Egypt. J. Chem. **Vol. 63,** No. 9, pp. 3381 - 3390 (2020)

Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

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

S. M. Al-Mahmoud
Department of Chemistry, College of Education for Women, Tikrit University, Tikrit, Iraq.

IN THIS work, Hordeum murinum as a sustainable and cost-effective biosorbent material isutilized 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 temperatureareinvestigated. The results show that 94% of Methylene blueisremoved 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 isindicated 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.

Introduction

Water pollution isoneofthe largest problemsfacing the worldin recent years [1]. Discharging wastewater from industrial and agricultural activities without suitable treatment is the main source of water pollution [2]. Wastewater contains different contaminations. Dyes are the major type of contaminants thatarereleased from various industrial processes, for instance, manufacturing of textiles, paper, cosmetics and plastics [3, 4]. It has a complex chemical structure that makes it resist the biological degradation, which can harm the environment and cause hazardous damage to the aquatic life [5, 6].

Methylene blue (MB) is a water-soluble dye having a good adsorption efficiency onto solid surfaces [7]. Itis a cationic dye thathad been widelyused in the medical field for treatment of some diseases such as psoriasis, and commonly used in analytical chemistry as a redox indicator [8]. Itis considered one of the most important dyes that extensively employed in textile industries [9]. Despite its various applications, MB can cause many health problems to human beings such as anemia, vomiting, nausea [10, 11]. Therefore, using a proper treatment method can be a significant issue for the removal of MB from wastewater.

Various treatment techniques have been used to remove methylene blue dye such as adsorption [12],photocatalysis [13], coagulation/flocculation [14], Fenton [15], and ultrafiltration [16]. Among these treatment processes, adsorption is a very effective treatment methodthat has been widely used for the removal of contaminants from wastewater due to its cost, simplicity, and ease of operation [17-19]. Variety of adsorbent materials areused for wastewater treatment.Adsorption using activated carbon is highly effective and the

*Corresponding author e-mail: s_almahmoud@tu.edu.iq
Received 19/8/2020; Accepted 29/4/2020
DOI: 10.21608/ejchem.2020.16008.1970

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 analternative 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,isconsidered as one of the common undesirable annual weeds that grow naturally in different regions in the world [34,35]. Due to itsabundant 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 ischaracterized using field emission scanning electron microscopy (FESEM). UV–Visible Spectrophotometer (UV-1800, Shimadzu) isused for MB absorbance measurements. pH measurement isperformed using (WTW pH 7310). Controlled shaking water bath (GFL, Germany) isemployed for better agitating performance. To isolate the biosorbent from the solution (Gallenkamp centrifuge, England)isutilized in this study.

Adsorption Experiments

A stock solution of MB dye with a concentration of 500 mg/Lisprepared by dissolving MB in deionized water and used itfurther to get therequired dye concentrations. Batch adsorption experiments areconductedin 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 areinvestigated. Each solution isshaken using a controlled shaking water bath at 120 rpm. After adsorption, the solutionsarecentrifuged at 3000 rpm for 10 min to obtain the supernatant that contains the residual MB concentrationin order to monitor its absorbance at 663 nm. Each experiment istriplicate 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)) areobtained using the following equations:

$$\% \, Removal = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

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

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (3)$$

Where, C_0(mg/L), is the initial dye concentration, C_e and C_t (mg/L) are the dye concentration after equilibriumand 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 isemployed in this study. The FESEM images for the surface morphology of H. murinum is shown in Fig. 1. It can be clearly observednon-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 allowmore contact between biosorbent and sorbate (Fig. 1 (b)).

