of the adsorbent per unit volume (g/L), K_{bq} is the constant obtained by multiplying q_m and K_L, S_s is the external surface area of the adsorbent per unit volume (m^{-1}), β is the mass transfer coefficient (cm/min) and t is the contact time (min). The values of mass transfer coefficient and β were determined graphically from the plot of $\ln(C_t/C_o - 1/(1+MK_{bq}))$ vs. t.

3. Results and discussion

3.1. Adsorbent characterization

3.1.1. FT–IR analysis

Fig. 1 shows the FT–IR spectra of CTB before and after the adsorption of MB dye. The FT–IR spectrum exhibits a broad peak at 3,412.08 cm^{-1} which is distinctive of the O–H stretching vibrations of cellulose, pectin, hemicelluloses and lignin components. Free hydroxyl groups and bonded O–H bands of carboxyl group were found as the O–H stretching vibrations which happened within a broad range of frequencies [46]. The band at 2,364.73 cm^{-1} is attributed to C–H stretching vibration of methyl, methylene and methoxy groups. The peak observed at 2,370.71 cm^{-1} is the stretching vibration due to non-ionic carboxyl groups (–COOH, $–COOCH_3$). The peaks at 1,760 and 1,620 cm^{-1} may be due to asymmetric and symmetric stretching vibrations of the presence of (N–H) amide group. Peaks between 1,111.00 and 1,039.63 cm^{-1} may be due to stretching vibration of C–OH of alcohols and carboxylic acids [47]. Peak at 611.43 cm^{-1} implies the presence of C–H stretching.

From Fig. 1, it can be seen that before adsorption CTB surface is affluent in functional groups and after adsorption of MB dye onto CTB surface, a number of functional groups either shifted in frequency or fade away in some cases when MB molecules are jumped onto adsorbent surface. These phenomena indicate that the promising involvement of those functional groups on the surface of CTB in the adsorption process.

3.1.2. BET analysis

BET analysis was done to identify the adsorption of MB onto the CTB surface. Adsorbent having more surface area contains more active sites that are responsible for adsorption. From the experiment, it can be observed that average surface area of CTB sample was found to be 117.17 m^2/g whose pore diameter and pore volume were obtained 9.20 nm and 0.69 cm^3/g, respectively. In comparison with that of some other adsorbents such as activated carbon (1,688 m^2/g) and carbon nanotubes (177 m^2/g) [48], it can be understood that surface area of CTB is not higher than those but CTB is bio-based low-cost and locally available adsorbent; might be a better alternative to carbonaceous high-priced adsorbents.

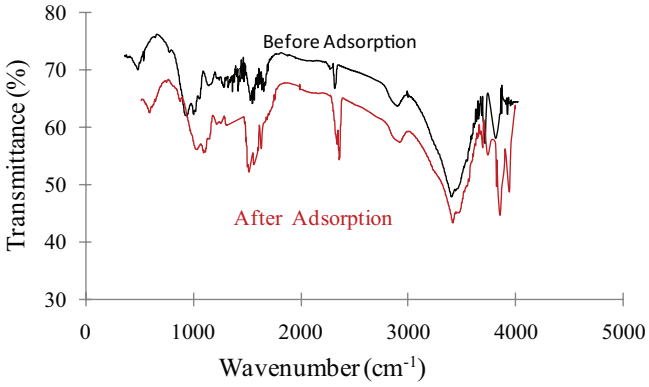

Fig. 1. FTIR spectra of CTB surface before and after adsorption of MB dye.

3.2. Removal properties of MB

3.2.1. Effect of initial pH

Adsorption of MB dye onto CTB surface is mostly pH dependent as shown in Fig. 2. The removal of MB increased remarkably as the pH of the solution increased but lower adsorption of MB at acidic pH was accounted for by the competition of adsorption sites between the MB surface charges and excess H^+ ions in solution. MB is a cationic dye which has a net positive charge and at higher pH values, CTB surface adopts negative charges, which contribute to improve uptake of positively charged dye species via attractive electrostatic force and similar behavior was observed for MB removal using different types of bio-adsorbent [49–54]. In this study, the maximum dye removal was obtained at pH 10 and values higher than this condition (pH > 10); the removal of dye was decreased due to less number of positive charges on MB dye surface. For this, pH level 10 was used as optimum condition in further adsorption studies herein.

