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Biochar from Empty Date Fruit Bunch as an Adsorbent to Remove Eriochrome Black T and Methylene Blue from Aqueous Solution

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Abstract

Date fruit has a significant role in Sahara countries' economies. In this study, a bunch of empty dates waste was used to produce biochar, which will be used to adsorb Eriochrome black T (EBT) and methylene blue (MB) dyes from aqueous solution. The dates bunch was washed, dried, and ground into small particles. Then it was heated in a muffle furnace at 850 °C. The biochar from empty date bunches (BEDB) characteristics before and after adsorption was determined by using scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. The experiment has used different parameters notably initial concentration (25 – 100 mg L^{-1}), contact time (0 – 90 min), BEDB amount (0.01 – 0.05 g), and different solutions pH (2 – 10) in batch adsorption. This investigation has shown that Langmuir and pseudo-second-order isotherm models were well-fitted than Freundlich and pseudo-first-order. The maximum capacity of adsorption was 58.47 and 80.64 mg g^{-1} for EBT and MB removal, respectively at 25°C. The results obtained show that BEDB sorbent has an important adsorption capacity of dyes removal and has a performance to eliminate EBT and MB dyes from aqueous solution.

Keywords: Adsorption; Aqueous solution; Biochar; Empty bunch date; Eriochrome black T; Methylene blue

Introduction

Dyes can be used in textile, paper, paint, food, and colorant industries for different purposes [1]. The production of dye worldwide was estimated at about 1 million tons per year, where hundreds of thousands of kinds of dyes were commercialized [2]. In fact, wastewater contains a percentage of dyes discharged by industrial factories, which are very toxic for the environment (animals, fish, insects, and plants) and life cycle because of their complex structures, thereby affecting directly the human health (ecotoxicology, carcinogenic and mutagenic) [3]. In the last decade, many environmental types of research had been directed to treat industrial

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wastewaters from dyes using different methods, including adsorption, coagulation, electrochemical or photochemical treatment, oxidation flocculation, inverse osmosis, and others [1].

The adsorption by waste materials was considered as an effective method, low cost, and green. Various waste materials were used to produce different adsorbents to treat wastewater such as olive stones [4], palm tree [5], mung bean husk [6], peanut husk [7], tea leaves wastes [8], mint plant waste [9], banana peels [10], oak acorns [11] and date seeds [12]. The use of biomaterial (biomass) as an adsorbent to eliminate dyes from aqueous solution is related to the chemical structure since functional groups and carbon content are mainly responsible for adsorption [13]. The pyrolysis of biomass at high temperatures (biochar) enhances the adsorption of dyes from aqueous solution thanks to its carbon content, large number of active sites, and high surface area. Therefore, biochar can be used as a bio-adsorbent [14].

Date fruit productivity has a crucial role in economic development worldwide, especially among Sahara countries. Algeria has 19 million date palm trees in 170000 hectares, with 800 kinds of palm trees, and produces about 11 million quants of date per year [15]. Waste date fruit is considered as renewable and low-cost waste so, it can be exploited as a green material for organic adsorption. Empty dates bunch (EDB) are the principal waste date. Therefore, they can be used as charcoal to treat aqueous solution from dyes.

Eriochrome Black T (EBT) and methylene blue (MB) are the most of dyes contained in the wastewater. Many researchers used the adsorption process to remove EBT and MB dyes from aqueous solutions as will be outlined in what follows: Almeida et al. [16] used expanded perlite modified with orthophenanthroline to remove EBT dye. Benallou et al. [17] studied MB adsorption on olive stones. Azlina et al. [18] used raw empty fruit for MB sorption. Erradi et al. [19] also eliminated MB dye using an adsorbent produced from snail shells. In the present study, The biochar produced from empty date bunches were used to eliminate EBT and MB dyes from aqueous solution.

The study aimed to evaluate the biochar produced from empty date fruit bunches as an adsorbent to eliminate eriochrome black T and methylene blue from aqueous solution. This study included parameters including time of contact, pH solution, initial dye concentration, and adsorbent dose. Langmuir and Freunlich isotherms were used to determine the maximum adsorption capacity of this adsorbent. Moreover, a kinetic study was considered by using pseudo-first and pseudo-second-order models.