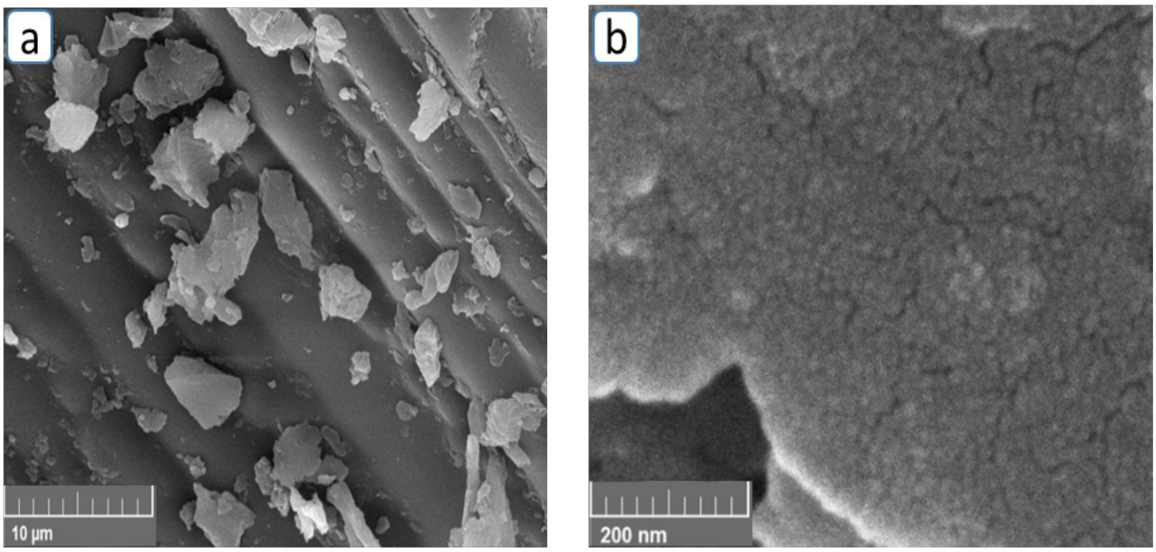

Fig. 1. FESEM images of H. murinum biosorbent material.

Effect of pH on theRemoval 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 isexamined 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. murinumispresented in Fig. 2. Aminimum adsorption value of about 43% isobserved at low pH of 2.0, and as the pH increased to 5.0, the MB dye removal isalso increased to 92%. Further increase of the pH doesnot affect the dye removaland 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 uptakeisobservedat higher pH values.Similar behavior isobserved 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 sensibledegradation 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 wasinvestigatedbyusing a normal pH of 5.6, initial dye concentration of 20 mg/L, 0.1 g of H. murinumat 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 isobserved, and the adsorptionrate 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 isreached 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].

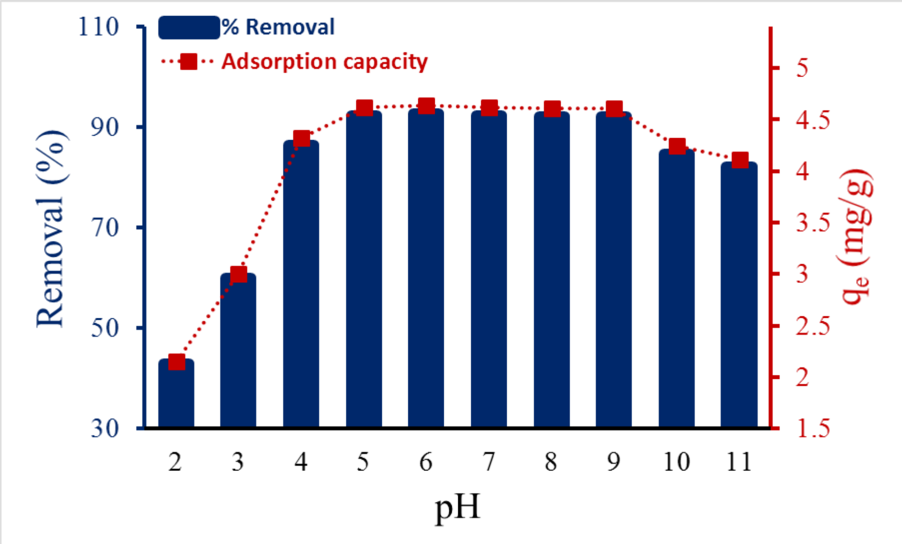

Fig. 2. Effect of the pH on the removal of Methylene blue on H. murinum.