3.2.2. Effect of adsorbent dosages

Fig. 3 demonstrates the effect of CTB adsorbent dosages for the removal of MB dye. From this figure, it can be seen that the highest level (~86%) of MB removal was achieved using 1.5 g/L CTB adsorbent. Normally increasing the adsorbent dose provides a larger surface area and increasing the availability of the binding sites [55]. For this reason, increasing amount of the adsorbent and maintaining fixed adsorbate concentration make a huge number of sites available for a fixed concentration of adsorbate; hence enhanced the percentage of adsorption. Similar results are reported elsewhere [34,52,56,57].

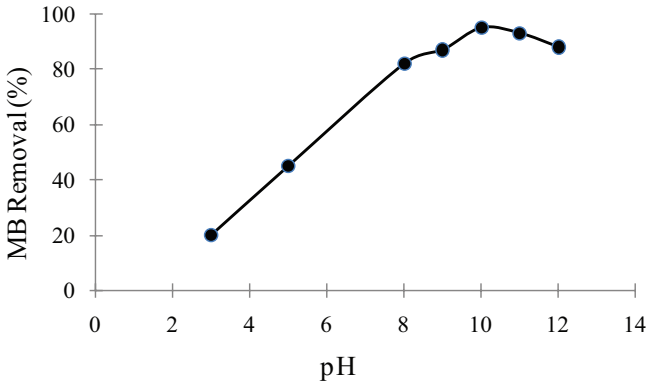

Fig. 2. Effect of pH on the removal of MB by CTB as bio-adsorbent where concentration: 100 ppm, dose: 1.5 g/L, contact time: 150 min and shaking speed: 211 osc/min.

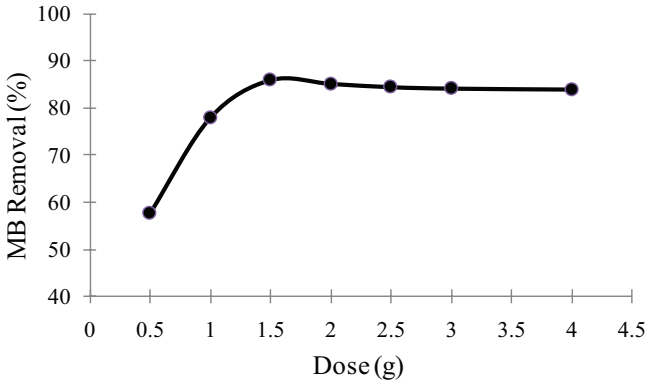

Fig. 3. Effect of adsorbent dosage on MB dye removal (%) by CTB as bio-adsorbent where concentration: 100 ppm, contact time: 150 min, pH: 10 and shaking speed: 211 osc/min.

3.2.3. Effect of dye concentration and contact time on MB adsorption

The consequence of contact time on the adsorption of MB onto CTB adsorbent was studied at different initial dye concentrations presented in Fig. 4. From the figure, it can be observed that the dye removal percentage increased with decreasing initial MB dye concentration from 100 to 200 ppm. This is due to the fact that for fixed adsorbent dosage, at higher initial dye concentration the number of active sites of adsorbent becomes fewer [58]. On the other hand, the percentage of adsorption increases with increasing contact time at all initial dye concentrations and equilibrium is attained at 150 min where maximum recovery was found to be 92%. Similar types of results were reported elsewhere [57,59].

