Removal of a cationic dye -Methylene Blue- from aqueous media by the use of animal bone meal as a new low cost adsorbent

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Abstract

The Animal Bone Meal (ABM) prepared from the animal bone has been used as a new low cost adsorbent for the removal of Methylene Blue (MB) dye from aqueous solutions. Kinetics and equilibrium adsorption experiments were conducted to evaluate the adsorption characteristics of a cationic dye onto ABM. Results showed that the ABM could remove the dye effectively from aqueous solutions. The adsorption rate was fast and about 75% of adsorbed MB and was removed in less than 15 min.
The effects of various process parameters *i.e.*, temperature, pH, initial MB concentration, stirring speed, ionic strength and contact time on the adsorption capacity of ABM were investigated. The kinetic models for MB adsorption onto the ABM were studied. Langmuir isotherm showed better results for the ABM. The rates of adsorption were found to conform to the pseudo-second-order kinetic with good correlation. The separation factor (R_L) revealed the favorable nature of the isotherm of the (MB-ABM) system. An activation energy of 25.2, 56.2 and 18.9 kJ/mol corresponding to initial concentrations of 25, 50 and 100 mg/L respectively were determined suggesting that the adsorption involved as a chemical reaction mechanism. The thermodynamic parameters, ΔG°, ΔH° and ΔS° were determined.

Keywords: Animal Bone Meal, Adsorption, Methylene blue, Kinetic model, Adsorption isotherm.

1. Introduction

The effluents of wastewater in some industries such as dyestuff, textiles, leather, paper, plastics, etc..., contain various kinds of synthetic dyestuffs [1]. The effluents of these industries are highly colored and the discharge of these wastes into receiving waters causes severe damages to the environment [2]. The introduction of waste products into the environment is an important problem that has been highlighted by various environmentalist groups [3]. The dyestuffs have complex chemical structures and are stable to light, heat and oxidation agents [4]. The source of such pollution lies in the rapid increase in the use of synthetic dyes. More than 10 000 chemically different dyes are being manufactured. The world dyestuff and dye intermediates production are estimated to be around 7.10^8 kg per annum [5, 6]. Discharging of these dyes into water resources even in a small amount can affect the aquatic life and food web. Dyes can also cause allergic dermatitis and skin irritation. Some of them have been reported to be carcinogenic and mutagenic for aquatic organisms [3].

Although, some existing technologies, such as chemical coagulation/flocculation [7], ozonation, cloud point extraction, oxidation processes, nanofiltration, chemical precipitation, ion-exchange, reverse osmosis and ultra filtration [3, 8-10] may be efficient for the removal of the dyestuffs. These techniques are rather expensive.

Application of biological processes to treat colored wastewater is yet to be fully established. Among treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. Activated carbon is the most effective and widely used adsorbent [11]. However, its high cost has prevented its application, at least in developing countries. So, it’s necessary to search for an alternative low cost adsorbent which can be used as a substitute for activated carbon. A number of low cost adsorbents are reported in the literature. These include phosphate [12], bagasse pith [13,14], maize cobs [11], sunflower [15], fly ash [16], peat [17], saw dust [18], marine algae [19], fungal biomass [20], wasted activated sludge [21], digested sludge [22], red mud [23], coir pith [24], Neem leaf [25], waste organic peel [26] and tree fern [27]. However, adsorption potential of most of these low cost adsorbents is generally low [28].

This work aims to study a convenient and economic method for Methylene Blue (MB) removal from water by adsorption onto animal bone meal (ABM) as an abundantly available and a low cost adsorbent. To gain an understanding of the adsorption kinetics, it was necessary to describe the rate and mechanism of adsorption, to determine the factors controlling the rate of adsorption and to calculate the activation energy of system. The effects of stirring speed, initial MB concentration, solution pH, ionic strength and temperature on MB adsorption rate have been evaluated.

