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Adsorption of Methylene Blue by Low-Cost Biochar Derived from Elephant Dung

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Abstract

Elephant dung biochar (ED350) prepared by controlled heating at 350 ºC was used to adsorb methylene blue (MB) in an aqueous solution. The effects of adsorption time, pH, adsorbent dosage, and initial MB concentration were examined. Kinetic, isotherm, and thermodynamic models were then further analyzed to determine the adsorption. The results show that ED350 was found to be efficient within 180 min. The optimum pH of MB adsorption was 11. The Langmuir isotherm model was found to be the most suitable fit for the adsorption equilibrium data, with ED350 having a homogeneous surface. The calculated equilibrium parameter (R_L) values were greater than zero and less than one, indicating a favorable adsorption process and that ED350 was an efficient adsorbent for MB removal. The kinetics of MB adsorption onto ED350 obeys the pseudo-second-order model. The results of thermodynamic data consideration reveal that the adsorption process is spontaneous and exothermic in nature. This finding suggests that ED350 may prove to be an efficient low-cost adsorbent of MB from wastewater.

Keywords: Biochar; Elephant dung; Methylene blue; Adsorption

Introduction

Dyes are colored compounds widely used in industries such as textiles, printing, rubber, cosmetics, plastics, and leather to dye products, producing large quantities of colored wastewater [1]. Nowadays, there are more than 10,000 commercial dyes in existence and the quantity of dye produced from wastewater worldwide is approximately 750,000 ton a^{-1} [2]. Dyes can be highly toxic and carcinogenic to microbes and animals. They also reduce light penetration, cannot be biologically degraded and are problematic substances which need to be treated from industrial wastewater [3]. Moreover, the contamination of dyes can pose potential hazards to

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the assimilation of organisms in groundwater [4].

Methylene blue (MB) is a cheap cationic dye widely applied to cotton, silk, leather, wool, and coating paper [5]. Compared to differently classified dyes, cationic dyes are identified as being more toxic than other types. Among the cationic dyes, MB is no more toxic than others. However, chronic exposure to MB can lead to severe health issues such as vomiting, increased heart rate, cyanosis, shock, limb paralysis, jaundice, eye burns, tissue necrosis, and mental confusion [6]. To decrease its harmful effects on human beings, wastewater contaminated with MB should be removed before being released into a water environment.

Numerous methods can be used to treat dye wastewater including ozone oxidation, coagulation, advanced oxidation, and biological treatment [7]. Among these methods, adsorption is not a complex process and has great potential in the treatment of dyes. Therefore, it is extensively applied to treat dye in wastewater. Activated carbon is applied frequently as a conventional adsorbent owing to its high surface area but expensive to regenerate and results in losses during regeneration [8]. Previous studies evidence the development of low-cost alternatives to the activated carbons derived from natural products such as modified sawdust, peanut hulls, peanut shells, sunflower stalks, rice husk, corn cobs and barley husk, pineapple stem, and orange peel [9]. However, their applications are limited by the high investment required, high energy consumption, and multifaceted preparation processes [10]. Consequently, it would be useful to develop an improved ecofriendly, economical, and abundant adsorbent [2].

Biochar is a carbon-rich solid material, produced from slow biomass pyrolysis under the absence of oxygen [10]. Biochar is superior to other alternatives due to its simple production process, low cost, enormous surface area, rich oxygen-containing functional groups, and highly aromatic structure, providing excellent adsorption and stability [11]. Most previous studies of biochar use plant or industrial sources as raw materials in its preparation; however, MB adsorption treatment from biochar derived from animal manure has rarely been reported. Elephants (*Elephas maximus*) at the Thai Elephant Conservation Center (Lampang Province, Thailand) produce large quantities of dung, equating to about 540–720 ton a^{-1} [9]. The biochar produced from elephant dung is a good management option for solving environmental problems caused by excess manure. Accordingly, the biochar in this study was produced from low-cost biomass material such as elephant manure for MB adsorption. The feasibility of MB adsorption was evaluated to assess the adsorption time, effects of pH, biochar dosage, and initial concentration of MB required for adsorption efficiency. Additionally, to determine the adsorption mechanism, kinetic, isothermal, and thermodynamic models were further analyzed for use in fecal-sourced biochar to treat MB in wastewater and research a new technique for the utilization of animal feces.

