

Chapter 59

Adsorption of Methylene Blue from Aqueous Solution by Natural Clays

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Abstract The objective of this study is the valorization of certain local natural clays by their use in treatment of industrial wastewater. For this purpose, we carried out discoloration tests of effluents by adsorption using two natural clays from two different deposits, one located in Maghnia (MC) and the other in the region of Bechar (BC). The adsorption tests were conducted on a basic dye methylene blue (MB). The effects of temperature, initial dye concentration, contact time, and solution pH on adsorption were studied. The adsorption capacity increased with an increase in adsorbate dosage and a decrease in ionic strength. The equilibrium time was found to be 90 min for full equilibration. Langmuir isotherm model fitted well the equilibrium data for the two sorbents (BC and MC) comparing to the Freundlich isotherm models. The monolayer adsorption capacity of AB and AM for methylene blue (MB) was found to be 223.714 and 510.204 mg/g, respectively. Also, the adsorption processes were endothermic and spontaneous in nature.

Keywords Algerian clays • Adsorption • Dye • Water treatment

59.1 Introduction

Many industries such as the textile, cosmetic, food, leather, pharmaceutical, paper, and printing industries consume large quantities of water to color their products [1]. The effluents from these industries and from manufacturing are highly colored and undesirable, even at very low concentrations in the case of some dyes. Discharge of the dye wastewater into receiving water bodies prevents photosynthetic activity in

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aquatic life by reducing sunlight penetration [2]. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic [3]. The conventional methods for removing dyes include adsorption, coagulation and flocculation, oxidation, ion exchange, reverse osmosis, and ultra filtration [4]. Due to economic considerations, adsorption has gained favor in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above conventional treatment methods [5]. This led to a search for cheaper, easily obtainable materials for the adsorption of dye [6]. Clays such as sepiolite, zeolite, montmorillonite, smectite, and bentonite are being considered as alternative low-cost adsorbents. The wide usefulness of clays is a result of their specific surface area, high chemical and mechanical stability, and variety of surface and structural properties. The chemical nature and pore structure usually determine the sorption ability of clays [7]. In relatively recent years, there has been an increasing interest in utilizing natural clay materials for the removal of toxic metals and some organic pollutants from aqueous solutions [8].

This chapter examines the elimination of MB present in an aqueous solution using MC and BC as adsorbent material. In this study, the effects of various parameters including contact time, temperature, and solution pH on the adsorption were investigated. The kinetic and thermodynamic parameters were also calculated to determine rate constants and adsorption mechanism. The experimental data were fitted into Langmuir and Freundlich equations to determine which isotherm gives the best correlation to experimental data.

59.2 Experimental

59.2.1 Materials

The clay samples used in this study were MC and BC. They were obtained from the north and south, respectively, region of Algeria. The sorbent solids were collected and washed. They were grounded and sieved into different particle sizes ranging in diameter range of 0.5–1 mm for BC and MC.

59.2.2 Dye

Methylene blue was chosen as adsorbate in this study as a model molecule for basic dyes. A stock solution of the dye was prepared by dissolving an accurately weighed amount of MB in ultrapure water to give a concentration of 1 g/L. Experimental solutions of different concentrations were obtained by diluting the stock solution with ultrapure water. The characteristics of methylene blue are: $C_{16}H_{18}ClN_3S$ chemical formula, 319.86 g/mol molecular weight and 665 nm maximum wavelength.

59.2.3 Batch Mode Adsorption Study

MB solutions were prepared with ultrapure water at natural pH. Batch experiments were carried in a glass beaker by shaking a fixed mass BC or MC (20 mg) with 20 mL diluted solution (20–800 mg/L). After agitation, the solution was centrifuged at 5,000 rpm with a required time at 25 °C. Then, the MB concentration in the supernatant solution was analyzed using a Spectronic 21 MV spectrophotometer by monitoring the absorbance changes at a wavelength of maximum absorbance (665 nm). Each experiment was carried out in duplicate and the average results are presented. Calibration curves were obtained with standard MB solutions using ultrapure water as a blank. Mass capacity of adsorption, q_e , is calculated from the difference between the initial and the final MB concentration as followed in Eq. (59.1).

$$q_e = (C_0 - C_e)V/W \quad (59.1)$$

where C_0 and C_e (mg/L) are the concentrations of MB initially and at time (t), respectively, V (L) is the volume of the solution, and W (g) is the mass of adsorbents used.