Materials and methods

1) Biochar preparation

EDB was used to pro-duce biochar as an adsorbent. The raw material was washed with distilled water several times until the dirt was removed. Then, it was dried in the oven at 107 °C for 24 h, to eliminate moisture. The dried EDB was crushed to small pieces inferior to 20 mm. The sample was heated in a digital muffle furnace (DAIHAN Scientific) at different pyrolysis temperatures 550 and 700 °C for 30 min and 850 °C for 1 h with 5 °C min^{-1} ramp rate. The biochar prepared from the empty date bunch (BEDB) was grounded by mortar (MICROTRON SYSTEM MB 800) and then sieved using a 0.08 mm sieve mesh. The biochar powder was stored in a glass container for later use.

2) Solution preparation

The dye solutions used in this study are EBT and methylene blue (MB) purchased from Biochem laboratory, Tortolabri- United Kingdom. The molecular structure was $C_{20}H_{12}N_3NaO_7S$ and $C_{16}H_{10}CIN_3S$ for EBT and MB, respectively. EBT and MB molar masses were 461 and 319 g mol^{-1} respectively. The main aqueous solution (1,000 mg L^{-1}) were prepared by dissolving 1 g

of dye in 1 liter of distilled water. Then, the pollutant solutions (25 – 100 mg L^{-1}) were prepared by diluting the main solution with demineralized water. Hydrochloride acid (HCl) and sodium hydroxide (NaOH) were used in these experiments to adjust the pH of different dye solutions.

3) Point of zero charge of BEBD sorbent

The point of zero charge of the sorbent was conducted using Erlenmeyer flasks with 50 mL of 0.1 M KNO_3 solution. The pH of KNO_3 solutions were adjusted by 0.1 M of HCl and NaOH. After then 0.15 g of BEBD sorbent was added to the samples containing 50 mL of KNO_3 solutions under different pH values and shaken for 24 h. After filtration, the values of pH finale (pH_f) were measured using a pH meter. The PZC value of BEDB was deter-mined from the plot $pH_i - pH_f = f(pH_i)$ [20].

4) Batch adsorption

Batch adsorption experiments were carried out using Erlenmeyer flasks containing 100 mL dye solutions. The initial concentration was 25-100 mg L^{-1}, the adsorbent dosage was 0.01–0.05 g, and the contact time was 15–90 min. To study the effect of pH on dyes adsorption, different pH solutions from 2 to 10 were used. All samples were filtered using filter paper mesh 3 to separate BEDB from the aqueous solution. The EBT and MB dyes concentrations at equilibrium were measured using a UV-vis spectrophotometer at 529, 663-nm wavelength each. All tests were carried out in triplicate; the average values were used for the upcoming work. The amounts of dyes removed by BEDB adsorbent at equilibrium and t time q_e, q_t (mg g^{-1}) were determined by Eq. 1 and Eq. 2, respectively.

$$q_m = (C_0 - C_e)\frac{V}{m} \quad \text{(Eq. 1)}$$

$$q_t = (C_0 - C_t)\frac{V}{m} \quad \text{(Eq. 2)}$$

Where; C_0: initial concentration of dye (mg L^{-1}), C_e: concentration of dye at equilibrium (mg L^{-1}), C_t: concentration of dye at time t (mg L^{-1}) and m: BEDB adsorbent weight (g).

The percentage of EBT and MB adsorbed were calculated using Eq. 3.

$$R = \frac{C_0 - C_{eq}}{C_0}\ 100 \quad \text{(Eq. 3)}$$

5) Analysis methods

The surface morphology of BEDB before and after dye sorption was taken by scanning electron microscopy SEM (model: Hitachi TM-1000). The functional groups of BEDB were determined using a Fourier Transform Infrared FTIR spectrometer (Agilent technologies Cary 600). The Absorbance of solutions after EBT and MB adsorption were determined by UV-vis spectrophotometer (Optizen 3220 UV) to find a concentration of dye solutions at equilibrium.

Results and discussion

1) Surface morphology of BEDB

The micrograph shown in Figure 1 represents a surface morphology of BEDB with 4000-time magnification before and after EBT and MB dyes sorption. Before adsorption, the BEDB micrograph shows a porous structure. The porosity was high and the permeability was important to allow the penetration of dye between BEDB pores. After sorption, the BEDB has no porous structure than before dye adsorption. This result can be explained by the fact that the majority of active sites were closed and less permeable. The pores of BEDB were occupied by BET and MB dyes after adsorption.