Materials and methods

1) Main reagents and instruments

All the chemicals in this study were of analytical grade and used without further purification. The dye solution of synthetic wastewater was prepared using methylene blue (MB), supplied by Fisher Scientific. This dye has an empirical formula of $C_{16}H_{24}ClN_3O_3S$. The concentration of MB was studied using a spectrophotometer (Hitachi U-2900) at a wavelength of 665 nm to measure its color concentration.

The following instruments were used: the Brunauer-Emmett-Teller (BET) surface area (Micromeritics 3Flex) and Field Emission Scanning Electron Microscope (FESEM JEOL/JSM-7800F).

2) Elephant dung biochar preparation

Elephant (*Elephas maximus*) dung for this study was collected from the Thai Elephant Conservation Center, Lampang Province, Thailand. The dung was sun-dried for a week, then placed in a hot air oven at 103 ˚C for 24 h, and finally an airtight container. The biochar was prepared using a slightly modified method as proposed by Xu et al. [12]. The dried elephant dung was put into a crucible and ignited in an electric muffle furnace (Nabertherm L LT^{-1}) for 15 min at 350 ºC. The biochar materials were ground, sieved with apertures of 250 μm, and carefully stored in an airtight container.

3) Adsorption experiment

This study was conducted using different adsorption operational parameters. The adsorption performance and reaction of adsorbents and adsorbate behavior depend significantly on various parameters including pH, adsorbate concentration, adsorbent dosage, contact time of adsorbent-adsorbate, and adsorption temperature. The aforementioned parameters were used: initial pH (3–11), initial MB concentration (10–40 mg L^{-1}), adsorbent dosage (0.4–2.0 g L^{-1}), contact time (10–300 min), and temperatures (298–328 K). Each of these parameters was examined using 50 mL of dye solution in a series of 250 mL Erlenmeyer flasks with adjustable parameters, whereas other parameters were fixed. The mixture was shaken by a temperature-controlled water bath shaker (Memmert WNB7-45) at a constant speed of 100 rpm. At specific time intervals, the samples were withdrawn from the shaker. The supernatants were then placed in a centrifuge machine (MIKRO 220) at 8000 rpm for five min and the residual dye concentrations measured by a spectrophotometer. The adsorption capacity at equilibrium q_e was determined [13], and the percentage of MB removal calculated as follows.

4) Adsorption isotherm model

The adsorbate interaction is described by an adsorption isotherm. This is critical for the optimum usage of adsorbents and essential for realizing the appropriate correlation for the equilibrium curve [15]. There are several isotherm models, such as the Langmuir and Freundlich mathematical calculations, which are designed to study the mode of interaction between MB and adsorbents at equilibrium. The Langmuir (Eq. 3) and Freundlich (Eq. 4) isotherms were plotted using standard straight-line equations and related by the two parameters C_e and q_e for MB.

$$Removal\ capacity\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad \text{(Eq. 1)}$$

where C_i and C_f represent the initial and final concentration of MB in an aqueous solution (mg L^{-1}). The adsorption capacity for each concentration of MB at equilibrium was investigated by the following expression [14].

$$Adsorption\ capacity\ = q_t\ = \frac{C_i - C_f}{m} \times V \quad \text{(Eq. 2)}$$

where q_t represents the quantity of MB uptake (mg g^{-1}), m is the mass of the adsorbent used (g) and V is the volume of solution (L).

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m}\frac{1}{C_e} \quad \text{(Eq. 3)}$$

where C_e is the concentration at equilibrium (mg L^{-1}) and q_e is the amount of MB adsorbed at equilibrium (mg g^{-1}). The Langmuir isotherm parameters consist of q_m (mg g^{-1}), b (L mg^{-1}) and K_L (L mg^{-1}) [16].

$$log\, q_e = [logK_f + \left(\frac{1}{n}\right) logC_e] \quad \text{(Eq. 4)}$$

where C_e is the concentration at equilibrium (mg L^{-1}) and q_e is the amount of MB adsorbed at equilibrium (mg g^{-1}). K_f and n are Freundlich isotherm parameters, while n is the heterogeneity factor. K_f and n can be examined from a linear plot of log q_e against $log\ C_e$ [17].