59.3 Results and Discussion

59.3.1 Effect of Contacts Time

It is essential to evaluate the contact time required to reach equilibrium. In fact, a kinetic study helps to determine the nature of the process and serves as a reference for the assessment of the residence time required for the adsorption process. Hence, experiments were conducted, varying contact time from 10 to 120 min for both samples. Figure 59.1 shows the effect of contact time at initial dye concentration of 200 mg/L. The adsorption capacity increases with an increase in contact time and reaches a plateau at 90 min for BC and MC. Moreover, it is seen that the adsorption of MB is very rapid in the first 10 min and then slowly declines with time until equilibrium. The initial rapid phase may be due to an increase in the number of vacant sites available at the initial stage. Similar trends have been reported for the adsorption of MB by giant duckweed [6].

59.3.2 Adsorption Kinetics

In order to investigate the adsorption kinetics of MB, four kinetic models, namely pseudo-first-order, pseudo-second-order, Bangham equation, and intraparticle diffusion models, were used in this study.

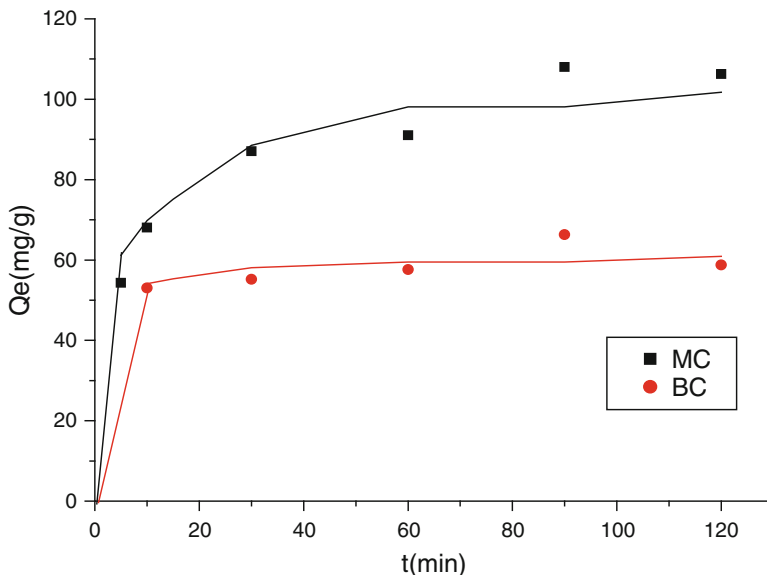


Fig. 59.1 Effect of contact time and initial dye concentration on adsorption of MB by MC and BC (adsorbent dosage 1 g/L, natural pH, 25 °C)

59.3.2.1 Pseudo-First-Order Model

The pseudo-first-order Lagergren equation [9] is given by:

$$dq_t/dt = k_1(q_e - q_t) \quad (59.2)$$

where q_t and q_e (mg/g) are the amounts adsorbed at time t and equilibrium, respectively, and k_1 (min^{-1}) is the pseudo-first-order rate constant for the adsorption process. The integrated linear form of Eq. (59.3) can be expressed as:

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t \quad (59.3)$$

From the plots of $\log(q_e - q_t)$ vs. t , it was observed that the pseudo-first-order model was applicable for the initial 10 min (Fig. 59.2a). Thereafter, the experimental data deviated from theory (results not shown).

Ho et al. [10] reported that the sorption data were well represented by the Lagergren first-order model only in the first stage where rapid sorption took place, confirming that it was not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics of MB by adsorbents for the entire adsorption process. The rate constants k_1 and calculated equilibrium adsorption capacities $q_{e,cal}$ obtained from the slopes and intercepts of the plots are given in Table 59.1. The correlation coefficient values R^2 were 0.825 and 0.443 for MC and BC, respectively.