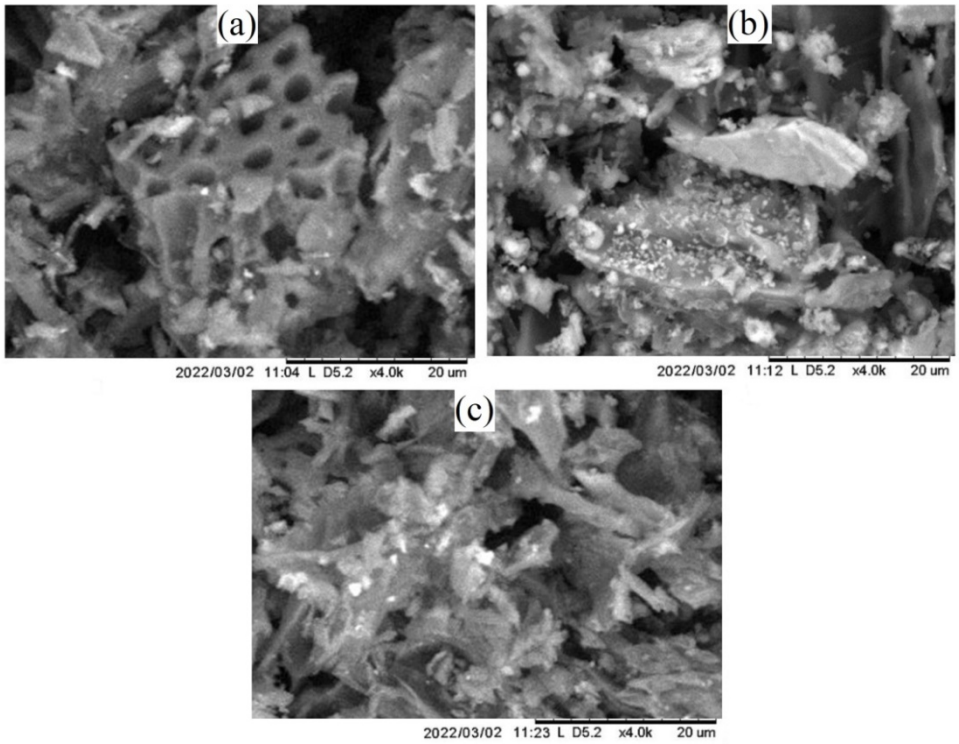

Figure1 Surface morphology of BEDB with 4000 time magnification, (a) before absorption, (b) after EBT absorption, (c) after MB absorption.

2) FTIR analysis

Figure 2 shows the FTIR spectrum of BEDB adsorbent before and after adsorption. The main transmittance peaks of the BEDB absorbent were shown at 3,451, 1,588, 1,470, and 1,122 cm^{-1}. The peak at 3451 cm^{-1} is attributed to the hydroxyl groups (OH^-), the peak at 1588 cm^{-1} is assigned to N-H stretching (amine groups), and the peak at 1,470 cm^{-1} is linked to C-H bonding vibration. Finally, the last peak at 1,122 cm^{-1} can be assigned to the C-C bonding vibration. After the adsorption of EBT and MB, new peaks appeared due to the formation of new bondings between the BEDB adsorbent surface and organic pollutants. The new peak observed at 1,061 cm^{-1} corresponds to C-OH stretching (alcoholic group), while the peak at 669 and 617 cm^{-1} is assigned to C-Cl bonding (alkyl halide). Furthermore, the transmittance peak at 1,588 cm^{-1} disappears after adsorption. This fact can be explained by the interactions between EBT, MB, and aromatic functional groups of BEDB surface. The FTIR spectra demonstrate this biochar from empty date bunch BEDB can be used as an absorbent to remove EBT and MB from aqueous solutions, because of its different functional groups which include; hydroxyl, aromatic, amino, alkyl groups [21].