5) Kinetic study

To determine the adsorption rate and mechanism of ED350 onto MB, the pseudo-first order and pseudo-second order are commonly used in kinetic studies to test the fit of ED350 with the experimental data. The pseudo-first-order and pseudo-second-order equations can be expressed as in Eq. 5 and 6, respectively [18].

$$log(q_e - q_t) = log\, q_e - \frac{tk_1}{2.303} \quad \text{(Eq. 5)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{(Eq. 6)}$$

where q_e is the adsorbed amount of MB at equilibrium (mg g^{-1}) and q_t is the amount of MB adsorbed (mg g^{-1}) at any time t (min). k_1 is the adsorption rate constant and the value can be calculated from the slope of log (q_e–q_t) versus the t graph. For the pseudo-second order, k_2 is the adsorption rate constant. In this model, linear regression is obtained from the plot of $t\ q_t^{-1}$ versus t. k_2 which is the adsorption rate constant, determined from the intercept of the plot.

6) Thermodynamic model

To explain the nature of adsorption, it is important to determine the thermodynamic parameters, including Gibbs free energy of adsorption (ΔG^0), enthalpy of adsorption (ΔH^0), and entropy of adsorption (ΔS^0), examined by a series of experiments using 50 mL of 40 mg L^{-1} MB concentration at various temperatures (298, 308, 318, and 328 K). ΔG^0, ΔH^0, and ΔS^0 were calculated using the mathematical formulae shown in Eq. 7 and 8 [19].

$$log\frac{q_e}{C_e} = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad \text{(Eq. 7)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{(Eq. 8)}$$

where T is the temperature in Kelvin and R is the gas constant. The values of ΔH^0 and ΔS^0 can be obtained from the plot of log $q_e\ C_e^{-1}$ versus $1\ T^{-1}$.

Results and discussion

1) Structural characteristics of ED350

The specific ED350 surface area of 5.69 $m^2\ g^{-1}$ is within the range of biochars (1–50 $m^2\ g^{-1}$) produced from industrial organic waste or dairy manure [12, 20]. A FESEM image of ED350 is presented in Figure 1.

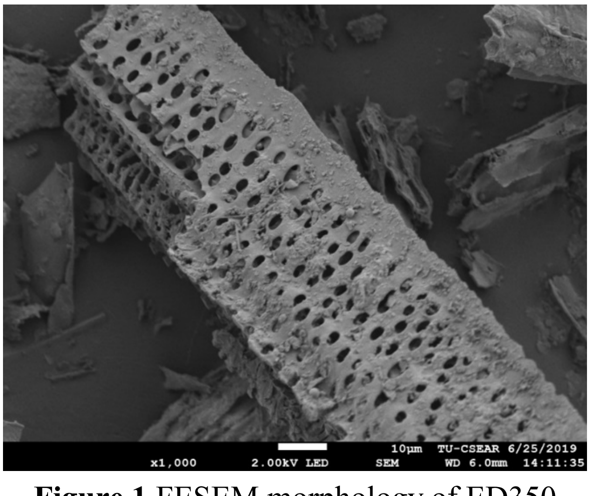

Figure 1 FESEM morphology of ED350 at 1,000 x magnification.

2) Adsorption capacity of MB

The effect of contact time is an important factor in determining the equilibrium time allowed for maximum adsorption capacity. In this study, the uptake of MB was conducted using initial solutions of pH 7; an initial MB concentration in the range of 10 to 40 mg L^{-1} and an adsorbent concentration of 0.100 g. Figure 2 shows the kinetic adsorption plots of MB at 25 °C. The MB molecules were readily adsorbed to the adsorbent surface; resulting in rapid MB adsorption during the first five min of contact.

The results show that the MB adsorption increased in accordance with the length of contact time, with equilibrium being established in less than 180 min, while a corresponding decrease was found after the treatment of the adsorbent, for example, desorption occurred with longer contact times [10]. Hence, the selected equilibrium time for MB adsorption was 180 min. These results were similar to those in previous studies [21–22].

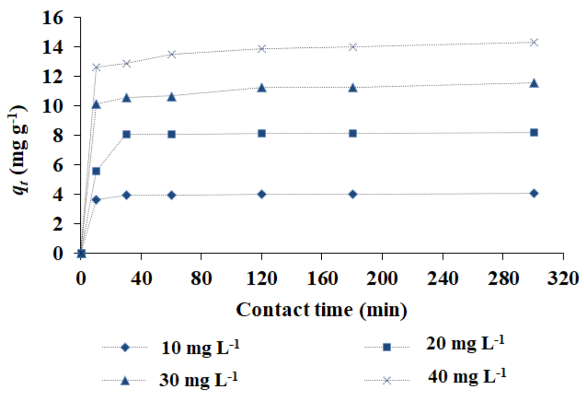

Figure 2 Effect of contact time and different initial concentrations (10, 20, 30, and 40 mg L^{-1}) on the adsorption of MB by ED350.