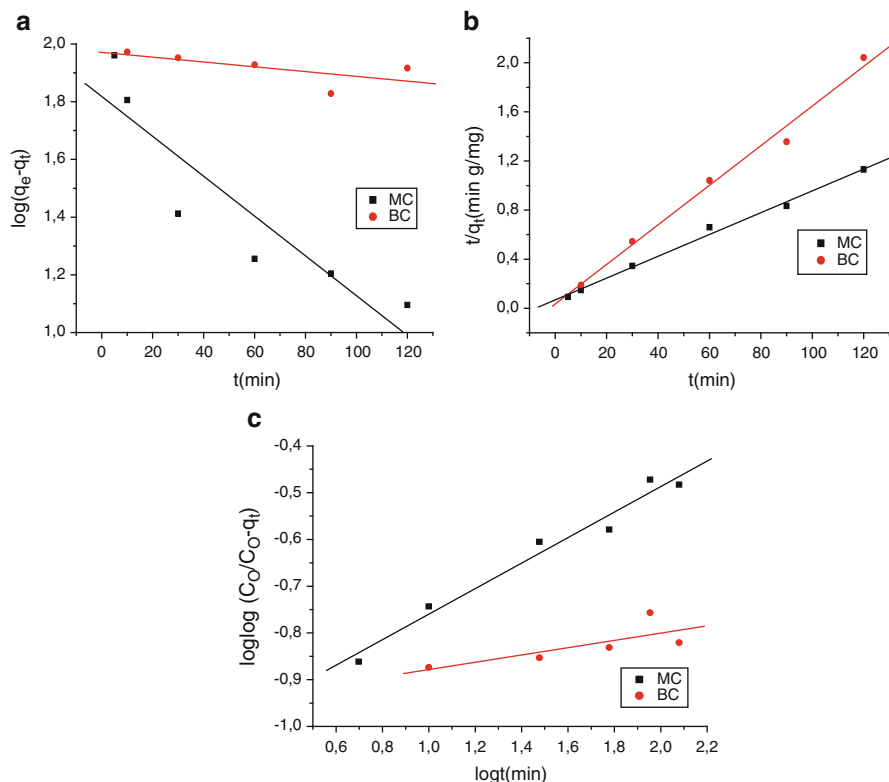


Fig. 59.2 Kinetic models for adsorption of MB by MC and BC: (a) pseudo-first-order model; (b) pseudo-second-order model; (c) Bangham equation model; (adsorbent dosage 1 g/L, natural pH, 25 °C)

The $q_{e,\text{cal}}$, calculated values and the experimental values $q_{e,\text{exp}}$, are not similar, showing that the adsorption kinetics for the entire process did not follow the pseudo-first-order model.

59.3.2.2 Pseudo-Second-Order Model

In order to characterize the adsorption kinetics, several kinetic models were applied to the experimental data. However, in the last years, the pseudo-second-order kinetic model has been considered to be the most appropriate. The pseudo-second-order equation can be expressed following Eq. (59.4) [10].

$$dq_t/dt = k_1(q_e - q_t)^2 \quad (59.4)$$

Table 59.1 Kinetic parameters for adsorption of MB by MC and BC

	Pseudo-first-order model			Pseudo-second-order model			Bangham equation model			
	$q_{e,exp}$ (mg/g)	k_1 (1/min)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg min)	R^2	h (g/mg min)	R^2	k_0 (mL/g L)	α
BC	66.33	19.16	0.443	93.56	2.13	0.988	29.41	0.988	0.25	0.078
MC	108.01	0.016	0.825	65.78	0.0012	0.992	14.74	0.992	0.214	0.27

where k_2 (g/mg min) is the pseudo-second-order rate constant. After integration, Eq. (59.4) becomes:

$$t/q_t = 1/k_2q_e^2 + (1/q_e)t \quad (59.5)$$

The initial sorption rate h (mg/g min) is defined as:

$$h = k_2q^2 \quad (59.6)$$

By plotting t/q_t against t for different initial concentrations, straight lines were obtained (Fig. 59.2b). The rate constants k_2 and calculated equilibrium adsorption capacities $q_{e,cal}$ obtained from the intercepts and slopes of the plots are given in Table 59.2. For all initial concentrations studied, the correlation coefficients were close to unity. In addition, the values of $q_{e,cal}$ showed good agreement with the experimental data. Thus, the sorption could be approximated more appropriately by the pseudo-second-order model, supporting the assumption of chemisorptions as the rate-limiting mechanism through sharing or exchange of electrons between sorbent and sorbate [10]. Similar results have been reported in the literature [11].

