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Investigation of equilibrium, kinetic and thermodynamic of methylene blue adsorption onto dehydrated hazelnut husk carbon

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ABSTRACT

In this study, adsorption of methylene blue (MB) on dehydrated hazelnut husk carbon (DHHC) was tested in batch adsorption system by investigating several factors including pH, contact time, initial concentration, mass dosage and temperature. MB adsorption was found to be favoured at pH values ≥7.0. The increase in temperature yielded an increase in MB adsorption. The MB adsorption was reached to equilibrium in 8 h. The MB equilibrium data agreed well with Langmuir equation with maximum monolayer capacity of 285.7 mg g^{-1}. MB adsorption kinetics was described well with the pseudo-second-order kinetic model. The thermodynamic investigations showed a spontaneity and endothermicity of MB adsorption onto dehydrated hazelnut husk. Eventually, DHHC could be utilized as an effective and useful adsorbent for the removal of MB from aqueous solutions.

Keywords: Adsorption; Activated carbon; Agricultural waste; Hazelnut husk; Kinetic; Isotherm

1. Introduction

For the protection of the environment, a lot of concern has been given on the removal and/or solid phase extraction of several dyes and metals from aqueous solutions [1–3]. The dyes are not desired in the environment due to bad appearance of coloured waters, inhibition of photosynthetic activities of aquatic plants by preventing sun light passage into water, and toxicological effects on living organisms. Among the dyes, methylene blue (MB) is important due to its' widely usage in several industries and adoption to be a model compound for measurement of dye adsorption ability of adsorbents [4–8]. Some toxic effects of MB can be listed as burning of eye by its contact with eye, difficulty in breathing and nausea by its inhalation, mental confusion and vomiting by its ingestion [9].

In order to treat waste water containing dyes, there is a need for an economical, effective and easily applicable method. For this purpose, adsorption method has been widely investigated for removal of pollutants from waste water in the last few decades [10–29]. The cost of adsorption technique, one of the effective treatment methods, depends on the price of adsorbent. For this reason, many scientists have tried for the synthesis of low cost adsorbent from agricultural wastes [30–35].

Hazelnut husks (HHs) appeared in Turkey about 140,000 tonnes per year after harvesting of hazelnut.

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HHs have not been utilized for any purpose and eliminated by incineration in threshing field. Consequently, HH could be considered as an appropriate agricultural waste for the preparation of activated carbon (AC) because of its zero economical value. HHs were utilized for this purpose using various AC preparation methods including sulphuric acid, zinc chloride and phosphoric acid [36–41]. Treatment of HH with sulphuric acid at ambient temperature produced carbonaceous material which is called as dehydrated hazelnut husk carbon (DHHC) [40]. Efficient adsorption ability of DHHC for metal ions such as Ni(II) [40] and Cr(VI) [41] ions directed us to examine and to investigate MB adsorption by DHHC.

In the present work, MB adsorption ability of DHHC was studied by investigating effective parameters including pH, time, temperature, mass dosage and initial MB concentration in batch adsorption model. Adsorption equilibrium, kinetics and thermodynamics were evaluated.

2. Materials and methods

2.1. Instruments and chemicals

An UV–vis spectrophotometer, (Shimadzu UV-2401, Japan) was used for the determination of MB concentrations at 663 nm. A Schott CG-840 model pH meter (Schott AG, Mainz, Germany) was used to measure pH values of the MB solutions. Temperature-controlled orbital shaker (IKA, KS 4000i) was employed for shaking of the suspension containing MB solution and DHHC.

Preparation and characterization of DHHC were given elsewhere [40]. Briefly, DHHC was prepared by the treatment of grinded HH (53–106 μm) with sulphuric acid at ambient temperature for 24 h. The obtained DHHC contains high amount of surface functional groups (total acidic value: 3.0 mmol g^{-1}) and its pH_{pzc} value and BET surface area were reported to be 5.30 and 35.7 $m^2 g^{-1}$. C, H, N and S elemental analysis of DHHC (wt.%) was estimated to be 60.07, 3.61, 0.85 and 1.39, respectively [40].