2. Materials and methods

2.1. Preparation and characterization of ABM adsorbent

The animal bones used in this study were collected from the abattoir of Casablanca city. All of the attached meat and fat were removed and cleaned from the bones. The bones were then washed several times with tap water and left in open air for several days to get rid of odours. Later, they were transferred to the oven at 105°C for drying. The dried bones were crushed and milled into different particle sizes in the range 45-200 µm, calcined at 900°C for 2 hours. The residue was washed with distilled water and was used after drying 24 hours at 80°C. The residue was washed with distilled water and was dried overnight at 105°C in a conventional drying oven, and then calcined at a heating rate of 2°C/min to 400°C and kept at this temperature for 4 hours. The resulting material was denominated ABM. The final product is identified by X-ray diffraction (Philips X'Pert PRO), IR spectroscopy (spectrometer Bruker-Tensor 27) and chemical analysis. Elemental analysis shows a high yield of Ca (49.62%) and P (42.36%) compared to small amounts of Si (3.88%), Mg (1.32%), Na (0.77%), Al (0.35%), Fe (0.24%), Cl (0.24%), S (0.11%), K (0.07%), Sr (0.03%), Cu (0,03%) and Zn (0.02%). X-ray diffraction analysis confirms the presence of hydroxyapatite as shown in Figure1.

The characteristic phosphate and calcium bands are observed in Infrared spectra analysis as depicted in Figure 2. The specific surface area of ABM was determined by BET method from adsorption-desorption isotherm of nitrogen at its liquid temperature (77K) and was found to be $S_p = 85 \, m^2/g$. The specific surface area of the ABM was measured by Quantachrome Nova 2200e BET N2 instrument.

2.2. The dye

The chemical formula of MB dye is $C_{16}H_{18}N_3SCl$, presented in Figure 3. The aromatic moiety is planar and the molecule is charged positively. Dimensions of MB molecule are 16.9 Å for the length, 7.4 Å for the breadth, and 3.8 Å for the thickness [29]. Distilled water was used for preparing all solutions.

