Kinetic and Thermodynamic Studies for the Efficient Removal of Methylene Blue Using Hordeum Murinum as a New Biosorbent

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In this work, Hordeum murinum as a sustainable and cost-effective biosorbent material is utilized without any further treatment to remove Methylene blue dye from aqueous solutions. The effects of various parameters including pH, biosorbent amount, reaction time, initial concentration, and temperature are investigated. The results show that 94% of Methylene blue is removed using the optimal adsorption conditions of pH 5.6, biosorbent dose of 0.1 gm, 60 min equilibrium contact time, 20 mg/L of initial dye concentration at a temperature of 25°C. Experimental results reveal that the adsorption kinetics can have the best description by employing the pseudo-second order model. The spontaneous and exothermic nature of the adsorption process is indicated by the negative values of the Gibbs free energy change and the enthalpy change, respectively. These results reveal that Hordeum murinum exhibited excellent performance for the removal of Methylene blue from aqueous solutions, which can make it very interesting as an alternative and effective low-cost biosorbent material.

Keywords: Methylene blue, Hordeum murinum, Adsorption.
most widely used in dyes removal, however, the economic issue is the most important concern in the industrial applications limits its commercial utilization [5, 20].

Recently, many researchers use agricultural waste materials as alternative and cost-effective adsorbents [21]. Different biosorbent materials including, tea waste [22], rice husk [23], pumpkin seed hull [24], fruitpeel [25-27], coconut [28], Viscose waste [29], Artist’s Bracket fungi [30, 31], nut shells [32] and sawdust [33] have been utilized for the removal of MB from aqueous solutions.

Hordeum murinum (H. murinum) also called false barley or wall barley, is considered as one of the common undesirable annual weeds that grow naturally in different regions in the world [34,35]. Due to its abundant availability, H. murinum can be an effective alternative source as a natural and renewable biosorbent material. As far as we know, there is no research has studied the adsorption of MB using H. murinum. This paper aims to study the ability of H. murinum as a new, efficient and economic biosorbent for the effective removal of MB from aqueous solutions.

**Materials and Methods**

**Materials**

Methylene blue purchased from Fluka and used as received without further purification. H. murinum was collected from the local area around Tikrit city in Iraq. It was washed several times using distilled water and dried in the oven for 48 hr. at 95 °C. It was crushed using food grinder and sieved to obtain particles with a size less than 100 µm.

**Material Characterization**

The surface morphology of the biosorbent material is characterized using field emission scanning electron microscopy (FESEM). UV–Visible Spectrophotometer (UV-1800, Shimadzu) is used for MB absorbance measurements. pH measurement is performed using (WTW pH 7310). Controlled shaking water bath (GFL, Germany) is employed for better agitating performance. To isolate the biosorbent from the solution (Gallenkamp centrifuge, England) is utilized in this study.

**Adsorption Experiments**

A stock solution of MB dye with a concentration of 500 mg/L is prepared by dissolving MB in deionized water and used ifurther to get therequired dye concentrations. Batch adsorption experiments are conducted in 100 ml conical flask with 20 ml of MB solution. The effects of the different parameters such as the pH (2-11), contact time (5-100 min), biosorbent amount (0.01-2.0 g), initial dye concentration (5-100 mg/L) and temperature (25, 35, and 45°C) on the adsorption of MB on H. murinum are investigated. Each solution is shaken using a controlled shaking water bath at 120 rpm. After adsorption, the solutions are centrifuged at 3000 rpm for 10 min to obtain the supernatant that contains the residual MB concentration in order to monitor its absorbance at 663 nm. Each experiment is triplicate and the presented results represent the average of these experiments.

The removal efficiencies (%), and the quantity of MB adsorbed on H. murinum surface at equilibrium \( q_e \) (mg/g) and at time \( t \) \( (q_t \) (mg/g)) are obtained using the following equations:

\[
\%\text{Removal} = \frac{(C_0 - C_e)}{C_0} \times 100
\]

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

Where, \( C_e \) (mg/L), is the initial dye concentration, \( C_0 \) and \( C_t \) (mg/L) are the dye concentration after equilibrium and after time \( t \), respectively. \( V \) (L) is the volume of the dye solution, and \( m \) (g) is the mass of the biosorbent.