59.3.2.3 Bangham Equation

Three sequential steps are involved in the adsorption of sorbate onto sorbent: film diffusion, particle diffusion, and adsorption on the pore surface [12]. Among these steps, the third one is very fast and is not considered as a rate-limiting step. The overall adsorption process may be controlled by the film or particle diffusion step. The Bangham equation is applied in this study to check whether pore diffusion is the only limiting step or not. The Bangham equation is given as

$$\log(\log([C_0/(C_0 - q_{tm})])) = \log(k_0m/2.303) + \alpha \log t \quad (59.7)$$

where C_0 (mg/L) is the initial dye concentration, m (g/L) is the adsorbent mass used per liter of solution, V (mL) is the volume of the solution, and α (<1) and k_0 (mL/g L) are Bangham constants. The parameters of Bangham model as well as the correlation coefficient are listed in Table 59.1. The experimental data are not fitted well by the Bangham equation (Fig. 59.2c), the plots have low correlation coefficients, indicating that the diffusion of MB into pores of the adsorbent is not the only rate-controlling step [13].

59.3.3 Adsorption Isotherms

It is important to study the equilibrium adsorption isotherm for the design of the adsorption system. Two adsorption isotherm models, namely Langmuir and Freundlich models were used to fit the adsorption experimental data in this study.

The Langmuir isotherm [14] assumes that sorption occurs at specific homogeneous sites within the adsorbent and that the capacity of the adsorbent is finite. The Langmuir equation is represented as:

$$q_e = K_L q_m C_e / (1 + K_L C_e) \quad (59.8)$$

where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e (mg/L) is the equilibrium dye concentration in the solution, q_m (mg/g) is the monolayer adsorption capacity, and K_L (L/mg) is the Langmuir isotherm constant, which is related to the affinity of the binding sites and the energy of adsorption. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L [15], which is defined as:

$$R_L = 1 / (1 + K_L C_0) \quad (59.9)$$

where C_0 (mg/L) is the initial dye concentration and K_L (L/mg) is the Langmuir isotherm constant. The R_L value indicates whether the type of isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The linear plots of C_e/q_e versus C_e are used to determine the value of q_m (mg/g) and K_L (L/mg).

The Freundlich isotherm [16] is based on the assumption of a heterogeneous surface with a nonuniform distribution of adsorption heat over the surface. It is an empirical equation expressed as

$$q_e = K_F C^{1/n} \quad (59.10)$$

where K_F (mg L^{1/n} mg^{1/n}/g) is the Freundlich constant and $1/n$ is the heterogeneity factor, which is related to the capacity and intensity of the adsorption, respectively.

A plot of $\log q_e$ against $\log C_e$ gives a straight-line graph with $(1/n)$ as the slope and $\log K_F$ as the intercept. Both K_F and n determine the curvature and the steepness of the isotherm.

Relevant isotherm parameters and the values of q_m , K_L , R_L , K_F , $1/n$, and R^2 for all the experiments for removal of MB are presented in Table 59.2.

The linear calculations reveal that the equilibrium data agree well with the Langmuir equation comparing to Freundlich isotherms, for AB and AM adsorbents. This reasonable fit of the mode is indicated by a high correlation coefficient $R^2 > 0.98$. The comparison of correlation coefficients (R^2) of the linearized form of the two isotherm models indicates that the Langmuir model yields a better fit for the experimental equilibrium adsorption data than the Freundlich isotherm models.

According to the values of $R_L < 1$, all the systems show favorable adsorption of MB. The low values of R_L indicate high and favorable adsorption of methylene blue on to MC and BC. The maximum capacity obtained from Langmuir equation are 510.2 and 223.7 mg/g at 25 °C for MC and BC, respectively. Table 59.3 compares between the adsorption capacities of AM, AB, and other adsorbents from the literature. From Table 59.3 the maximum capacity of AM and AB was found to be comparable to those of some other adsorbent.