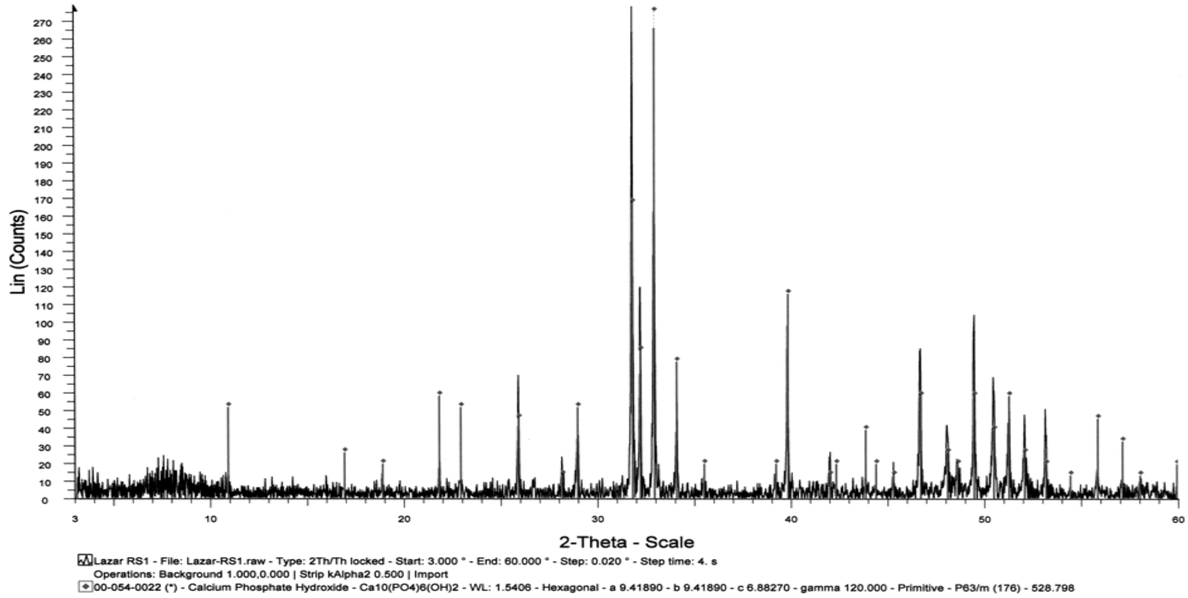

Figure 1: X-ray diffraction of ABM

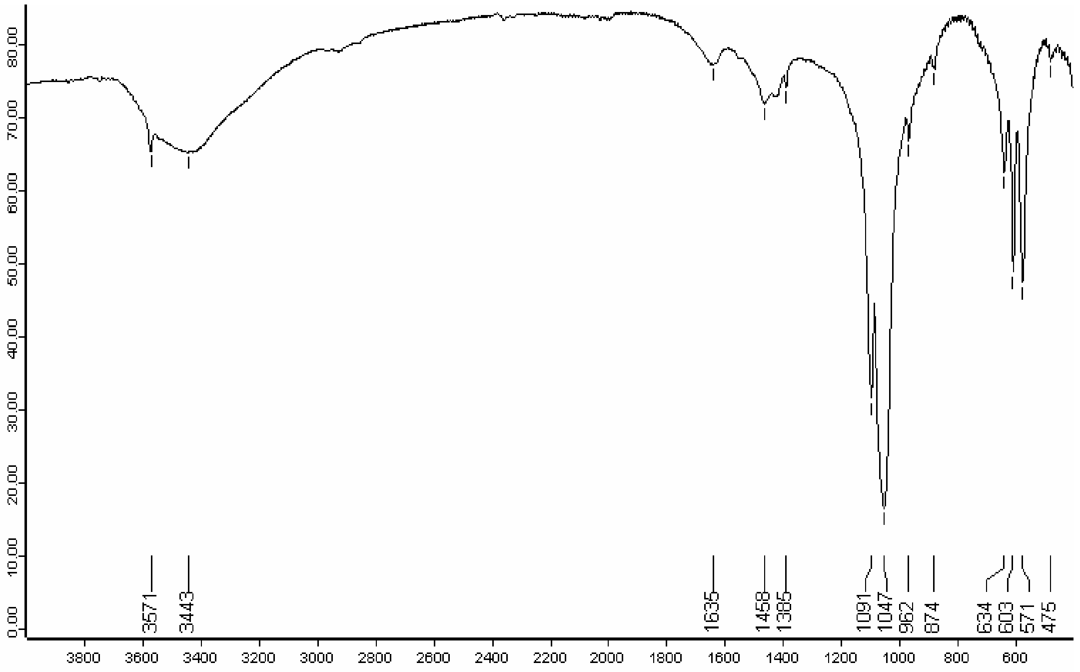

Figure 2: IR spectra of ABM

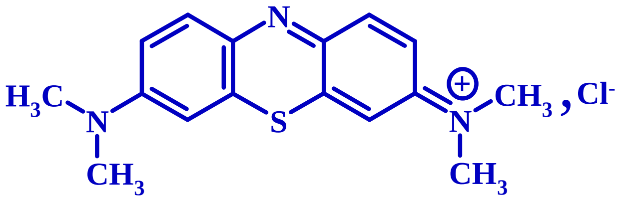

Figure 3: Molecular structure of MB

2.3. Methods

The effects of experimental parameters, initial dye concentrations (25, 50 and 100 mg/L). Effect of stirring speed (300, 400 and 500 rpm), Ionic strength (0-0.5 mol/L), pH (2-10), Temperature (15, 25, 35 and 45°C) on the dye adsorption were studied in a batch mode of operation for a contact time of two hours. The pH of the adsorbate solution was adjusted by adding HCl (0.1 N) or NaOH (0.1 N) solution meauserd by a pH-Metre Basic 20+ model pH-meter. Dye samples were prepared by dissolving a known quantity of the dye in double-distilled water and used as a stock solution and diluted to the required initial concentration. 500 ml dye solutions were put into a glass bottle. The solution was continuously mixed by a magnetic mixer at a speed of 300 rpm. A given amount of ABM was dispersed in the dye solution. After a given contact time, 10 mL mixture of the dispersion was taken, filtered and the absorbance of the filtrate was determined with a UV/visible spectrophotometer (BioMate 6, England) at λ_{max} = 665 nm, the concentration of dye was calculated from a calibration curve. The amount of dye adsorbed was determined by the difference between the initial and remaining concentrations of MB solution. Each experiment was repeated 2 times. The amount of adsorbed MB at equilibrium, q_e (mg/g) was calculated by the following equation (1):

$$q_e = \frac{(C_0 - C_e)}{w} V \qquad (1)$$

where, C_0 and C_e (mg/l) are the liquid phase initial and equilibrium concentrations of the dye respectively. V (l) is the volume of the solution, and w (g) is the mass of dry adsorbent used.