3) Effect of contact time on EBT and MB removal

Figure 3 illustrates the effect of contact time on EBT and MB removal. The percentage of dyes eliminated by BEDB increased rapidly in the first 15 min of adsorption for each pollutant. This result is due to the availability of active sites on BEDB [22]. Then the adsorption process increased gradually because there was a less active site. After 60 min, the sorption reached the equilibrium at which EBT and MB percentage of eliminated dyes was fixed at 34 and 93% respectively. This outcome means that there are no more dyes to adsorb and all active sites were occupied by EBT and MB dyes. It can be explained by the presence of the repulsive force between absorbent and adsorbate [23].

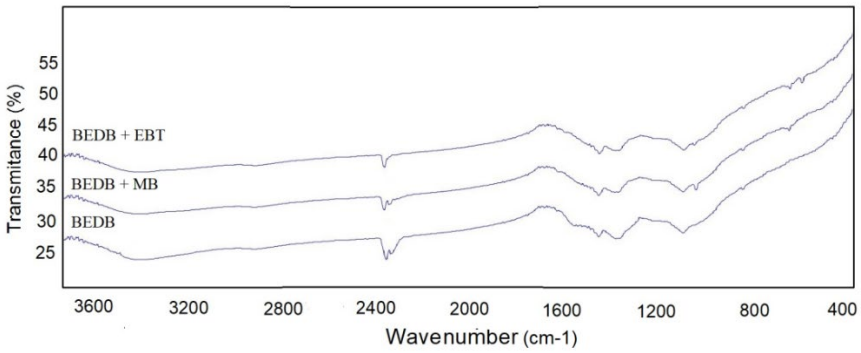

Figure 2 FTIR/kbr spectra of BEDB before and after adsorption.

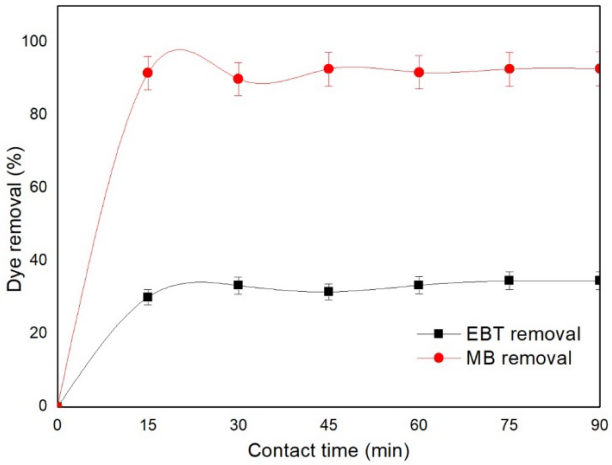

Figure 3 Effect of contact time on EBT and MB removal onto BEDB.

4) Effect of pH solution and pHPZC on EBT and MB removal

The point of zero charge (PZC) represents the pH at which the adsorbent surface charge is neutral [24]. According to Figure 4(a), the pH PCZ value of the BEDB surface is 5.8, which means that at this pH rate, the cation and the anion exchange capacities are equal. When the pH solution is higher than the pHPCZ, the surface charge of biochar is negative, which can be explained by the desorption of proton (H+). However, when the pH of the solution is lower than pHPCZ, the BEDB surface charge becomes positive. That results are due to the absorption of positive charge (H^+) [24].

Figure 4(b) shows the effect of pH solution from 2 to 10 on EBT and MB adsorbed at initial concentration 25 mg L^{-1}, adsorbent dose 0.02 g, contact time 45 min and 25°C. For MB removal, data demonstrates the minimum adsorption capacity of the BEDB observed at pH 2 (71 mg g^{-1}), then MB sorption increased up to pH 6 (89 mg g^{-1}) and then decreased at pH 10. This figure can be explained as follows: at pH > pHPCZ, the surface charge of the BEBD became negative, which enhanced the interaction between the positive charge of methylene blue solution and the BEDB sorbent surface. The low capacity adsorption of MB onto the BEBD sorbent is due to the inexistent electrostatic forces between MB dye and BEBD surface at pH < pHPCZ. In fact, at this pH, both MB dye and sorbent surface are positively charged [25]. However, EBT is an anionic dye, so it has a negative charge [26]. The peak of EBT amount adsorbate from solution by BEDB was observed at pH 2 (66 mg g^{-1}), after then the adsorption decreases with increasing the pH value. The results at pH 2 (pH < pHPCZ) are attributed to the electrostatic force between the positive charge of the active site of BEDB

absorbent and the hydroxyl ions present on the EBT dye solution [27]. The decrease of EBT adsorption capacity due to the charge of BEDB became negative as the charge of adsorbent surface at (pH < pHPCZ).