MB ($C_{16}H_{18}N_3SCl$, Mw: 319.86 g mol^{-1}) was purchased from Riedel-de Haen AG (Seelze-Hannover, Germany) and not purified prior to use. A stock solution of MB was prepared at 1,000 mg L^{-1} and working and standard solutions were prepared from subsequent dilutions from the stock solution with deionized water. Other chemicals were of analytical reagent grade supplied from Merck KGaA, Darmstadt, Germany. Distilled and deionized water, chemical resistivity: 18 MΩ cm, (Millipore Milli-Q Gradient, Millipore, MA, USA) was used throughout the study. pH of the MB solutions were adjusted to desired value by adding 0.1 M HCl and NaOH solutions.

2.2. Adsorption experiments

MB adsorption studies were conducted using batch adsorption model. For this purpose, a known amount of DHHC (50 mg) was added to 50 mL of MB solutions at various concentration in an Erlenmeyer flask (250 mL) and then, the obtained suspension was agitated on the orbital shaker at 298 K for predetermined time intervals (8 h, except contact time studies). In the end, the equilibrium concentration of MB was determined by UV–vis. spectrophotometer. Adsorbed amount of MB per gram of DHHC and removal per cent of MB were calculated by well-known basic stoichiometric equations [40]. For the investigation of temperature on the MB adsorption, the temperature of the medium was changed between 298 and 318 K.

3. Results and discussion

3.1. Effect of pH on the MB adsorption by DHHC

The pH of the aqueous medium not only affects the ionization degree of the adsorbates but also changes the surface charge of adsorbents, and hence, pH is a key parameter for the uptake of dyes [42]. In order to investigate the effect of pH on the MB adsorption by DHHC, initial pH of the MB solutions was changed from 3.0 to 9.0 at two initial concentrations, namely, 200 and 300 mg L^{-1}. According to the results illustrated in Fig. 1, MB adsorption is higher at pH values ≥7.0 than at acidic pH values for both MB

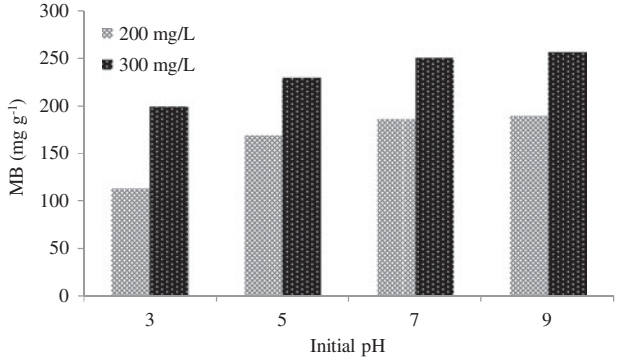

Fig. 1. Effect of initial pH on the MB adsorption by DHHC (initial MB concentrations: 200 and 300 mg L^{-1}, DHHC: 50 mg, volume of the solution: 50 mL, contact time: 8 h and temperature: 298 K).

concentrations. Hence, the subsequent experiments were carried out at pH of 7.0.

3.2. Effect of time on the MB adsorption by DHHC and adsorption kinetics

The effect of contact time on the MB adsorption was investigated at time intervals between 1 and 24 h at two different concentrations of MB, namely, 200 and 300 mg L^{-1}. The results (Fig. 2) revealed that MB adsorption was increased by increment of the time from 1 to 8 h and then was not changed. So, the equilibrium time of MB adsorption onto DHHC was found to be 8 h.

In order to search MB adsorption kinetics, pseudo-first-order and second-order models were used. The pseudo-first-order model of Lagergren [43] was given in the linear form by Eq. (1).

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amount of the MB adsorbed on the DHHC at equilibrium and at any time t, respectively; and k_1 (min^{-1}) is the rate constant of the pseudo-first-order model. The value of k_1 and q_e can be computed from the slope and intercept of the linear plot of ln ($q_e - q_t$) vs. t, respectively.