The procedures for the kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at present time intervals, and the concentrations of MB were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by the following equation (2):

$$q_t = \frac{(C_0 - C_t)}{w} V \qquad (2)$$

where, C_0 and C_t (mg/g) are the liquid-phase concentrations of MB at initial and any time t, respectively. V (L) is the volume of the solution, and w (g) is the mass of dry adsorbent used.

The absorbance value obtained in each case was then used to calculate the percentage adsorption of the dye on ABM [30], by using the formula (3):

$$\%Adsorption = \frac{(A_i - A_t)}{A_i} x100 \qquad (3)$$

where A_i and A_t are the initial and any time t absorbance values, respectively.

3. Results and discussion

3.1. Effect of stirring speed

The variation in the adsorption of MB as a function of stirring speed was studied using 25 mg/L initial dye concentration at 25°C and initial pH solution. The effect of three stirring speeds was investigated: 300, 400 and 500 rpm. It appeared that stirring speed has no important influence on the adsorption of MB. Therefore, the stirring speed was taken at 300 rpm in the follow experiments.

3.2. Effect of contact time and initial dye concentration

The variation of percentage removal of dye with contact time at different initial concentrations from 25 to 100 mg/L at 25°C and initial pH (9.16) of ABM are shown in Figure 4. It's observed that the maximum amount of dye adsorption taking place within the contact time of 10 min and becomes gradual thereafter. This indicates that the rate of adsorption is very fast. Data has been taken up to 15 min of operation which close to attain equilibrium. Thus, after that no significant change in the extent of observed adsorption.

As shown in Figure 4, with increasing initial dye concentration from 25 to 100 mg/L, the amount of dye adsorbed by ABM increases from 75 to 87%. It would be for that a large number of vacant surface sites are available for adsorption during the initial stage of the treatment time, and after a few time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between MB dye adsorbed on the surface of ABM and solution phase. It is clear that the adsorption process is highly dependent on initial concentration of solution.

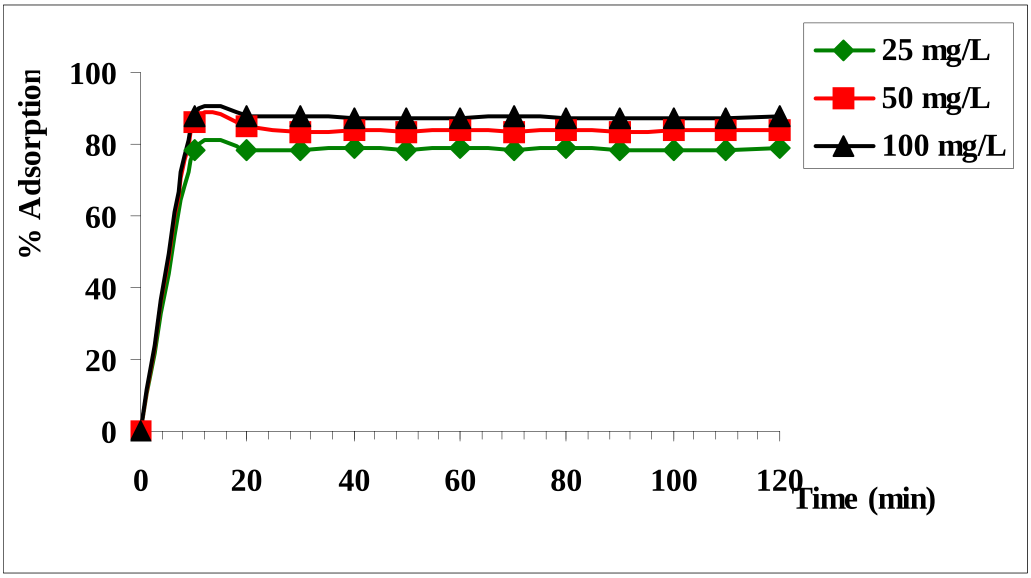

Figure 4: Variation of percent of adsorption with adsorption time and with various initial dye concentrations at 25°C (pH initial, W = 1 g/L)

3.3. Effect of ionic strength

Extensive investigations carried out on adsorption of dyes revealed that the extent of dye uptake was strongly influenced by the concentration and nature of the electrolyte ionic species added to the dye-bath [31]. The effect of inorganic salt (NaCl) on adsorption rate of MB on ABM is presented in Figure 5. So, the presence of inorganic salt has influenced the adsorption rate of MB. The dye adsorption lightly decreases with the increasing chloride sodium concentration, and this effect decrease when increasing the concentration of the dye from 25 to 100 mg/L.