**Results and Discussion**

**Characterization of H. murinum**

To characterize H. murinum, FESEM analysis is employed in this study. The FESEM images for the surface morphology of H. murinum is shown in Fig. 1. It can be clearly observed non-uniform shapes with less than 100 µm particle sizes (Fig. 1 (a)). Moreover, the high resolution FESEM image for the biosorbent shows unsmooth and rough surface with grooves, which can give more surface area to allow more contact between biosorbent and sorbate (Fig. 1 (b)).
Effect of pH on the Removal of MB on H. murinum

The pH of a solution is a significant factor that affects the adsorption of dye onto the adsorbent. The effect of pH is examined between 2.0 - 11.0 using initial dye concentration of 20 mg/L, 0.1 g of H. murinum, 60 min contact time at a temperature of 25 °C. The pH of dye solutions was adjusted to appropriate value using solutions of 0.1 M HCl or NaOH. The effect of pH on MB removal onto H. murinum is presented in Fig. 2. A minimum adsorption value of about 43% is observed at low pH of 2.0, and as the pH increased to 5.0, the MB dye removal increased to 92%. Further increase of the pH does not affect the dye removal and it remained nearly constant within the pH ranges 5.0 to 9.0 (pH 5.6 is found to be the normal pH value of MB dye solution used in this study). In addition, a slightly decreased of the dye uptake is observed at higher pH values. Similar behavior is observed for the variation of the pH as a function of the dye adsorption capacity \(q_e\) as seen in Fig. 2.

This can be explained from knowing that dissolving cationic dye in water would provide ions with a positive charge. Thus, in low pH medium, the surface of the biosorbent becomes more positively charged, and this will decrease the attraction between the cationic dye and biosorbent [27]. On the other hand, as the pH increases, the biosorbent surface becomes more negatively charged, which allow a strong electrostatic attraction between negatively charged biosorbent and positively charged dye to take place, resulted in a greater MB dye removal [10]. Further increase of the pH after 9 can be attributed to the sensible degradation of the investigated biosorbent material by a strong alkaline solution [20].

Effect of Contact Time on the Removal of MB on H. murinum

The effect of contact time on the removal of MB onto H. murinum is displayed in Fig. 3. It was investigated by using a normal pH of 5.6, initial dye concentration of 20 mg/L, 0.1 g of H. murinum at a temperature of 25 °C. Fast uptake of MB dye by H. murinum biosorbent can be seen in the first few minutes indicating a high affinity between the dye and the biosorbent surface, which attributes to the presence of a large number of vacant adsorption sites on the biosorbent surfaces. As time increases, a gradual increase is observed, and the adsorption rate becomes slower due to the decrease in the number of adsorption sites. After 60 minutes, the removal process remains constant, and no further dye uptake can occur, which reveals that equilibrium is reached at about 60 minutes. This may occur as a result of the decrease of the vacant adsorption sites, and after equilibrium, the residual sites are difficult to occupy because of the resistance between the dye particles on the surface of the biosorbent and the incoming dye particles [36].
Effect of H. murinum Amount on the Removal of MB

The adsorbent amount is an important affecting factor for the adsorption behavior of MB onto H. murinum. The variation of the biosorbent dosage as a function of dye removal efficiency has been studied with normal pH solution of 5.6, using initial dye concentration of 20 mg/L, 60 min contact time at a temperature of 25 °C. Figure 4 displays the influence of the H. murinum amount on the removal of MB. The adsorption efficiency of MB dye increases from about 52% to 94% with an increase in the amount of H. murinum from 0.01 to 0.1 g. It is more likely that utilizing a small amount of the biosorbent can adsorb a small amount of the dye, which can be related to the available number of adsorption sites on the H. murinum surface. Increasing the biosorbent amount can provide more adsorption sites to adsorb more dye particles, which leads to a greater increase in the removal percentage [37]. After that, no significant change in adsorption percentage is observed during increasing the biosorbent amount, which can contribute to attaining the equilibrium state. This indicates that 0.1 g can be considered the optimal amount for H. murinum loading. It can also be seen that the adsorption capacity for a given fixed dye concentration is highly dependent on the biosorbent amount. A decrease in the adsorption capacity is observed from 26.2 to 2.3 mg/g with the increase of H. murinum amount from 0.01 to 0.2 g, which can be referred to the ratio of a certain initial number

Fig. 2. Effect of the pH on the removal of Methylene blue on H. murinum.