3.3. Adsorption kinetics

3.3.1. Pseudo-first-order and pseudo-second-order kinetic models

Pseudo-first-order and second-order kinetic models were investigated for CTB–MB adsorption system. In this study, the values of K_1, K_2 and q_e are calculated from the corresponding slope and intercept of the plots which are incorporated in Table 1. The values of correlation coefficient R^2 which was obtained from the analysis of different kinetic models clearly notify that the experimental results can be best represented by the pseudo-second-order kinetic model. Table 1 indicates that the experimental value of adsorption capacity (12 mg/g) is nearer with the value of 16.95 mg/g as calculated by employing pseudo-second-order equation than the calculated

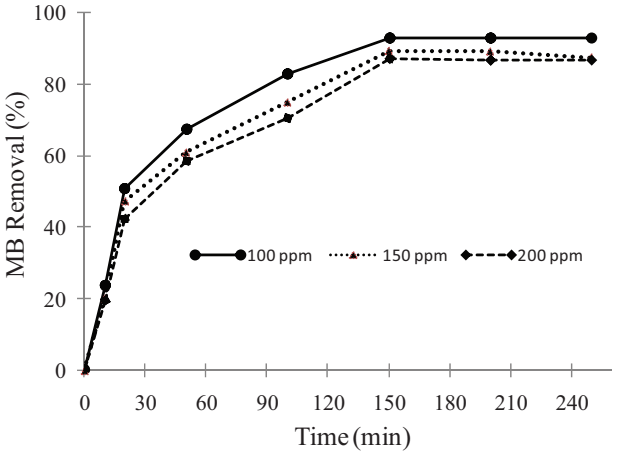

Fig. 4. Effect of initial MB dye concentration and contact time onto CTB surface where adsorbent dose: 1.5 g/L, shaking speed: 211 osc/min and pH: 10.

Table 1
Kinetics parameters for adsorption of MB onto CTB surface

Pseudo-first-order					Pseudo-second-order				
	K_1 (min^{-1})	q_e (mg.g^{-1})		R^2		K_2 (mg.g^{-1}min^{-1})	q_e (mg.g^{-1})		R^2
		Exp.	Calc.				Exp.	Calc.	
1.5 g/L	0.016	12	4.16	0.8981	1.5 g/L	29.75×10^{-3}	12	16.95	0.9952

value by employing pseudo-first-order model. This further authenticates that the kinetics of CTB–MB system obeys pseudo-second-order model. On the other hand, the value of K_2 is lower than the corresponding value of K_1 which indicates the best fit of kinetic data with pseudo-second-order model (Fig. 5) as well as linearity of t/q_t vs. t plot confirmed that the nature of adsorption process is pseudo-second-order and similar phenomena are found elsewhere [28,57,60,69–71].

3.3.2. Intraparticle diffusion model

According to the Weber–Morris intra-particle diffusion model, the plot of q_t vs. $t^{0.5}$ shows a linear plot passing through the origin indicating that intra-particle diffusion is the rate controlling step in the adsorption process [34,42]. From Fig. 6, it can be seen that the plot demonstrates linear relationship but does not pass through the origin resembling that intra-particle diffusion is not a rate determining step. The Weber and Morris plot (Fig. 6) can be divided into two regions: the first region is accredited to intra-particle diffusion, while the second region is attributed to slow equilibrium. On the other hand, larger intercept value (I = 12.73) indicates a greater boundary layer effect on the adsorption process and similar results are available in the literature [52,61,72]. Calculated value of diffusion coefficient (K_{id}) was found to be 0.38 according to Eq. (5).

3.4. Adsorption isotherm study

3.4.1. Langmuir model

In the present study, the plot of C_e/q_e vs. C_e shows almost linear fitting (Fig. 7) with a slope of $1/q_m$ and intercept of $1/q_mK_L$. The values of adsorption capacity (q_m) and Langmuir isotherm constant (K_L) are calculated from the slope and intercepts of this plot and the results are inserted in Table 2. From the plot, it can be seen that the value of regression correlation coefficient is very close to 1 (R^2 = 0.9976) indicating the obtained data are well-fitted with Langmuir isotherm which suggests that monolayer sorption exists under the tentative conditions.