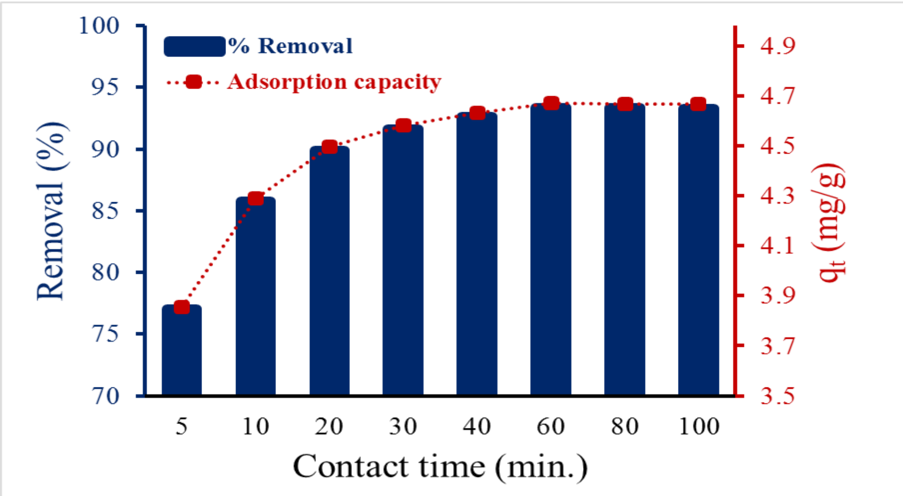

Fig. 3. Effect of the contact time on the removal of Methylene blue on H. murinum.

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 studiedwith 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. murinumamounton the removal of MB.The adsorption efficiency of MB dye increases from about 52% to 94% with an increase in the amountof 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 isobserved during increasing the biosorbent amount, which can contribute to attaining the equilibrium state. This indicates that 0.1 g canbe considered the optimal amount for H. murinum loading. It can also be seen that the adsorption capacity for a given fixed dye concentrationis 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 of dye molecules exist in the solutionto 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 theavailable 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. murinumcan 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 observeda lowpercentage removal of about 89 % with low dye concentration, and as the dye concentration increases, the uptake level increasesto 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].

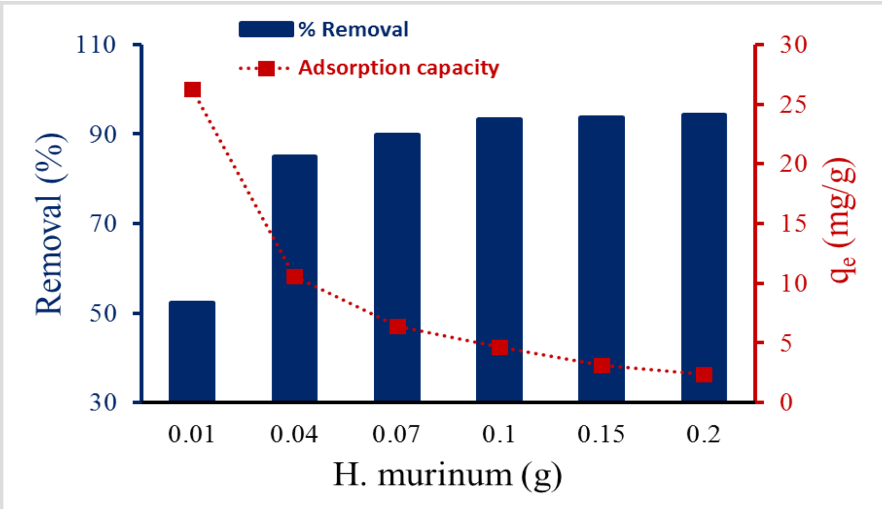

Fig. 4. Effect of the H. murinum amount on the removal of Methylene blue.