Fig. 3. Effect of the contact time on the removal of Methylene blue on H. murinum.
of dye molecules exist in the solution to the free adsorption active sites on the adsorbent surface. As the adsorbent dosage increases, the number of available adsorption active sites increases. This result in a decrease in the adsorption capacity attributed to the available adsorption active sites remain unsaturated within the removal process as reported earlier [38, 39].

Effect of Initial Concentration on the Removal of MB on H. murinum
The effect of initial dye concentration on the removal efficiency of MB on H. murinum can be illustrated in Fig. 5. It was investigated using different dye concentrations ranging from 5.0 – 100.0 mg/L, 0.1 g of H. murinum, 60 min contact time at a temperature of 25 °C. It can be clearly observed a low percentage removal of about 89% with low dye concentration, and as the dye concentration increases, the uptake level increases to reach its maximum value of 94% at a concentration of 20 mg/L. Thus, the dye concentration of 20 mg/L found to be the optimal concentration for MB removal by H. murinum biosorbent. Further increase in MB concentration would reduce the removal efficiency due to the decline of available adsorption sites required for the removal of dye [40, 41]. While, the adsorption capacity of MB increased from 1.1 to 21.2 mg/g as the initial concentration increased from 5 to 100 mg/L, which can be related to the driving force resulted from the concentration gradient at higher dye concentration [42].

![Fig. 4. Effect of the H. murinum amount on the removal of Methylene blue.](image-url)

![Fig. 5. Effect of the initial concentration on the removal of Methylene blue on H. murinum.](image-url)
Kinetic Study

In order to understand the removal mechanism of the dye molecules migration through the bulk solution to the biosorbent surface, the rate of the adsorption process is analyzed by fitting the results using two modules, the pseudo-first order model and pseudo-second order model, represented by Eqs 4 and 5, respectively:

\[
\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right) t
\]

(4)

\[
t/q_t = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t
\]

(5)

Where \(q_e\) and \(q_t\) (mg/g) are the adsorption capacity at equilibrium and at time \(t\), respectively, \(k_1\) is the pseudo-first order rate constant (1/min) and \(k_2\) is the pseudo-second order rate constant (g/(mg.min)).

The kinetic parameters for the removal of the MB dye onto H. murinum surface acquired from fitting the kinetic models on the experimental data are shown in Table 1. It can clearly be observed that the adsorption capacities (\(q_e\)) have a better fit between the experimental and the calculated values by applying the pseudo-second order model. In addition, the pseudo-second order model shows a higher correlation coefficient (\(R^2\)) in comparison to the pseudo-first order model. Based on these results, it emphasizes that the removal process follows the pseudo-second order kinetics.

Effect of Temperature on the Removal of MB on H. murinum and the Thermodynamic Study

The effect of the temperature is also investigated. Fig. 6 (a) displays the relationship between the removal efficiency of MB dye with H. murinum amount using three different temperatures 25, 35, 45 °C, normal pH solution of 5.6, initial dye concentration of 20 mg/L and 60 min contact time. At low biosorbent amount 0.01 g, a low adsorption efficiency is observed, and as the temperature increases from 25 to 45 °C, the uptake level decreases from 52 to 36%. Rising the temperature might have the ability to break the intermolecular forces between dye molecules and H. murinum, and this would increase the tendency of dye molecules to escape from biosorbent particles to the bulk solution [43]. Thus, resulted in reducing the dye uptake level. The results suggest that the removal of MB on H. murinum is an exothermic process, and increasing the temperature would decrease the removal efficiency. In spite of changing the temperature, the three cases show similar behavior of adsorption efficiency rising with increasing the biosorbent dosage that refers to the availability of more active adsorption sites as mentioned earlier in section 3.4.