Removal efficiency of MB dye by CTB adsorbent can be explained through dimensionless separation factor R_L which is expressed by the following equation:

$$R_L = \frac{1}{\left(1 + bC_o\right)} \tag{9}$$

The value of R_L is obtained to be 0.0684 which is in the range of 0–1 point out that the Langmuir isotherm model is favorable for adsorption and similar results are discussed in

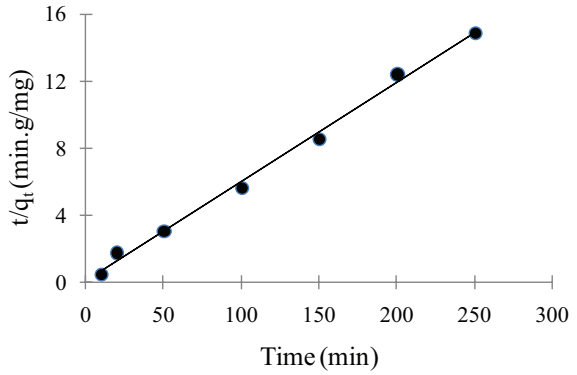

Fig. 5. Pseudo-second-order kinetics for the removal of MB by CTB adsorbent at various optimum operating conditions.

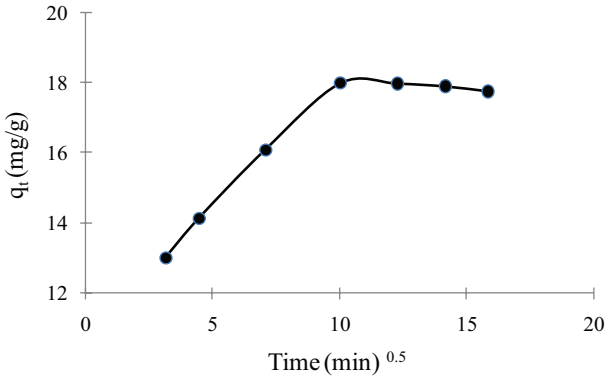

Fig. 6. Intra-particle diffusion kinetic model for the removal of MB onto CTB surface.

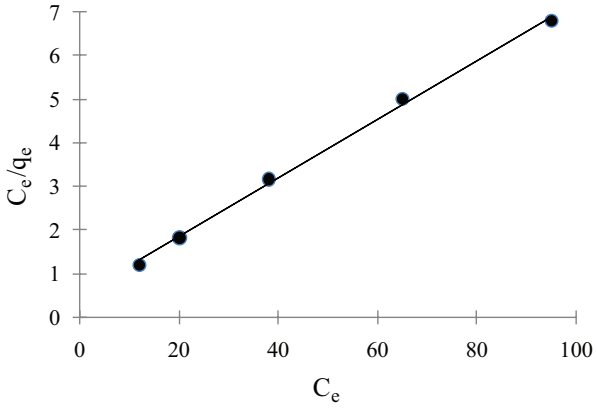

Fig. 7. Linear fitting of Langmuir equation for the adsorption of MB by the adsorbent where pH: 10, adsorbent dosage: 1.5 g/L and contact time: 150 min.

Table 2
Isotherm parameters for adsorption of MB dye onto CTB surface

Langmuir isotherm		Temkin isotherm	
Parameters	Value	Parameters	Value
q_m (mg/g)	14.925	K_T (L/mg)	1.32
K_L (L/mg)	0.136	B	2.60
R^2	0.9976	R^2	0.9586

Table 3
Maximum MB adsorption capacities of different types of bio-adsorbents

Adsorbents	Adsorption capacity (mg/g)	Sources
Coconut tree bark	14.925	Present study
Casuarina equisetifolia needle	110.8	[38]
Fine wheat straw	2.23	[62]
Neem leaf	3.67	[63]
Coarse wheat straw	3.82	[62]
Eggshell	0.80	[64]
Neem bark	5.71	[65]
Potato peel	10.4	[65]
Coconut tree sawdust	4.70	[66]