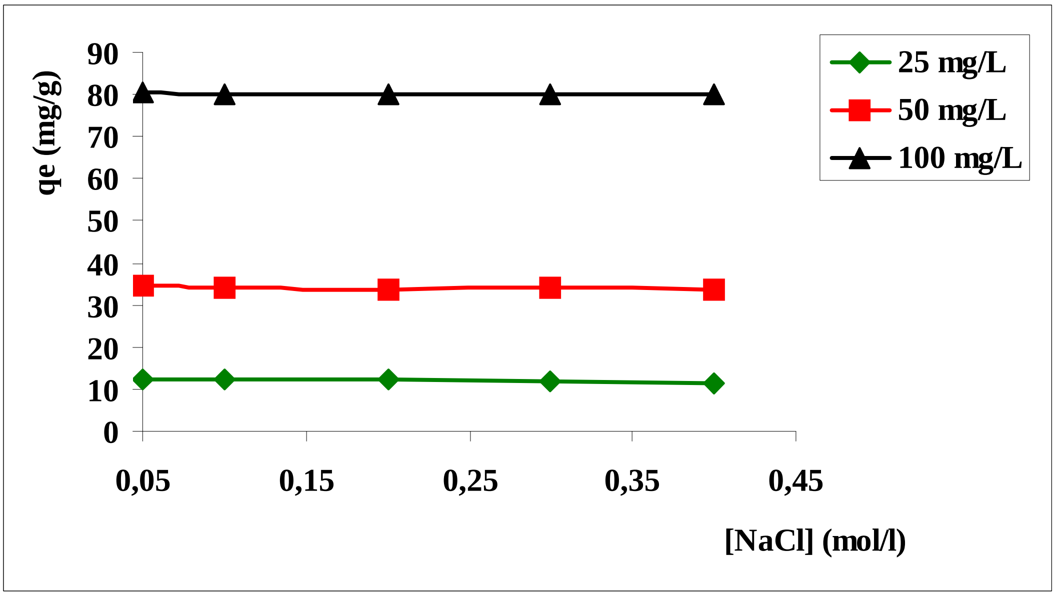

Figure 5: Effect of ionic strength at various initial dye concentrations at 25°C, (pH initial, W = 1 g/L)

3.4. Effect of initial solution pH

The pH is one of the most important factors controlling the adsorption of dye onto suspended particles. The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of different pollutants. The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. Change of pH affects the adsorptive process through dissociation of functional groups on the adsorbent surface active sites [32]. The effect of initial pH of the dye solution on the amount of dye adsorbed was studied by varying pH under constant process parameters (Figure 6). As seen, the removal efficiency of MB increased with increasing initial MB concentration and remained constant values over values of initial pH (2-10) for the dye concentration 100 mg/l. However the solution pH affects the amount of dye adsorbed for the dye concentration 25 and 50 mg/L. The MB adsorption by ABM was significantly affected over the pH range of (2-4) and at higher pH values (5-10) the dye adsorption was almost constant.