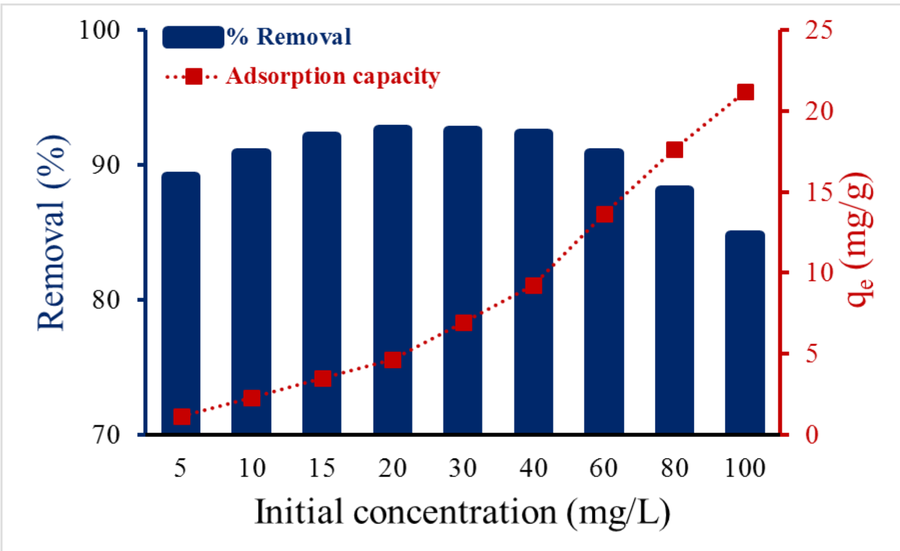

Fig. 5. Effect of the initial concentration on the removal of Methylene blue on H. murinum.

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 isanalyzedby fitting the results using two modules, the pseudo-first order model and pseudo-second order model, represented by Eqs 4 and 5, respectively :

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)\,t \quad (4)$$

$$t/q_t = (1/k_2\, q_e^2) + (1/q_e)\,t \quad (5)$$

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 isalso 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 isobserved, 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 efficiencyrising 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 beseen 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 doesnot show any significant change, and constant adsorption capacity isobserved 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 ΔH° the enthalpy change (J/mol), ΔS° the entropy change (J/mol K), and ΔG° 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. murinumsurface.

Pseudo-first order model			Pseudo-second order model			q_e exp. (mg/g)
k_1 (min^{-1})	R^2	q_e cal. (mg/g)	k_2 (g.mg^{-1}. min^{-1})	R^2	q_e cal. (mg/g)	
0.08359	0.9867	1.03	0.22163	1.0	4.72	4.669