Figure 2 shows the adsorption effect of ED 350 with different concentrations of MB (10, 20, 30, and 40 mg L^{-1}). It can be observed that the adsorption capacity of ED350 increases in accordance with MB concentrations. When the difference in MB concentration between the biochar surface and the aqueous solution increased, a high mass transfer rate would result in greater adsorption [23]. Additionally, when a certain quantity of biochar was dispensed into the aqueous solution, this limited the ability of active surface sites to adsorb MB. As the initial concentration of MB increased, the MB concentration in the solution increased accordingly. After the saturation of biochar adsorption, the adsorption rate was reduced [10].

3) Effect of pH on adsorption

Different initial pH values of the solution were examined to assess the protonated charge state on the adsorbent surface and the effects of the contaminants present [10]. Figure 3 shows the effects of initial pH on the biochar adsorption of MB.

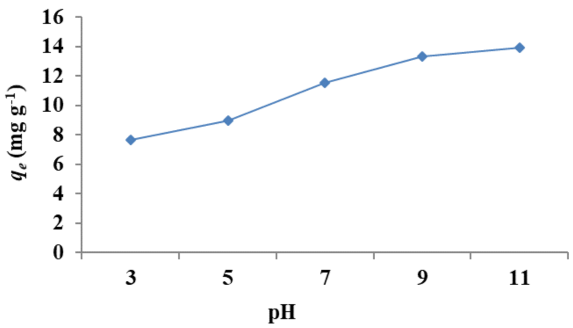

Figure 3 Effect of contact time on the adsorption of MB by ED350.

The results show better adsorption capacity in alkaline conditions than in acidic. At a pH of 11, the ED350 adsorption capacity reached 13.93 mg g^{-1}, which is 1.82 times greater than at a pH of 3. Two phenomena explain the influence of pH on MB adsorption: (1) at the low pH, H^+ ions surround the active adsorption sites on the biochar surface, reducing the number of its potential binding sites; and (2) when the pH is low, the biochar surface can be highly protonated which increases the positive charge and contributes to electrostatic repulsion with the MB cation in the solution, leading to reduced adsorption [10]. When the pH increases, the quantity of H^+ ions on the potential absorption sites is reduced, and adsorption of MB using biochar tends to increase. At higher pH values, deprotonating occurs on the biochar surface and becomes negatively charged, which is advantageous to the mutual attraction of MB cations via electrostatic interactions, thus improving the adsorption outcome. This result is similar to that reported by Huang et al. (2018) in their study of MB adsorption by biochar [10], whereby changes in pH resulted in regular adsorption for sheep, rabbit, and pig manure.

4) Adsorption kinetics

The MB adsorption kinetics and mechanism of ED350 were examined using pseudo-first-order and pseudo-second-order models. The correlation coefficient (R^2) of the pseudo-second-order model was expressed as 0.9998 (Figure 4 and Table 1), which was greater than the pseudo-first-order value. Similar results using a pseudo-second-order kinetics model were reported by Huang et al. (2018) for the adsorption of MB from an aqueous solution by biochar prepared from sheep, rabbit, and pig manure [10]. The (theoretically) calculated value of q_e from the pseudo-second-order model showed similar good agreement with the experimental data. Consequently, these findings indicate that the pseudo-second-order model correlated more consistently and precisely with the experimental results compared to the pseudo-first-order model. The pseudo-second-order kinetic model assumes that the rate-limiting step is physicochemical, with the adsorption process being conducted through electronic sharing, transfer, and exchange [24]. Therefore, it can be observed that the mechanism of the MB adsorption process onto ED350 is complex.

5) Analysis of adsorption isotherms

The curves of the Langmuir and Freundlich models were used to analyze the adsorption isotherms, as illustrated in Figure 5. The adsorption constants of both models were obtained from the slopes and intercepts of these figures along with the corresponding correlation coefficients as presented in Table 2.