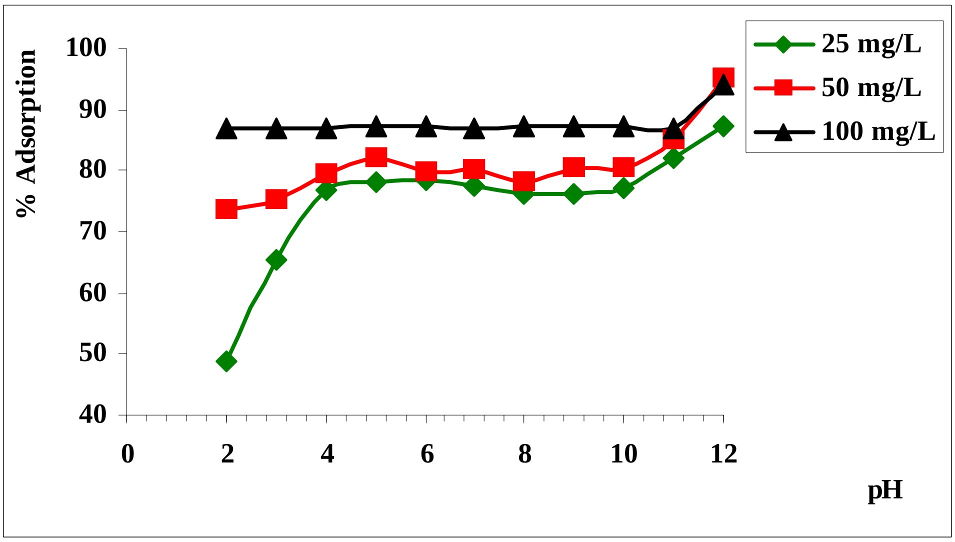

Figure 6: Effect of pH on Methylene blue adsorption (W = 1 g/L, T = 25°C)

3.5. Adsorption kinetics

Adsorption is a physiochemical process that involves the mass transfer of a solute (adsorbate) from the fluid phase to the adsorbent surface. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. The applicability of the pseudo-first-order and pseudo-second-order model was tested for the adsorption of MB onto ABM particles. The best fit model was selected based on the linear regression correlation coefficient, R^2 values.

3.5.1 The first-order kinetic modelg

The Lagergren rate equation is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseudo-first-order kinetic model of Lagergren [33] is represented by the equation (4):

$$\frac{dq_e}{dt} = K_1(q_e - q_t) \tag{4}$$

Integrating this equation for the boundary conditions (t = 0 to t = t and q = 0 to q = q_t), gives the following equation (5):

$$Ln(q_e - q_t) = Lnq_e - K_1 t \tag{5}$$

where q_e and q_t are the amounts of MB adsorbed (mg/g) at equilibrium and at time t (min), respectively, and K_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. The validity of the model can be checked by linearized plot of Ln($q_e - q_t$) *versus* time t. The rate constant of pseudo-first-order adsorption is determined from the slope of the plot. It was found that the application of the first-order kinetic model to the present experimental data gave a poor fit, however, so that it is clearly not appropriate for the (MB-ABM) system.

3.5.2. The second-order kinetic model

Kinetic data were further treated with the pseudo-second order kinetic model [34]. The differential equation is as follows (6):

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{6}$$

where K_2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg.min). Integrating Equation (6) for the boundary condition (t = 0 to t and q_t = 0 to q_t) gives the following equation (7):

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2 t \tag{7}$$

which is the integrated rate law for a pseudo-second-order reaction. Equation (7) can be rearranged to obtain a linear form (8):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where is (q_e) the equilibrium adsorption capacity, and the second-order constants K_2 (g/mol.min) can be determined experimentally from the slope and intercept of plot (t/q_t) *versus* t [35]. The K_2 and q_e values under different conditions were calculated and listed in Table 1.

Table 1 depicts the results of the rate constant studies for different initial dye concentrations by the second-order models. The correlation coefficients for the second-order kinetics model (R^2) are greater than 0.992, and its calculated equilibrium adsorption capacity, $q_{e\ cal}$ is consistent with experimental data. These facts suggest that the pseudo-second-order adsorption mechanism is predominant, and that the overall rate of the dye adsorption process appears to be controlled by the chemisorption process [34, 36].

3.6. Adsorption isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [37].

The Langmuir [38], Tempkin [39] and Freundlich [40] models are commonly used to describe the adsorption isotherm.

The Freundlich equation, which is essentially empirical, is the earliest known relationship describing the adsorption process. The isotherm assumes that adsorbent surface sites have a spectrum of different binding energies.

The Tempkin isotherm contains a factor that explicitly takes into account adsorbing species adsorbate interactions. This isotherm assumes that: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [39].

Application of the Freundlich and tempkin models to the present experimental data gave a poor fit, however, so that it is clearly not appropriate for the (MB-ABM) system.

The adsorption isotherm data were also analyzed on the basis of the Langmuir model. Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer adsorption without interaction between sorbed molecules. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation [41] is represented by the following equation (9):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{9}$$

where q_e is the equilibrium MB concentration on the ABM (mg/g), C_e is the equilibrium MB concentration in the solution (mg/L), q_{max} is the monolayer adsorption capacity of the Adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg). The plots of (C_e/q_e) *versus* C_e for the adsorption of MB onto the ABM at different temperature give a good correlation (Table 2).