The pseudo-second-order model [44] can be written in the linear form by Eq. (2).

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

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second-order model. The values of q_e and k_2 can be determined from the slope and intercept of the plot of t/q_t vs. t, respectively [40].

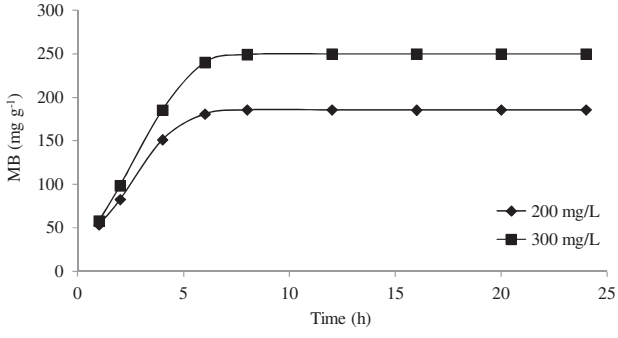

Fig. 2. Effect of contact time on the MB adsorption by DHHC (initial MB concentrations: 200 and 300 mg L^{-1}, DHHC: 50 mg, volume of the solution: 50 mL, pH of the solution: 7.0 and temperature: 298 K).

The predicted and experimental q_e values, calculated rate constants and correlation coefficients were listed in Table 1. The linearity of the kinetic model plots is very important to decide which model is appropriate for the adsorption systems. As can be seen from the results, values of r^2 of second-order model were higher than first-order model. The second criterion for deciding which kinetic models describe the adsorption system is the closeness of experimental and predicted q_e values. The pseudo-second-order model produced these values more closely than the first-order model. Hence, it could be concluded that MB adsorption onto DHHC followed by second-order model. Similar approaches were reported in the literature for the adsorption of dyes [26,45].

3.3. Effect of DHHC dosage on the MB adsorption

The effect of the DHHC dosages on the MB adsorption was conducted at two different MB concentration 200 and 300 mg L^{-1} using various amount of the sorbent. The results were presented in Fig. 3. The adsorption percents of MB were increased by increasing of DHHC dosage for both initial concentrations of MB. These findings were expected results. The increasing of DHHC mass provided a more available adsorption site for the MB uptake from solution [46]. Also, similar findings were reported for the adsorption of MB on tobacco stem ash [31] and AC from HH [38] in literature.

3.4. Effect of Initial MB concentration on the adsorption by DHHC

It is well known that the adsorbed amount of adsorbate is a function of its concentration [7]. In order to understand the MB adsorption onto DHHC whether monolayer or multilayer, the experiments were carried out by changing of initial MB concentration in the range of 150–600 mg L^{-1} and using fixed adsorbent dosage 50 or 75 mg. According to the results depicted in Fig. 4, MB adsorption was significantly increased by increasing of its concentration from 150 to 400 mg L^{-1} and after this point increasing of MB concentration caused a little enhancement in MB adsorption showing monolayer adsorption.

3.5. MB adsorption isotherm by DHHC

The experimental MB adsorption isotherms, MB equilibrium concentration against adsorbed amount of

Table 1
Pseudo-first-order and Pseudo-second-order constants for MB adsorption on DHHC

		Pseudo-first-order			Pseudo-second-order		
C_0 (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	$k_1 \times 10$ (h^{-1})	$q_{e,cal}$ (mg g^{-1})	r^2	$k_2 \times 10^3$ (g mg^{-1} h^{-1})	$q_{e,cal}$ (mg g^{-1})	r^2
200	185.7	6.6	336.8	0.9556	2.7	204.1	0.9901
300	250.2	5.9	443.1	0.9399	1.4	285.7	0.9833

