Cationic Dye (Methylene Blue) Removal from Aqueous Solution by Montmorillonite

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Color impurity in industrial effluents pose a significant risk to human health and the environment, so much effort has been expended to degrade them using various methods, including the use of clay minerals as adsorbent. The purpose of this study was to advance understanding of the mechanisms for the removal of methylene blue (MB) from aqueous solutions onto montmorillonite as an adsorbent. Preliminary experiments showed that montmorillonite was effective for this purpose and adsorption equilibrium could be reached in about 24 h. Adsorption capacity of the clay decreased with increase in temperature and ionic strength, and increased with in pH. The fitness of equilibrium data to common isotherm equations such as the Langmuir, Freundlich, Elovich, Temkin and Dubinin-Radushkevich were tested. The Langmuir equation fitted to equilibrium data better than all tested isotherm models. Thermodynamic activation parameters such as ΔG^0, ΔS^0 and ΔH^0 were also calculated and results were evaluated. As result montmorillonite clay was found as effective low cost adsorbent for removal of cationic dyes from waste waters.

Key Words : Montmorillonite, Methylene blue, Clay, Adsorption isotherms, Thermodynamic

Introduction

Dye effluents from dye manufacturing and dye consuming industries such as food, paper, plastic, textile, *etc.* are one of the most problematic water pollution causes. Besides, most of the dyes are resistant to biodegradation and release of the effluents to the aquatic medium increases the biological load.[1] The discharge of these effluents to receiving environments results in serious health problems as some dyes (*e.g.* Azo dyes) are of carcinogenic effects on the living organisms.[2] Dyes in surface waters are of barrier effect on the sun light penetration and aeration of water body, and thus reduce photosynthetic activity. The toxic nature of the dye effluents causes to death of soil microorganisms when they are used for irrigation purposes and this affects agricultural productivity.[3]

Methylene blue (MB) is the cationic dye that is most commonly used for coloring. It is generally used for dyeing cotton, wool, and silk. MB can cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, dyspnea, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, nausea, vomiting, and diarrhea.[4]

Therefore, decolonization of dyes is important aspects of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems. Generally biological aerobic wastewater systems are not successful for decolonization of majority of dyes. Therefore, color removal was extensively studied with physco-chemical methods as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation.[5] Adsorption is widely used in the removal of contaminants from wastewaters. The design and efficient operation of adsorption processes require equilibrium adsorption data. The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems.[6]

Activated carbon is the effective alternate for the concentration of dye ions even in the case of lower solute concentration. However activated carbon adsorption is limited due to the high cost of activated carbon and the cost involved in regenerating it. The use of cheap adsorbents for the removal of color from its aqueous solution will provide as a potential alternate to the conventional treatment techniques. Recent investigations by several researchers proved onto use of low-cost, reusable, locally available, biodegradable adsorbent made from natural sources like peat,[6] coconut husk,[7] chitosan,[8] mesoporous silica,[9,10] chitosan-*g*-poly (acrylic acid)/montmorillonite nanocomposite,[11] bituminous coal,[12] activated palm ash,[13] palygorskite,[14] kudzu,[15] fly ash[16] and peanut husk.[17] Natural and modified clays like kaolinite,[18,19] activated clay,[20] vermiculite,[21,22] clinoptilolite,[23] smectite,[24,25] natural and modified zeolites,[26] Maghnia montmorillonite,[27] perlite[28] and bentonite[29,30] are being considered as alternative low-cost adsorbents. A large variety of non-conventional adsorbent materials have been also proposed and studied for their ability to remove dyes.[31]

The main objects of this paper are: (i) to study the feasibility of using montmorillonite as an adsorbent for the removal of a cationic dye, methylene blue, (ii) to determine the various parameters affecting sorption, such as pH, ionic strength and temperature, (iii) to determine the applicability of various isotherm models (*i.e.*, Langmuir, Freundlich,

Table 1. Chemical composition of montmorillonite (a) and physicochemical properties of montmorillonite (b)

	Component	Weight (%)
	SiO_2	49.40
	Al_2O_3	19.70
(a)	MgO	0.27
	CaO	1.50
	Fe_2O_3	0.30
	Na_2O	1.50
	H_2O	25.67

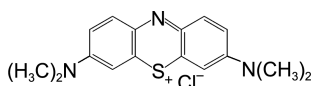|	Parameters	Value
	Color	White
	Density (g/cm^3)	2.3-3
(b)	Transparency	Semi-transparent and opaque
	Brightness	Matt
	Surface area (m^2/g)	95.36
	Reflective index	1-2

Temkin, Elovich and Dubinin-Radushkevich) to find out the best-fit isotherm equation, and (iv) to determine thermodynamic and kinetic parameters and explain the nature of adsorption.

Material and Methods

Materials. The montmorillonite sample was obtained from Süd-Chemie Processing Plants (Balikesir, Turkey). The chemical composition and physicochemical properties of the montmorillonite found in Turkey were given in Table 1. The montmorillonite sample was treated before using in the experiments as follows: the bulk containing 10 g L^{-1} montmorillonite was mechanically stirred for 24 h, after waiting for about two minutes the supernatant suspension was filtered through a what-man filter paper (Φ = 12.5 cm (diameter of filter paper)). The solid sample was dried at 110 ^{o}C for 24 h, and then sieved by 45-90 mesh sieve. The specific surface area of montmorillonite was measured by BET N_2 adsorption.