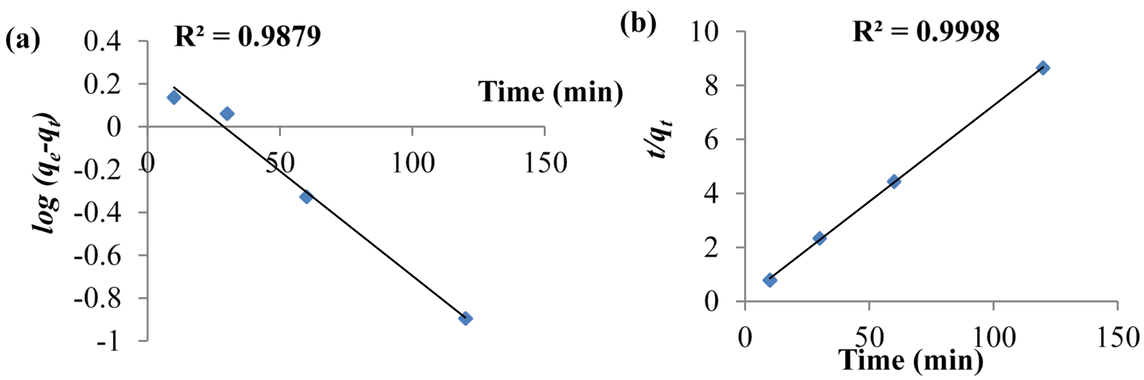

Figure 4 Adsorption kinetic curves of MB onto ED350: (a) pseudo-first-order model, (b) pseudo-second-order model.

Table 1 Kinetic model parameters of MB adsorption onto ED350

q_e experiment (mg g^{-1})	Pseudo-first order			Pseudo-second order		
	q_e calculated (mg g^{-1})	k_1 (min^{-1})	R^2	q_e calculated (mg g^{-1})	k_2 (min^{-1})	R^2
14.0019	2.0678	0.0104	0.9879	14.0647	0.0352	0.9998

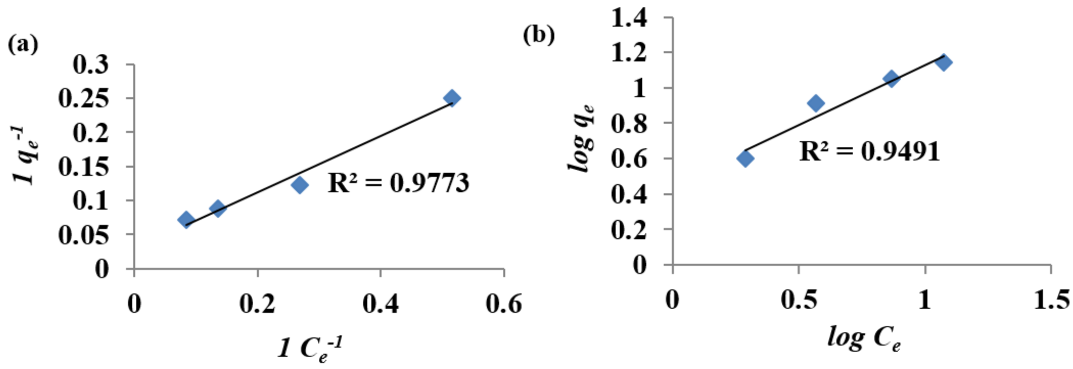

Figure 5 Adsorption isotherm curves of MB onto ED350; (a) Langmuir isotherm model, (b) Freundlich isotherm model.

Table 2 Langmuir and Freundlich isotherm model constants and correlation coefficients for MB adsorption

Langmuir isotherms				**Freundlich isotherms**		
q_m (mg g^{-1})	K_L (L mg^{-1})	R_L	R^2	K_F (mg g^{-1})(L mg^{-1})$^{1\ n-1}$	n	R^2
34.36	0.0701	0.5879	0.9773	2.8562	1.4843	0.9491

The corresponding correlation coefficient (R^2) values derived from the Freundlich fitting were less than those of the Langmuir model for each adsorbent. Thus, the Langmuir isotherm was the most suitable fit for the data. This finding is similar to that of Choi and Yu (2019) [2], who studied the adsorption of MB by bio-adsorbent corncob. This suggests that the adsorption of MB on ED350 is a monolayer adsorption process on a homogenous biochar surface. The effect of the isotherm shape can be observed in the values of the dimensionless separation factor (R_L). The R_L value of ED350 was between 0 and 1, indicating that the maximum adsorption process is favorable. The maximum monolayer adsorption capacity of ED350 was highest at 34.36 mg g^{-1}. Furthermore, the Freundlich exponent n can be used to describe the intensity of adsorption. In this study, the value of n was measured as 1.48. Therefore, the MB adsorption process is more likely to be performed by a physical process. In accordance with the general interpretation of n and $1\ n^{-1}$ values, n = 1 indicates linear, $n > 1$ illustrates a physical process, $n < 1$ illustrates a chemical process, $1\ n^{-1}$ = 0.1 to 0.5 which shows that an excellent adsorption process, $1\ n^{-1}$ = 0.5 to 1 shows a straightforward adsorption process, and $1\ n^{-1} \geq 1$ shows a difficult adsorption process [25]. In this experiment, the value of $1\ n^{-1}$ was found to be 0.67, indicating that the MB dye adsorption process onto ED350 was very straight-forward.