Table 59.2 Isotherm parameters obtained for adsorption of MB by MC and BC

Isotherm	Parameter	Temperature (°C)	BC values	MC values
Langmuir	q_m (mg/g)	25	223.714	510.204
		45	175.438	196.078
	K_L (L/mg)	25	0.194	0.143
		45	0.792	0.127
	R^2	25	0.794	0.884
		45	0.984	0.993
	R_L	25	0.0251	0.0337
		45	0.0063	0.0378
Freundlich	K_F (mg L ^{1/n} mg ^{1/n} /g)	25	46.581	63.755
		45	39.241	45.897
	$1/n$	25	0.480	0.669
		45	0.309	0.258
	R^2	25	0.664	0.888
		45	0.834	0.912

Table 59.3 Comparison of sorption capacities of MB between MC, BC, and other related sorbents

Adsorbent	Q_m (mg/g)	References
Clay of Maghnia (MC)	510.204	This study
Clay of Bechar (BC)	223.714	This study
Softstem bulrush	53.8	Y. Li et al. (2008)
Rice husk	40.5	V. Vadivelan et al. (2005)
Banana peel	20.8	G. Annadurai et al. (2002)
Orange peel	18.6	G. Annadurai et al. (2002)

59.4 Thermodynamic Studies

The thermodynamic parameters of the adsorption process are obtained from experiments at various temperatures using the following equations:

$$\Delta G = -RT \ln K_e \quad (59.11)$$

where R is the universal gas constant (8.314 J/mol K), T is temperature (K), and K_e is the distribution coefficient for the adsorption calculated from the following equation:

$$K_D = C_a/C_e \quad (59.12)$$

C_a is the amount of dye (mg) adsorbed on the adsorbent per liter of the solution at equilibrium and C_e concentration (mg/L) of the dye in the solution.

Table 59.4 Thermodynamic parameters for adsorption of MB on MC and BC

Sorbent solid	Parameters	Temperature (K)		
		298	308	318
BC	K_e	1.355	1.128	0.950
	ΔG (J/mol)	-754.188	-308.918	134.352
	ΔH (J/mol)	-13,993.434		
MC	ΔS (J/mol K)	-44.427		
	K_e	1.437	1.217	1.042
	ΔG (J/mol)	-898.422	-503.922	-109.422
	ΔH (J/mol)	-12,654.522		
	ΔS (J/mol K)	-39.45		

The enthalpy (ΔH) and entropy (ΔS) parameters are estimated from the following equation:

$$\ln K_e = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (59.13)$$

ΔH and ΔS were calculated from the slope and intercept of Van't Hoff plots of $\ln K_e$ versus $1/T$ (see Fig. 59.3). The results are listed in Table 59.4.

The obtained values for Gibbs free energy change (ΔG) are -898.422, -503.922, and -109.422 J/mol for MB adsorption on MC at 25 °C, 35 °C, and 45 °C, respectively. The negative ΔG values indicate a spontaneous nature of the adsorption. However, ΔG values are, -754.188, -308, and 134.352 J/mol for MB adsorption on BC at 25 °C, 35 °C, and 45 °C, respectively. The obtained ΔG values indicate that increasing temperature leads to decrease in feasibility of adsorption at higher temperatures.

The negative ΔH indicates the exothermic nature of the adsorption and also its magnitude gives information on the type of adsorption, which can be either physical or chemical. Therefore, the ΔH values show that the adsorption processes of MB on adsorbents were taken place via chemisorption. The negative values of ΔS suggest a decrease in randomness at the solid/solution interface [17] (Fig. 59.3).

59.5 The Effect of pH on the Adsorption Process

The effect of solution pH on the adsorption was investigated in the pH range 2.3–11 (adjusted with 0.1 mol/L HCl or NaOH solution) using a pH meter. The solution pH was an important parameter for the adsorption process owing to its impact on the surface binding sites of the clays and the ionization process of the dye molecule [11]. Figure 59.4 shows the dependence of MB dye removal on solution pH.