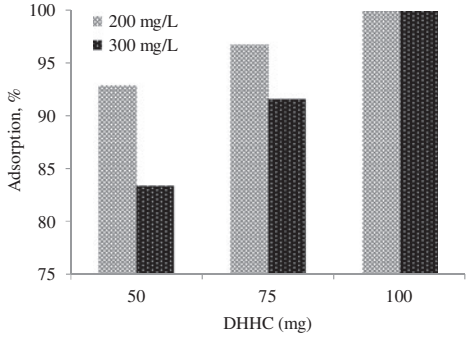

Fig. 3. Effect of DHHC amount on the MB adsorption per cent (initial MB concentrations: 200 and 300 mg L^{-1}, DHHC: 50, 75 and 100 mg, volume of the solution: 50 mL, pH of the solution: 7.0, contact time: 8 h and temperature: 298 K).

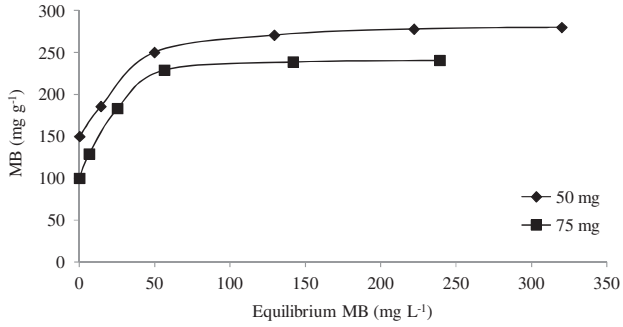

Fig. 5. Experimental adsorption isotherms of MB by DHHC (DHHC: 50 and 75 mg, volume of the solution: 50 mL, pH of the solution: 7.0, contact time: 8 h and temperature: 298 K).

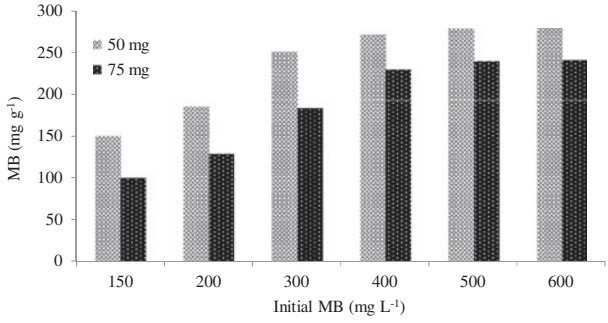

Fig. 4. Effect of initial MB concentration on the MB adsorption by DHHC (DHHC: 50 and 75 mg, volume of the solution: 50 mL, pH of the solution: 7.0, contact time: 8 h and temperature: 298 K).

MB at 298 K, were graphically plotted and presented in Fig. 5 This figure also showed that the MB adsorption increased by increasing of MB equilibrium concentration until monolayer coverage. The MB equilibrium data were analysed by Langmuir (Eq. (3)) [47] and Freundlich (Eq. (4)) [48] equation which are expressed by following formulas in the linear forms, respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where q_e (mg g^{-1}) is the amount of the MB adsorbed per unit mass of DHHC, C_e (mg L^{-1}) is the equilibrium MB concentration in the solution, q_{max} (mg g^{-1}) and K_L (L mg^{-1}) are the Langmuir constant related the maximum monolayer adsorption capacity and the equilibrium constant or bonding energy, respectively, and K_F (mg g^{-1}) and n are the Freundlich constants related to adsorption capacity and intensity (or surface heterogeneity), respectively [5,40,45].

The calculated constants and correlation coefficients for both equations were listed in Table 2. The correlation coefficients of Langmuir equation for both DHHC dosages were higher than Freundlich equation. For this reason, it could be resulted that MB adsorption on DHHC explained well by Langmuir model [49,50]. The maximum adsorption capacity of DHHC for MB was calculated to be 285.7 mg g^{-1} by the Langmuir equation.