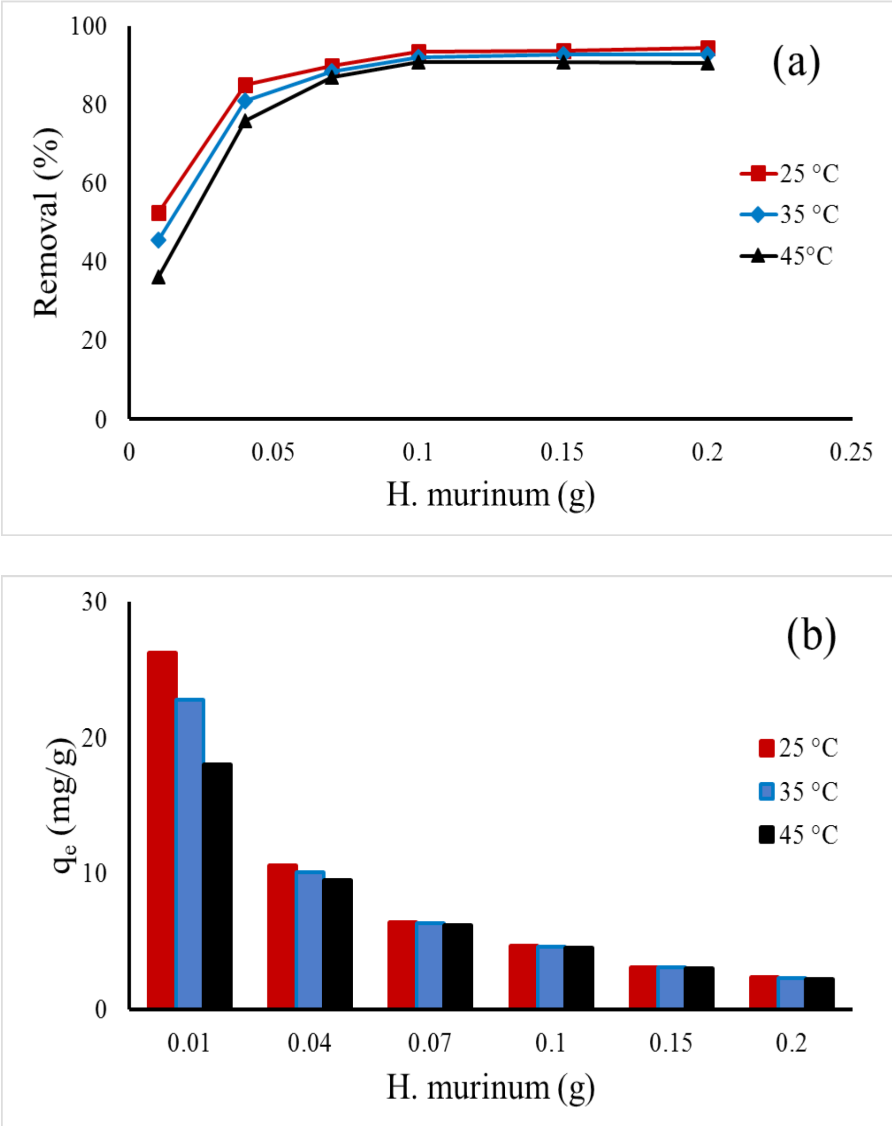

Fig. 6. Effect of the temperature on the (a) removal efficiency, (b) removal capacity of Methylene blue on H. murinum.

$$\ln K = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad (6)$$

$$\Delta G° = -RT \ln K \quad (7)$$

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

$$K = \frac{(C_0 - C_e)}{C_e} \quad (8)$$

ΔS° and ΔH° values aredetermined from the intercept and slope of the straight line of the plot between ln K versus 1/T. While ΔG° values arecalculated using Eq. 7. The calculated thermodynamic parameters are presented in Table 2.

The negative values of the enthalpy change ΔH° suggest that the removal process of MB dye onto H. murinum surfaceis exothermic. Theobtainedvalues 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 ΔS° indicate increasing randomness at the solid-solution interface through the removal process. Moreover,the negative values of the Gibbs free

TABLE 2. Thermodynamic parameters for the adsorption of MB onto H. murinum surface at different temperatures.

Biosorbent (g)	ΔH° *(J/mol)*	ΔS° *(J/mol^{-1}. K)*	ΔG° *(J/mol)*			R^2
			298 °K	308 °K	318 °K	
0.01	-26313.8	87.29	-243.23	456.30	1510.45	0.986
0.04	-22920.0	62.48	-4285.84	-3701.26	-3034.31	0.999
0.07	-11556.5	20.61	-5409.03	-5215.31	-4996.16	0.999
0.1	-14586.9	26.96	-6562.29	-6256.95	-6024.54	0.998
0.15	-16490.0	32.82	-6668.51	-6464.87	-6006.49	0.981
0.2	-21242.3	47.92	-6933.04	-6541.16	-5970.68	0.994

energy change ΔG° indicatethe spontaneous nature of the removal process.In addition, it can be observedfrom table 2 that raising the temperature leads to increasing the ΔG° values,whichreveals thatthe adsorption process is less favorable at the higher temperature [28].

Conclusions

The amount of methylene blue dye adsorbed on the Hordeum murinum surfaceisfound to vary with the variation of the adsorption factorsused in thisstudy. The optimal operating values of these factorsarefound to beat solution pH 5.6, a biosorbent amount 0.1gm, equilibrium contact time 60 min., initial dyeconcentration 20mg/L, and a temperature of 25°C. In addition, the kinetic modeling for the adsorption process is found to provide a better fitfor the resulted data by applyingthe pseudo-second order model with a higher correlation coefficient value. Moreover, the thermodynamic parameters confirmthe 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 effecting natural biosorbent material for the removal of methylene blue from aqueous solutions.

References

1. Mittal A., Thakur V., Mittal J., Vardhan H., Process development for the removal of hazardous anionic azo dye Congo red from wastewater by using hen feather as potential adsorbent, *Desalination and Water Treatment*, **52**, 227–237 (2014).
2. Babu S.A., Raja S., Sibi S., Neeraja P., Electrochemical oxidation of textile polluted water and its reuse, *Journal of Industrial Pollution Control,* **28**, 73–82(2012).
3. Hor K.Y., Chee J.M.C., Chong M.N., Jin B., Saint C., Poh P.E., Aryal R., Evaluation of physicochemical methods in enhancing the adsorption performance of natural zeolite as low-cost adsorbent of methylene blue dye from wastewater, *Journal of Cleaner Production,* **118**, 197–209 (2016).
4. Kharat D.S., Preparing agricultural residue based adsorbents for removal of dyes from effluents - a review, *Brazilian Journal of Chemical Engineering,* **32**, 1–12 (2015).
5. Wang H., Xie R., Zhang J., Zhao J., Preparation and characterization of distillers' grain based activated carbon as low cost methylene blue adsorbent: Mass transfer and equilibrium modeling, *Advanced Powder Technol*ogy,**29**, 27–35 (2018).
6. Bhattacharyya K.G., Sharma A., Azadirachtaindica leaf powder as an effective biosorbent for dyes : a case study with aqueous Congo Red solutions, *Journal of Environmental Management*, **71**, 217–229 (2004).
7. Hameed B.H., Spent tea leaves: A new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions, *Journal of Hazardous Materials,* **161**, 753–759 (2009).
8. Rangabhashiyam S., Lata S., Balasubramanian P., Biosorption characteristics of methylene blue and malachite green from simulated wastewater onto Carica papaya wood biosorbent, *Surfaces and*