Table 1: Kinetic parameters for the removal of MB by ABM

[MB] (mg/L)	[NaCl] (mol/L)	pH	T °C	$q_{e\ exp}$ (mg/g)	Second-order kinetic model		
					K_2 (g/mg.min)	$q_{e\ cal}$ (mg/g)	R^2
25	-	pH_i	15	20.90	0.125	21.74	0.992
	-	pH_i	25	20.05	0.177	20.83	0.997
	-	pH_i	35	19.96	0.054	21.28	0.975
	-	pH_i	45	19.35	0.024	21.28	0.988
50	-	pH_i	15	41.51	0.029	43.48	0.996
	-	pH_i	25	42.01	0.176	43.48	0.999
	-	pH_i	35	43.15	0.106	43.48	0.998
	-	pH_i	45	40.17	0.288	41.67	0.997
100	-	pH_i	15	87.62	0.061	90.91	0.999
	-	pH_i	25	87.60	0.017	90.91	0.998
	-	pH_i	35	87.33	0.121	90.91	0.999
	-	pH_i	45	87.37	0.121	90.91	1.000
25	-	2	25	12.19	3.362	12.20	1.000
	-	5	25	19.57	0.173	19.61	0.998
	-	8	25	19.03	0.901	19.23	0.998
	-	11	25	20.54	0.035	21.28	0.997
50	-	2	25	36.69	0.146	37.04	0.999
	-	5	25	41.08	0.010	43.48	0.996
	-	8	25	39.01	0.625	40.00	0.994
	-	11	25	42.47	0.058	41.67	0.997
100	-	2	25	86.82	0.121	90.91	1.000
	-	5	25	87.28	0.061	90.91	0.999
	-	8	25	87.21	0.121	90.91	1.000
	-	11	25	86.90	0.121	90.91	1.000
25	0.05	pH_i	25	13.46	0.782	13.51	0.997
	0.10	pH_i	25	13.60	0.166	13.70	0.996
	0.20	pH_i	25	13.42	0.148	13.70	0.998
	0.30	pH_i	25	12.59	0.156	12.82	0.996
	0.40	pH_i	25	12.34	0.033	12.99	0.996
50	0.05	pH_i	25	37.50	0.169	38.46	0.999
	0.10	pH_i	25	36.73	0.365	37.04	0.999
	0.20	pH_i	25	36.65	0.243	37.04	0.999
	0.30	pH_i	25	36.73	0.365	37.04	0.999
	0.40	pH_i	25	36.48	0.066	37.04	0.998
100	0.05	pH_i	25	87.40	0.121	90.91	1.000
	0.10	pH_i	25	86.60	0.121	90.91	0.999
	0.20	pH_i	25	86.93	1.210	90.91	1.000
	0.30	pH_i	25	86.50	0.061	90.91	0.999
	0.40	pH_i	25	86.65	0.121	90.91	0.999

Conformation of the experimental data with the Langmuir isotherm model indicates the homogeneous nature of ABM surface, *i.e.*, each dye molecule-ABM adsorption has equal to adsorption activation energy. The results demonstrate also the formation of monolayer coverage of dye molecule at the outer surface of prepared ABM. Values of q_{max} and K_L were calculated from the intercept and slope of the linear plot and are presented in Table 2.

Table 2: Adsorption isotherm constants for adsorption of MB onto ABM

	T °C			
	15	25	35	45
q_{max} (mg/g)	23.8095	22.7272	21.2766	20.8333
K_L (L/mg)	1.2727	1.2941	1.3428	1.3714
R_L	0.0305	0.0299	0.0289	0.0283
R^2	0.998	0.996	0.994	0.996

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor R_L [42], which is defined by the following relationship (10):

$$R_L = \frac{1}{1+K_L C_0} \tag{10}$$

Where C_0 is the highest initial solute concentration, K_L is the Langmuir's adsorption constant (L/mg). The R_L value implies the adsorption to be unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L = 0$). Values of R_L listed in Table 2 confirme that the prepared ABM is favorable for adsorption of MB dye under conditions used in this study.

3. 7. Estimation of activation energy

The magnitude of activation energy may give an idea about the type of adsorption. There are two main types of adsorption: physical and chemical. Activated chemical adsorption means that the rate varies with temperature according to activation energy comprised an (8.4-83.7 kJ/mol) in the Arrhenius equation. In non activated chemical adsorption, the activation energy is near zero [40].