3.6. Effect of temperature on the MB adsorption by DHHC

The effect of temperature on the MB adsorption by DHHC was studied at temperatures ranged from

Table 2
Freundlich and Langmuir isotherms constants for MB adsorption on DHHC

DHHC (mg)	Langmuir isotherms			Freundlich isotherms		
	q_{max} (mg g^{-1})	$K_L \times 10$ (L mg^{-1})	r^2	K_F (mg g^{-1})	n	r^2
50	285.7	2.0	0.9996	166.8	10.9	0.9281
75	243.9	2.2	0.9991	124.0	8.1	0.9147

298 to 328 using MB solution at 500 mg L^{-1} and 50 mg DHHC. The obtained results were illustrated in Fig. 6. The increasing of temperature caused an increase in the MB adsorption showing endothermicity of MB adsorption onto DHHC [38].

The thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes were calculated. ΔG values were computed using the following Eq. (5):

$$\Delta G = -RT \ln K_d \quad (5)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K) and K_d is the distribution coefficient. The K_d value was calculated by the following formula (Eq. (6)):

$$K_d = \frac{C_{ads}}{C_e} \quad (6)$$

where C_{ads} is the adsorbed concentration of MB onto DHHC and equal to difference of initial and equilibrium concentration of MB (mg L^{-1}) and C_e is the equilibrium concentration of MB (mg L^{-1}).

The relation between ΔG, ΔH and ΔS can be written by the following equations (Eq. (7) and (8)):

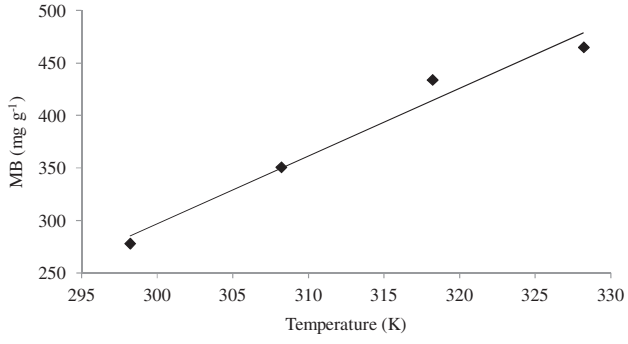

Fig. 6. Effect of temperature on the MB adsorption by DHHC (initial MB concentrations: 500 mg L^{-1}, DHHC: 50 mg, volume of the solution: 50 mL, pH of the solution: 7.0 and contact time: 8 h).

Table 3
Values of thermodynamic parameters for MB adsorption on DHHC

T (K)	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K)[a]	ΔH (kJ mol^{-1})[a]
298	−0.6		
308	−2.2	222.9	66.1
318	−5.0		
328	−7.1		

[a]Measured between 298 and 328 K

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (8)$$

The values of ΔH and ΔS for MB adsorption were calculated from the slope and intercept of the plot of $\ln K_d$ vs. $1/T$, respectively [45,51,52].

The obtained values of thermodynamic parameters for the MB adsorption onto DHHC are listed in Table 3. The positive value of ΔH revealed that the MB adsorption onto DHHC was endothermic [38]. The positive value of ΔS showed the increased randomness at the solid–solution interface during the MB adsorption onto DHHC [52–54]. The spontaneity of adsorption is depended on the Gibbs free energy and the obtained negative values of ΔG revealed the spontaneous nature of the adsorption process. The magnitude of ΔG also increased with increasing the temperature exhibiting that the MB adsorption was more favourable at higher temperatures [54–56].

4. Conclusions

In this study, batch adsorption of MB onto DHHC was investigated. The removal of MB was higher at neutral and slightly basic conditions than in acidic medium. MB adsorption reached the equilibrium in 8 h and followed with pseudo-second-order kinetic models. The MB equilibrium data well fitted to Langmuir equation with maximum adsorption capacity of 285.7 mg g^{-1}. Thermodynamic investigations exhibited

a spontaneity and endothermicity of MB adsorption onto DHHC. As a result, the HHs could be very useful precursor for the preparation of AC in order to remove MB from aqueous solutions.

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