On the other hand, it can be seen that the adsorption capacity \(q_e\) decreases as the temperature increases at the low biosorbent amount (Fig. 6 (b)). Increasing the temperature for a biosorbent dosage of 0.01 g displays a clear decrease in the capacity from 26.2 to 18.0 mg/g. At higher biosorbent dosage between 0.07–0.2 g, rising the temperature does not show any significant change, and constant adsorption capacity is observed for each certain biosorbent amount resulted from the increase of the accessible adsorption sites acquired from the added biosorbent. These active sites may provide more attraction force with the dye particles, which can make the release of the dye molecules from the adsorbent surface to the bulk solution more difficult.

In order to obtain the main thermodynamic factors for the adsorption of MB dye onto H. murinum, the analysis of the previous experimental data using three different temperatures 25, 35, 45 °C is carried out. These factors including \(\Delta H^0\) the enthalpy change (J/mol), \(\Delta S^0\) the entropy change (J/mol K), and \(\Delta G^0\) the Gibbs free energy change (J/mol), can be calculated using the following equations:

| TABLE 1. Kinetic parameters for the adsorption of MB onto H. murinum surface. |
|-----------------|-----------------|
| **Pseudo-first order model** | **Pseudo-second order model** | **q_e exp. (mg/g)** |
| **k_1** (min⁻¹) | **R²** | **q_e cal. (mg/g)** | **k_2 (g.mg⁻¹.min⁻¹)** | **R²** | **q_e cal. (mg/g)** |
| 0.08359 | 0.9867 | 1.03 | 0.22163 | 1.0 | 4.72 | 4.669 |

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Where, \( R \) is the gas constant (8.314 J/mol K), \( T \) is the absolute temperature (K), \( K \) is the equilibrium constant of the adsorption process, and can be calculated using the equation below:

\[
\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{6}
\]

\[
\Delta G^o = -RT \ln K \tag{7}
\]

Fig. 6. Effect of the temperature on the (a) removal efficiency, (b) removal capacity of Methylene blue on \( H. \) murinum.

\[
K = \frac{(C_0 - C_e)}{C_e} \tag{8}
\]

\( \Delta S^o \) and \( \Delta H^o \) values are determined from the intercept and slope of the straight line of the plot between \( \ln K \) versus \( 1/T \). While \( \Delta G^o \) values are calculated using Eq. 7. The calculated thermodynamic parameters are presented in Table 2.

The negative values of the enthalpy change \( \Delta H^o \) suggest that the removal process of MB dye onto \( H. \) murinum surfaces is exothermic. The obtained values are between (-11556.5) and (-26313.8) J/mol, which is within the range of physical nature of the adsorption process [32]. The positive values of entropy change \( \Delta S^o \) indicate increasing randomness at the solid-solution interface through the removal process. Moreover, the negative values of the Gibbs free

energy change $\Delta G^\circ$ indicates the spontaneous nature of the removal process. In addition, it can be observed from Table 2 that raising the temperature leads to increasing the $\Delta G^\circ$ values, which reveals that the adsorption process is less favorable at the higher temperature [28].

Conclusions

The amount of methylene blue dye adsorbed on the Hordeum murinum surface is found to vary with the variation of the adsorption factors used in this study. The optimal operating values of these factors are found to be: solution pH 5.6, a biosorbent amount 0.1 g, equilibrium contact time 60 min., initial dye concentration 20 mg/L, and a temperature of 25°C. In addition, the kinetic modeling for the adsorption process is found to provide a better fit for the resulted data by applying the pseudo-second order model with a higher correlation coefficient value. Moreover, the thermodynamic parameters confirm the spontaneous and exothermic nature of the adsorption process. The results of the present study indicate that Hordeum murinum can be employed as a new, non-conventional and cost-effective natural biosorbent material for the removal of methylene blue from aqueous solutions.

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