Interfaces, **10**, 197–215 (2017).

9. Mouni L., Belkhiri L., Bollinger J.-C., Bouzaza A., Assadi A., Tirri A., Dahmoune F., Madani K., Remini H., Removal of Methylene Blue from aqueous solutions by adsorption on Kaolin: Kinetic and equilibrium studies, *Applied Clay Science,***153**, 38–45 (2018).

10. Pathania D., Sharma S., Singh P., Removal of methylene blue by adsorption onto activated carbon developed from Ficuscaricabast, *Arabian Journal of Chemistry*,**10**, S1445–S1451(2017).

11. Nasuha N., Hameed B.H., Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea, *Chemical Engineering Journal*, **166**, 783–786(2011).

12. Hameed B.H., Din A.T.M., Ahmad A.L., Adsorption of methylene blue onto bamboo-based activated carbon: Kinetics and equilibrium studies, *Journal of Hazardous Materials*, **141**, 819-825 (2007).

13. Rauf M.A., Meetani M.A., Khaleel A., Ahmed A., Photocatalytic degradation of Methylene Blue using a mixed catalyst and product analysis by LC/MS, *Chemical Engineering Journal*, **157**, 373–378 (2010).

14. Liang C., Sun S., Li F., Ong Y., Chung T., Treatment of highly concentrated wastewater containing multiple synthetic dyes by a combined process of coagulation/flocculation and nanofiltration, *Journal of Membrane Science,***469**, 306–315 (2014).

15. Dutta K., Mukhopadhyay S., Bhattacharjee S., Chaudhuri B., Chemical oxidation of methylene blue using a Fenton-like reaction, *Journal of Hazardous Materials,***84**, 57–71(2001).

16. Zheng L., Su Y., Wang L., Jiang Z., Adsorption and recovery of methylene blue from aqueous solution through ultrafiltration technique, *Separation and Purification Technology*, **68**, 244–249 (2009).

17. Kausar A., Iqbal M., Aftab K., Bhatti H., Nazli Z.-H., Bhatti H.N., Nouren S., Dyes adsorption using clay and modified clay: A review, *Journal of Molecular Liquids*, **256**, 395–407 (2018).

18. Pyrzynska K., Removal of cadmium from wastewaters with low-cost adsorbents, *Journal of Environmental Chemical Engineering,***7**, 102795 (2019).

19. Esrafili A., Bagheri S., Kermani M., Gholami M., Moslemzadeh M., Simultaneous adsorption of heavy metal ions (Cu2 + and Cd2 +) from aqueous solutions by magnetic silica nanoparticles (Fe3O4 @ SiO2) modified using Simultaneous adsorption of heavy metal ions (Cu 2 + and Cd 2 +) from aqueous solutions by magnetic si, *Desalination and Water Treatment*, **158**, 207–215 (2019).

20. Nayak A.K., Pal A., Rapid and high-performance adsorptive removal of hazardous acridine orange from aqueous environment using Abelmoschusesculentus seed powder: Single- and multi-parameter optimization studies, *Journal of Environmental Management*, **217**, 573–591 (2018).

21. Mohammed M.A., Shitu A., Ibrahim A., Removal of Methylene Blue Using Low Cost Adsorbent : A Review, *Research Journal of Chemical Sciences*,**4**, 91–102(2014).

22. Uddin T., Islam A., Mahmud S., Rukanuzzaman M., Adsorptive removal of methylene *blue by tea waste, Journal of Hazardous Materials,***164**, 53–60 (2009).