5) Effect of initial concentration on EBT and MB removal

Figure 5 represents the effect of initial concentration on EBT and MB sorption. The experiment varied the initial dye concentration (25 – 100 mg g^{-1}) at pH 3, BEDB amount 0.05 g, and the contact time 45 min and 25 °C. The increase of initial dye concentration from 25 to 100 mg L^{-1}, results in an increase in adsorption capacity from 18 to 42 mg g^{-1} and from 49 to 140 mg g^{-1} for EBT and MB removal, respectively. The latter was explained by the increase of the resistance force between the active surface of BEDB and EBT, MB solutions. At the same time, the dyes molecular transfer was increased due to the increase of initial dyes concentration [28].

6) Effect of BEDB amount on EBT and MB removal

The effect of the BEDB dose on EBT and MB elimination is illustrated in Figure 6. The experiment was carried out using different BEDB quantities (0.01 – 0.05 g) at 25 mg L^{-1} as initial dye concentration, pH 3 and temperature 25°C. First, the percentage of EBT and MB adsorbed was increased quickly with the increase in BEBD quantities. The maximum yields of EBT and MB removal were at 51%, and 80%, respectively. This figure is due to the adsorption phenomenon on active sites of the biochar surface [29]. Then the percentage of EBT and MB removal also increased with the increase of the BEDB dose and was at 66 % and 98 %, respectively, as shown in Figure 6. As observed, the amount of MB dye was highly adsorbed by BEBD active sites compared to that of EBT dye. However, according the second Y axis, the increase in the BWV dose decreased the adsorption capacity of EBT and MB dyes from 44.3 to 33 mg g^{-1} and from 79.5 to 47 mg g^{-1}.

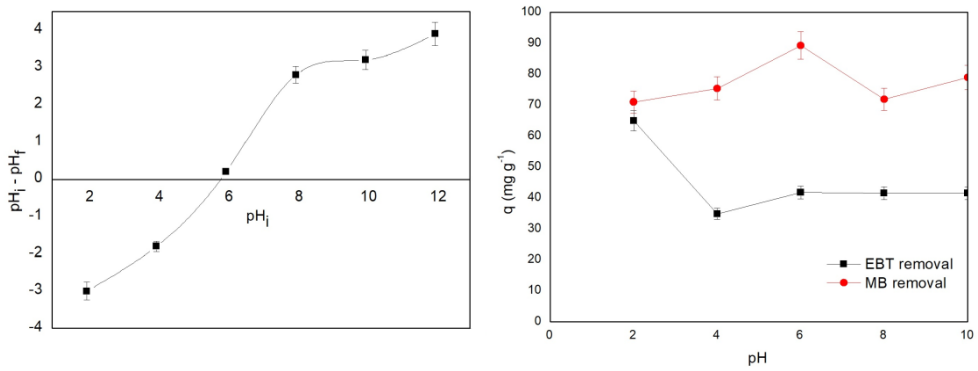

Figure 4 Graphs showing (a) determination point of zero charge of BEBD sorbent and (b) effect of pH solution on EBT and MB removal onto BEDB.

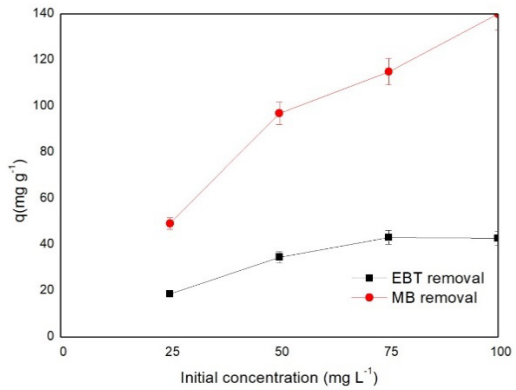

Figure 5 Effect of initial concentration on EBT and MB removal onto BEDB.