A comparison of the adsorption capacity of various sorbents for MB removal is presented in Table 3. The maximum adsorption capacity of ED350 is slightly larger than other adsorbents, its adsorption equilibrium time short, and the preparation temperature low, all of which are potential benefits.

6) Analysis of thermodynamics

Figure 6 shows the relationship between ΔG^0 and T while Table 4 presents the thermodynamic parameters of MB adsorbed onto biochar. The negative values of ΔG^0 under various temp-ratures indicate the spontaneous and favorable nature of the MB adsorption process onto ED 350 biochar. Moreover, the size of $|\Delta G^0|$ increases with rising temperature, that is,

$|\Delta G^0|$328K>$|\Delta G^0|$318K>$|\Delta G^0|$308K>$|\Delta G^0|$298K, indicating that as the temperature increases, the randomness of the solid/solution contact surface reduces [29]. Gibbs free energy can be used to describe the adsorption process, $|\Delta G^0|$ is −20 to 0 kJ mol^{-1} showing physical adsorption and $|\Delta G^0|$ is −80 to −400 kJ mol^{-1} indicating chemical adsorption [2]. In the adsorption experiments conducted for this study, the value of ΔG^0 is approximately −9.66 to −10.17 kJ mol^{-1}, which falls in the range of the physical adsorption process. The negative values of ΔH^0 for ED350 suggest that the adsorption process is exothermic in nature. The positive values of ΔS^0 reveal that randomness and disorder increase at the solid/solution interface during the adsorption of MB onto ED350 [30]. Furthermore, the positive value of ΔS^0 might suggest that adsorbate molecules obtain at least one degree of freedom when not adsorbed onto the biochar. This also confirms that randomness at the solid/solution interface is increased during the MB adsorption process. Considering all the results, the mechanism of MB adsorption onto ED350 indicates physical adsorption via van der Waals interaction.

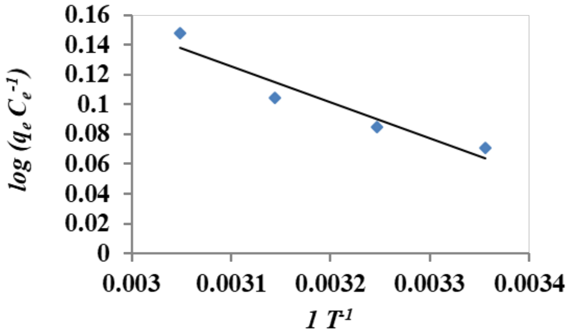

Figure 6 Relationship between log (q_e C_e^{-1}) and 1 T^{-1}.

Table 3 Comparison among several adsorbents applied to MB treatment

Adsorbents	Biochar producing temperature (°C)	Equilibrium time (min)	q_m (mg g^{-1})	Reference
ED350	350	180	34.36	This study
Pig manure biochar	500	210	53.68	[10]
Hickory biochar	350	1440	16.30	[26]
Anaerobic digestion residue biochar	400	120	9.50	[27]
Palm bark biochar	400	120	2.66	[27]
Eucalyptus biochar	400	120	2.06	[27]
Wheat straw biochar	550	300	12.03	[28]

Table 4 Thermodynamic parameters of MB adsorption onto ED350

Temperature (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})
298	-9.6625	-4.6493	0.0168
308	-9.9807		
318	-9.9989		
328	-10.1671		

Conclusion

The treatment of MB by ED350 in an aqueous solution was found to be effective within 180 min and at an optimum pH value of 11. The Langmuir isotherm model was the most appropriate fit with the adsorption equilibrium data, therefore ED350 had a homogeneous surface. The calculated equilibrium parameter (R_L) values were greater than zero and less than one, indicating a favorable adsorption process and that ED350 was an efficient adsorbent for MB removal. The kinetics of MB adsorption onto ED350 obeys the pseudo-second-order model, demonstrating that the adsorption process is spontaneous and exothermic in nature. This finding suggests that ED350 may prove to be an efficient low-cost adsorbent to adsorb MB from wastewater.

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