The amounts of MB adsorbed on each adsorbent in the acidic medium were slightly high as compared to those in the basic medium. In the present study, as the

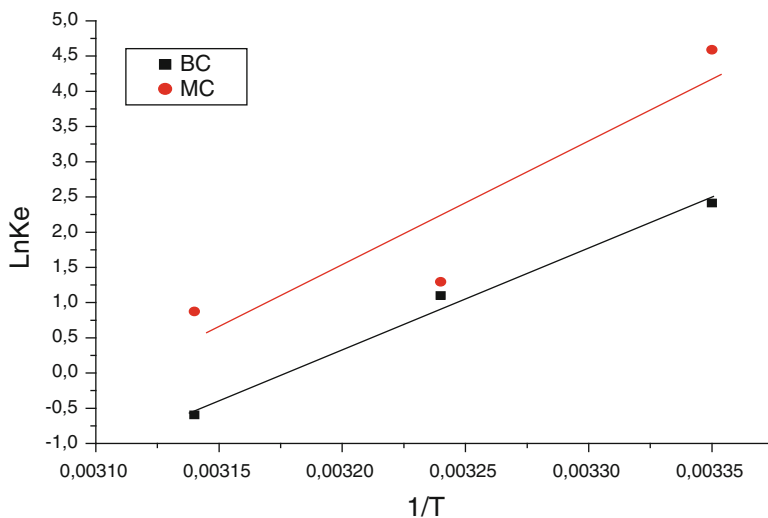


Fig. 59.3 Plot of $\ln K_e$ vs. $1/T$ for the estimation of thermodynamic parameters for adsorption of MB on MC and BC

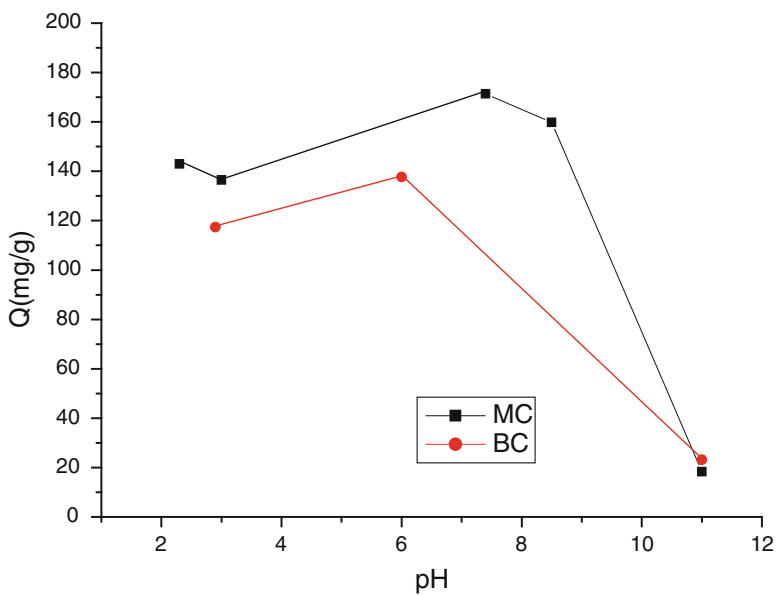


Fig. 59.4 Effect of solution pH on adsorption of MB by BC and MC ($C_0 = 200$ mg/L, adsorbent dosage 1 g/L, 25°C)

initial solution pH increased of 2.3–7, the number of negatively charged active sites increased. Therefore, the electrostatic attraction between the negatively charged adsorbent and positively charged MB ions increased, resulting in an increase in the adsorption on each adsorbent. In the pH range 7–11, the adsorption of MB decreases on each adsorbent, may be the OH^- ion can competitively exclude the adsorption of MB by exchanging with anion on the surface or in the interlayer region of the clay.

59.6 Conclusion

Adsorption of MB using BC and MC was performed in aqueous solutions. The amount of MB adsorbed on the MC was higher than that on the BC. The adsorption capacity was affected by various parameters including contact time, effect of temperature, and pH solution. Kinetic studies showed that the adsorption process followed the pseudo-second-order model. The experimental data were evaluated by Langmuir and Freundlich isotherms. Equilibrium data were well fitted to Langmuir isotherm model. The maximum adsorption capacities of BC and MC for methylene blue were 223.714 and 510.204 mg/g, respectively, at 25 °C. These values are in a high range for methylene blue adsorption when comparing to other adsorbents. The adsorption was spontaneous owing to the negative value of ΔG . The abilities of all the tested adsorbents to adsorb MB were relatively low in the alkaline medium as compared to those in the acidic medium. BC and MC are easily available and inexpensive, suggesting that it could be employed as an alternative adsorbent for the removal of MB.

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