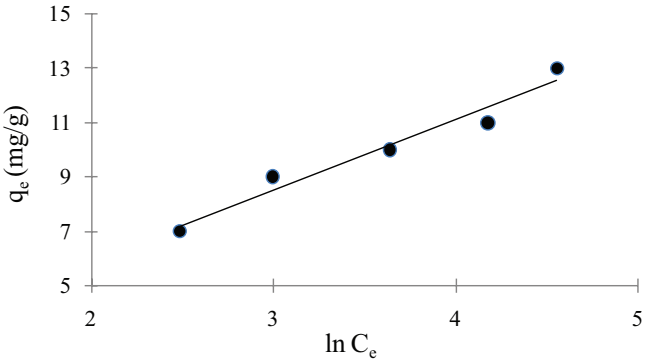

Fig. 8. Temkin isotherm plot for the adsorption of MB by the CTB adsorbent where pH: 10, adsorbent dosage: 1.5 g/L and contact time: 150 min.

[53,69–71,38]. The adsorption capacity (q_m) of CTB surface is 14.925 mg/g and maximum adsorption capacity of various bio-adsorbents are reported in Table 3. From the results, it can be perceived that CTB is a potential adsorbent for the removal of MB dye.

3.4.2. Temkin model

Fig. 8 represents the plot of q_e vs. lnC_e showing nearly a straight line and the values of Temkin isotherm constant (K_T) and B are determined from the slope and intercept of the graph inserted in Table 2. From the table, it can be suggested that the Langmuir isotherm model fitted better than Temkin isotherm model [53] and the value of B indicates the physical adsorption of the process. Identical phenomena are reported in the literature [67,71,73].

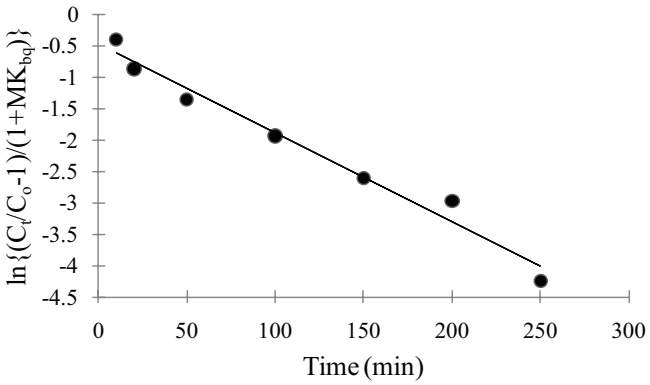

Fig. 9. Mass transfer plot for the adsorption of MB by CTB adsorbent where pH 10, initial dye concentration: 100 ppm and adsorbent dosage: 1.5 g/L.

3.5. Mass transfer analysis

The plot of $\ln(C_t/C_o - 1/(1+MK_{bq}))$ vs. t shows a straight line (Fig. 9) that representing the applicability of this model.

The value of mass transfer coefficient (β) was found to be 8.026×10^{-11} cm/s which was calculated graphically from the slope and intercept of the plot as well as correlation coefficient (R^2) value was found to be 0.975. The values obtained from the experimental study revealed that the velocity of the adsorbate MB for transporting from bulk, that is, solution phase to solid phase is quite good [68].

4. Conclusion

This work clearly represents that CTB is an efficient adsorbent for the removal of MB dye from the wastewater. The removal properties of the CTB–MB system investigated at various optimum conditions point out that the percentage removal of MB dye increased with increasing pH, adsorbent dosages, contact time and overturned result was obtained for initial dye concentration. The optimum dye removal (95%) by the CTB adsorbent was achieved at pH 10, concentration 150 ppm, dose 1.5 g/L for contact time 150 min. The adsorption properties were well-fitted with pseudo-second-order kinetic model and obtained result indicates that the adsorption process has some boundary layer effect. Equilibrium data fit nicely with the Langmuir isotherm model confirming monolayer adsorption capacity (14.925 mg/g) of MB onto CTB surface. Intra-particle diffusion model showed larger surface adsorption and mass transfer analysis indicated advanced movement of adsorbate towards CTB adsorbent.

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