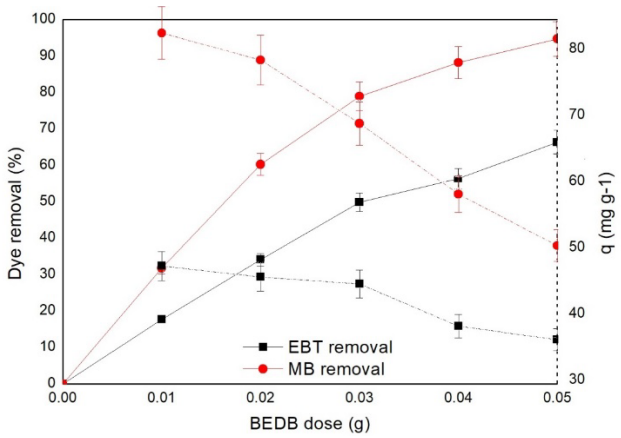

Figure 6 Effect of BEBD dose on EBT and MB removal.

7) Adsorption isotherm

Langmuir and Frendlich isotherm models were used to study the removal efficiency of the BDFB for EBT and MB dyes from aqueous solution. Langmuir adsorption model determines a monolayer capacity of adsorption qm (mg g^{-1}). This model is given by the Eq. 4.

$$\frac{Ce}{qe} = \frac{1}{q_m K_l} + \frac{Ce}{qm} \qquad \text{(Eq. 4)}$$

Where, C_e is the equilibrium concentration, q_m is the maximum monolayer adsorption capacity (mg g^{-1}), q_e is equilibrium adsorption (mg g^{-1}) and K_L is Langmuir coefficient.

Freundlich adsorption isotherm model was used to evaluate the adsorption capacity by assuming the heterogeneous surface. The Eq. 5 below gives the Freundlich model:

$$q_e = K_F\, Ce^{n^{-1}} \qquad \text{(Eq. 5)}$$

Where, KF is Freundlich coefficient, Ce is equilibrium concentration and n^{-1} is the adsorption intensity.

Figures 7(a), and 7(b) illustrate a plot of C_e qe^{-1} versus Ce to evaluate a monolayer capacity adsorption of Langmuir isotherm. This plot is linear. The values of q_m and K_L were calculated from the slope and the intercept of this graph with Ce qe^{-1}, which was compared with the experimental values. The results of the Langmuir isotherm are outlined in Table 1. The regression coefficients R^2 are 0.97 and 0.99 for BET and MB dye, respectively. The Langmuir results demonstrate that the distribution of active sites on the BEBD surface is homogeny, and the adsorption of EBT and MB dyes onto the BEDB sorbent is a monolayer. The KL value obtained from Langmuir data was 0,158 for BET and 0.925 for MB dye, (between 0 and 1). This figure reveals that the adsorption of BET and MB onto the BEDB is favorable [30]. The monolayer adsorption capacity of the BEBD was found 58.47 and 80.64 mg g^{-1} for EBT and MB removal, respectively. The Langmuir isotherm is a good model to evaluate BET and MB removal by the BEDB.

The plot ln q_e versus ln C_e shown in Figures 7(c) and 7(d) illustrates Freundlich isotherm. KF and R^2 values were determined based on the slope and the intercept of this graph. From the straight plot of Freundlich model, the correction coefficient Value R^2 was found 0.86 and 0.98 for EBT and MB adsorption, respectively as show in Table 1. These values indicate that the adsorption of MB dye is also multilayer and it was better fitted by the Freundlich model compared to EBT sorption with the same model. The n values of EBT adsorption is 2.96, while that of MB adsorption is 3.96 (between 1 and 10), which indicates that both adsorption dyes onto the BEBD sorbent are favorable. This can

be explained by increased heterogeneity of the BEDB with the increase of n values [31]. Both Langmuir and Freundlich models are the right models to study the adsorption of MB dyes from aqueous solution by BEDB adsorbent. However, for EBT sorption, the Freundlich model is not well fitted with experimental data.