The activation energy for MB adsorption was calculated by the Arrhenius equation [43, 44] as is defined by the following relationship (11):

$$K_2 = K_0 \exp(-\frac{E_a}{RT}) \tag{11}$$

Where K_0 (g/mg.min) is the temperature independent factor, E_a (kJ/mol) is the apparent activation energy of the reaction of adsorption, R (8.314 J/mol.K) is the gas constant, T is the adsorption absolute temperature and K_2 the linear form [45] is expressed by the following equation (12):

$$LnK_2 = -\frac{E_a}{RT} + LnK_0 \tag{12}$$

When Ln K_2 is plotted *versus* (1/T), a straight line with slope ($-E_a/R$) is obtained. The values of rate constant obtained analysis according to the pseudo-second-order can be used to calculate the activation energy of adsorption process. The energy of activation E_a was determined from the slope of the Arrhenius plot of Ln K_2 *versus* (1/T) according to Equation (12) and was found to be 25.2, 56.2 and 18.9 kJ/mol at the initial concentration of 25, 50 and 100 mg/L. This value, which is in the range of chemical adsorption, shows that MB adsorption is of a chemical nature. The thermodynamic parameters, namely free energy ΔG°, enthalpy ΔH° and entropy ΔS° have an important role to determine spontaneity and heat change for the adsorption process. Equilibrium constant can be used to evaluate the thermodynamic parameters [46]. The very useful relationship between standard free energy change and equilibrium constant [47] is given by the following equation (13):

$$\Delta G^0 = -RTLnK_L \tag{13}$$

where R is the universal gas constant, T is the temperature (K) and K_L value was calculated [41], using the following equation (14):

$$K_L = \frac{q_e}{C_e} \tag{14}$$

where q_e and C_e are the equilibrium concentration of MB ions on the ABM (mg/g) and in the solution (mg/L), respectively.

The enthalpy change ΔH° and entropy change ΔS° of the adsorption were estimated from the following equation (15):

$$LnK_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (15)$$

The values of ΔH° and ΔS° were determined from the slopes and intercept, of the linear plot of Ln K_L *versus* (1/T). Table 3 lists the calculated thermodynamic parameters.

Table 3: Thermodynamic parameters for the adsorption of MB onto ABM

[MB] (mg/L)	ΔH° (kJ/mol)	ΔS° (J/mol.K)	ΔG° (kJ/mol)			
			288.15 K	298.15 K	308.15 K	318.15 K
25	-9.33	-19.10	-3.90	-3.47	-3.53	-3.26
100	-0.758	13.64	-4.69	-4.85	-4.93	-5.12

The negative values of ΔG° of MB adsorption onto ABM were due to the fact that the adsorption processes were spontaneous with a high preference of MB onto ABM. For the low concentration of MB (25 mg/L), the negative value of ΔG° increases with an increase in temperature, indicating that the adsorption of MB is not spontaneous nature and higher temperature unfavorable the adsorption. The negative value of ΔS° (-19.1 J/K.mol) indicates that the adsorption leads to order through the formation of activated complex suggesting that methylene blue adsorption on ABM surface is an associated mechanism. Also the negative value of ΔS° normally reflects that no significant change occurs in the internal structure of the adsorbent during the adsorption process [28, 48]. For the high concentration of MB (100 mg/L), the negative value of ΔG° decreases with an increase in temperature, indicating that the spontaneous nature of adsorption of MB were inversely proportional to the temperature and higher temperature favored the adsorption, while the positive values of ΔS° (13.64 J/K.mol) corresponds to an increased degree of freedom in the system as a result of adsorption of the MB molecules [49]. The negative value of ΔH° suggests the exothermic nature of adsorption for the ABM.

4. Conclusion

The present study shows that The ABM was successfully used as an adsorbent for the quantitative removal of MB from aqueous solutions. The equilibrium adsorption is practically achieved in less than 15 min. Equilibrium data fitted well in the Langmuir model of adsorption, showing monolayer coverage of dye molecules at the outer surface of ABM. The value of R_L was found between 0 and 1, which confirmed that the prepared ABM is favorable for adsorption of MB dye blue. Kinetics of MB adsorption onto ABM followed the pseudo-second-order model. Thermodynamics parameters indicated spontaneous and exothermic process.

5. References

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