23. Vadivelan V., Kumar K.V., Equilibrium , kinetics , mechanism , and process design for the sorption of methylene blue onto rice husk, *Journal ofColloid and Interface Science,***286**, 90–100 (2005).

24. Hameed B.H., El-Khaiary M.I., Removal of basic dye from aqueous medium using a novel agricultural waste material: Pumpkin seed hull, *Journal of Hazardous Materials,* **155**, 601–609 (2008).

25. Amel K., Hassena M.A., Kerroum D., Isotherm and Kinetics Study of Biosorption of Cationic Dye onto Banana Peel, *Energy Procedia*, **19**, 286–295 (2012).

26. Hameed B.H., Krishni R.R., Sata S.A., A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solutions, *Journal of Hazardous Materials*, **162**, 305–311 (2009).

27. Hameed B.H., Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent, *Journal of Hazardous Materials,* **162**, 344–350 (2009).

28. Etim U.J., Umoren S.A., Eduok U.M., Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution, *Journal of Saudi Chemical Society,***20**, S67–S76 (2016).

29. Abdel Ghafar H., Salama M., Radwan E.K., Salem T., Recycling of pre-consumer viscose waste fibers for the removal of cationic dye from aqueous

solution, *Egyptian Journal of Chemistry*,**62**, 1457–1467(2019).

30. Naghipour D., Taghavi K., Moslemzadeh M., Removal of methylene blue from aqueous solution by Artist's Bracket fungi: kinetic and equilibrium studies, *Water Science and Technology*, **73**, 2832–2840 (2016).

31. Pourkarim S., Ostovar F., Mahdavianpour M., Moslemzadeh M., Adsorption of chromium (VI) from aqueous solution by Artist's Bracket fungi,*Separation Science and Technology,***52**, 1733–1741 (2017).

32. Modesto S., Brito D.O., Martins H., Andrade C., Frota L., Pires R., Azevedo D., Brazil nut shells as a new biosorbent to remove methylene blue and indigo carmine from aqueous solutions, *Journal of Hazardous Materials,***174**, 84–92 (2010).

33. Hameed B.H., Ahmad A.L., LatiffK.N., Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, *Dyes and Pigments*, **75**, 143–149 (2007).

34. Jakob S.S., Blattner F.R., Two extinct diploid progenitors were involved in allopolyploid formation in the Hordeummurinum(Poaceae : Triticeae) taxon complex,*Molecular Phylogenetics and Evolution*, **55**, 650–659 (2010).

35. Makarian H., MohasselM.H., Bannayan M., Nassiri M., Soil seed bank and seedling populations of Hordeummurinum and Cardariadraba in saffron fields,*Agriculture, Ecosystems and Environment*, **120**, 307–312 (2007).

36. Foya H., Mdoe J.E., Mkayula L.L., Adsorption of Maleic and Oxalic Acids on Activated Carbons Prepared from Tamarind Seeds, *International Journal of Engineering Research and Technology*,**3**, 1035–1042(2014).

37. Salleh M.A.M., Mahmoud D.K., Karim W.A., Idris A., Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review,*Desalination*, **280**, 1–13 (2011).

38. Aydin H., Bulut Y., Yerlikaya Ç., Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents, *Journal of Environmental Management,***87**,37–45 (2008).

39. Khobragade M.U., Pal A., Investigation on the adsorption of Mn(II) on surfactant-modi fi ed alumina : Batch and column studies, *Journal of Environmental Chemical Engineering*, **2**, 2295–2305 (2014).

40. Barka N., Qourzal S., Assabbane A., Nounah A., Ait-Ichou Y., Removal of Reactive Yellow 84 from aqueous solutions by adsorption onto hydroxyapatite, *Journal of Saudi Chemical Society*, **15**, 263–267 (2011).

41. Al-Mahmoud S.M., Adsorption of Some AlephaticDicarboxylic Acids on Zinc Oxide: A kinetic and Thermodynamic Study, *Baghdad Science Journal*,**16**, 892–897(2019).

42. Pal A., Pan S., Saha S., Synergistically improved adsorption of anionic surfactant and crystal violet on chitosan hydrogel beads, *Chemical Engineering Journal,***217**, 426–434 (2013).

43. Aljeboree A.M., Alshirifi A.N., Alkaim A.F., Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon, *Arabian Journal of Chemistry*,**10**, S3381–S3393 (2017).