The present adsorbent has a performance capacity to remove EBT and MB dyes from aqueous solution compared to other previous studies in the literature. Previous studies used biomass adsorbents for EBT removal as Peanut shell (40.81 mg g^{-1}) [32], sawdust (40.69 mg g^{-1}) [33] and Polyvinyl Alcohol/Starch/ZSM 5 Zeolite Membrane (16 mg g^{-1}) [34]. Also, many adsorbents from waste agriculture were used For MB removals, such as olive stones (107.4 mg g^{-1}) [35], Apricot Stone Activated Carbon (88.50 mg g^{-1}) [36], and biochar derived from menthe plant (86.96 mg g^{-1}) [9].

8) Kinetic study

Pseudo first/second-order equations were used in these investigations to study the kinetic of EBT and MB adsorption onto the BEDB. These isotherms present a relation between the number of available active sites of the absorbent and the adsorption rate [37]. Eq. 6 and Eq. 7 present pseudo-first and pseudo-second-order, respectively.

$$ln\,(q_e - q_t) = -\frac{K_1}{2{,}303}\,t + ln\,q_e \qquad \text{(Eq. 6)}$$

$$\frac{t}{q_t} = \frac{1}{q_e}\,t + \frac{1}{K_2 q_e^2} \qquad \text{(Eq. 7)}$$

Where, q_e and t: amount of dye eliminate at equilibrium and t (mg g^{-1}) t: time (min), K_1 and K_2: pseudo first and pseudo second order coefficient (min^{-1}), (g mg^{-1} min^{-1})

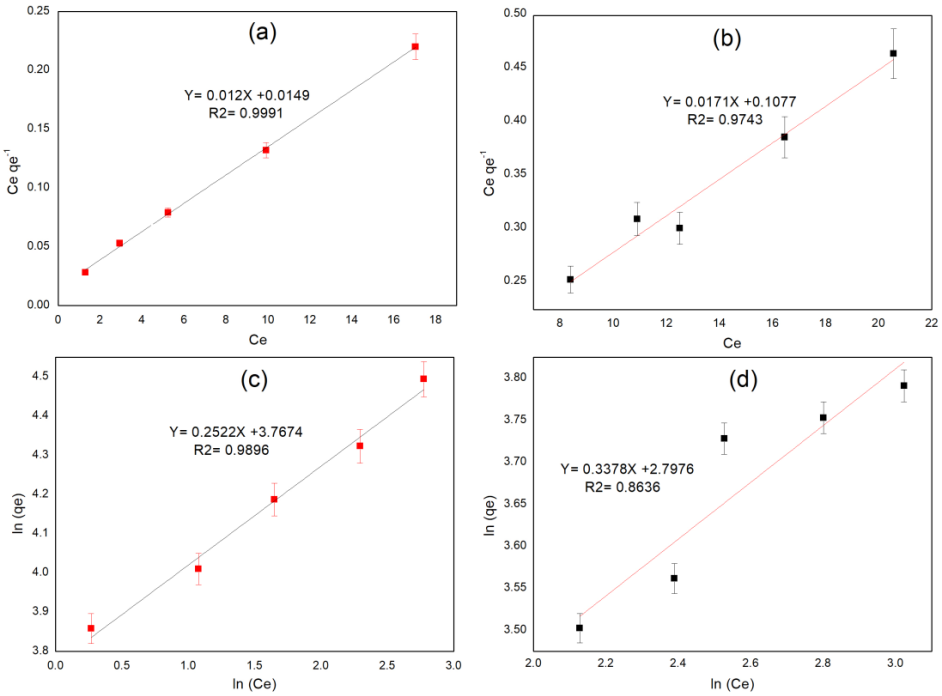

Figure 7 Graphs of (a), (c) Langmuir isotherm for MB adsorption /(b), (d) Freunlich for EBT adsorption.

Table 1 Langmuir and Freundlich parameters for EBT and MB removal onto BEDB

	Langmuir			Freundlich		
	q_m	K_L	R^2	K_F	n	R^2
EBT	58.47	0.158	0.9744	16.41	2.96	0.8636
MB	80.64	0.925	0.9986	43.26	3.96	0.9896

Figure 8 illustrates data from EBT and MB sorption for both kinetic models. The experiment parameters of EBT and MB adsorption onto the BEDB were obtained from the plots ln (q_e-q_t) versus t and t q_t^{-1} versus t of pseudo-first and pseudo-second-order, respectively. The results of these models are represented in Table 2. According to the parameters calculated, Pseudo second order is the better model to demonstrate the adsorption of EBT and MB dyes on BEBD sorbent, that is due to the R^2 values approach 1 (0.95 for EBT and 0.999 for MB). Also, the agreement between the experimental and the calculated values of maximum adsorption capacity approves this pseudo-second-order model, which can be considered to be the best model to study the adsorption of EBT and MB from aqueous solution by BEDB [38]. However, the pseudo-first-order model has R^2 values inferior to 1 for EBT and MB adsorption. Although, q_{exp} and q_{cal} values are different for both pollutants. Therefore, this model is not adequate to present EBT and MB adsorption onto BEBD sorbent.

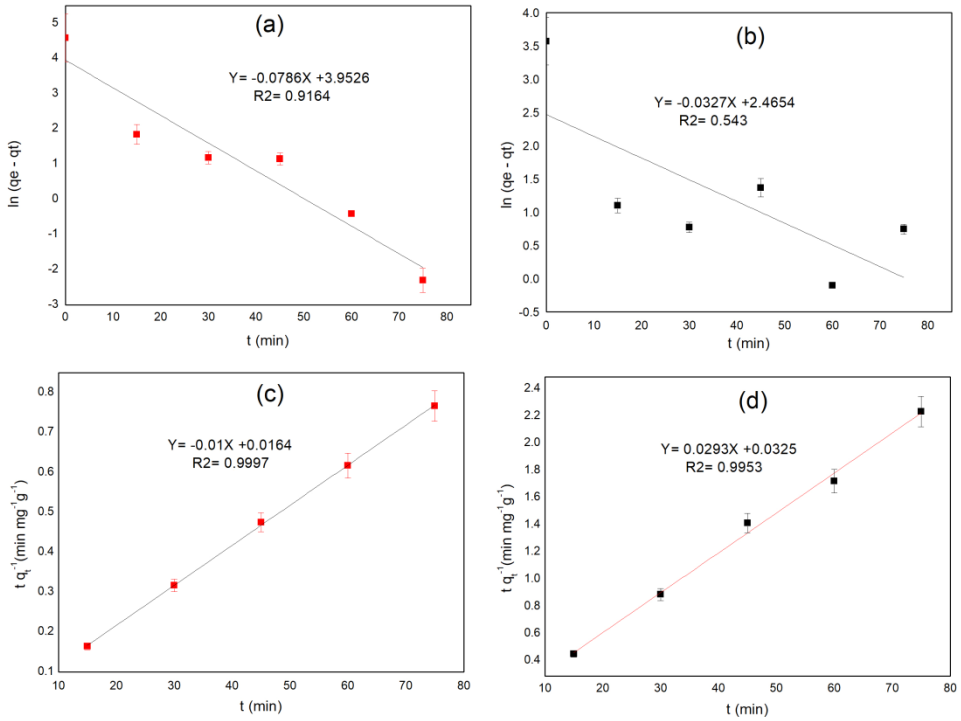

Figure 8 Graphs of (a), (c) Pseudo-first order kinetic for MB adsorption and (b), (d) Pseudo-second order kinetic for EBT adsorption.

Table 2 Pseudo-first and second order kinetic parameters for EBT and MB removal onto BEDB

		Pseudo-first-order			**Pseudo-Second-order**		
	q_{exp}	q_{cal}	K_1	R^2	q_{cal}	K_2	R^2
EBT	34.60	11.77	0.075	0.543	34.13	0.0264	0.95
MB	97.88	52.7	0.181	0.916	99.98	0.0061	0.999

Conclusion

The BEDB was used to remove EBT and MB from aqueous solution. This study has varied parameters in batch adsorption. The percentage of EBT and MB dyes eliminated were increased with a high contact time, BEDB dose, and initial dyes concentration. The maximum monolayer adsorption capacity of EBT and MB were found at 58.47 and 80.64 mg g^{-1}, respectively. Langmuir isotherm is a good model to fit the adsorption of

EBT and MB onto the BEDB sorbent. The kinetic data has followed the pseudo-second-order model. This new biochar from date bunch waste is an effective material to remove dyes from aqueous solution, due to its functional groups, porous structure, and high carbon content. BEDB is considered a bio adsorbent, low cost, and friendly for the environment.

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