All reagents were of analytical grade chemicals. All solutions were prepared with double distilled water. The cationic dye used in this study, MB was purchased from Merck Co., Germany. MB has a molecular weight of 373.9 g mol^{-1} and its chemical formula is $C_{16}H_{18}ClN_3S \cdot 3H_2O$.[32] The structure of MB dye is illustrated (Fig. 2) MB concentration in the sample solution was determined using a spectrophotometer (UNICAM UV-visible spectrophotometer) at a wavelength of 663 nm.[33] Calibration curves were plotted between absorbance and concentration of the dye solution.

Methods. The adsorption of methylene blue from aqueous

Figure 1. The structure of methylene blue.

solution onto montmorillonite was performed using batch equilibrium technique. The adsorption tests were continued until the equilibrium concentration was reached. The effect of contact time on the amount of dye adsorbed was investigated as a function of initial concentration of dye, pH, ionic strength and temperature. Each polyethylene flask was filled with 50 ml of a dye solution of varying concentrations (1×10^{-4} - 24×10^{-4} mol L^{-1}) and adjusted to the desired pH, ionic strength and temperature. 0.075 g of adsorbent was added to each polyethylene flask and agitated for the desired time periods; up to a maximum of about 24 h. Equilibration for longer times gave practically the same uptake. Therefore, a contact periods; up to 24 h was finally selected for all of the equilibrium tests. At the end of the adsorption period, the solution were centrifuged for 15 min at 5000 rpm and then the concentrations of the residual dye, C_e, was determined with a spectrophotometer (UNICAM UV-visible spectrophotometer) at a 663 nm wavelength, at which the maximum absorbency occurred. Blanks containing no dye were used for each series of experiments. The effect of pH was observed by studying the adsorption of dye over a pH range of 5-9. The pH of the solution was adjusted with 1 mol L^{-1} NaOH or HCl solution by using an Orion 920 a pH-meter equipped with a combined pH electrode. The sorption studies were also carried out at different temperatures, *i.e.*, 303, 313, 323 and 333 K, to determine the effect of temperature and to evaluate the sorption thermodynamic parameters. A thermostatic shaker bath was used to keep the temperature constant.

The amounts of dye adsorbed were calculated from the concentrations in solutions before and after adsorption. Each experimental point was an average of two independent adsorption tests.[34]

Following formula was used to determine adsorbed dye concentration q_e:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e (mol g^{-1}) is the amount of dyes adsorbed (mol g^{-1}), C_0 (mol L^{-1}) is the initial dye concentration, C_e (mol L^{-1}) is the concentration of dye in solution at equilibrium, V (L) is the volume, and m (g) is the amount of the adsorbent.

Result and Discussion

Adsorption Isotherm.
Langmuir Isotherm: The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface.[35] Graphically, a plateau characterizes the Langmuir isotherm. Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. Once a dye molecule occupies a site, no further adsorption can take place at that site. Langmuir isotherm can be given as follows.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

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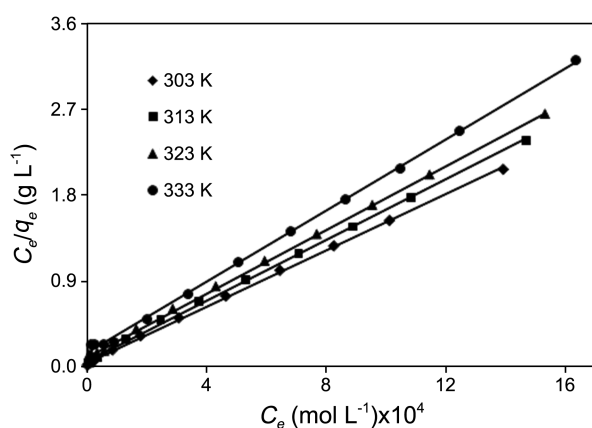
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Figure 2. Langmuir isotherm for methylene blue dye adsorption onto montmorillonite at different temperatures (natural pH, ionic strength 0 mol/L NaCl, 150 rpm of stirrer speed, adsorbent dosage 0.075 g/50 mL and contact time 24 h.)
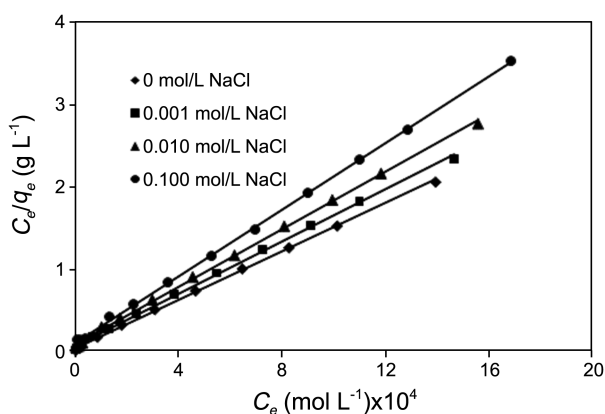

Figure 4. Langmuir isotherm for methylene blue dye adsorption onto montmorillonite at different pHs (temperature at 303 K, ionic strength 0 mol/L NaCl, 150 rpm of stirrer speed, adsorbent dosage 0.075 g/50 mL and contact time 24 h.)

Figure 3. Langmuir isotherm for methylene blue dye adsorption onto montmorillonite at different ionic strengths (temperature at 303 K, natural pH, 150 rpm of stirrer speed, adsorbent dosage 0.075 g/50 mL and contact time 24 h.)
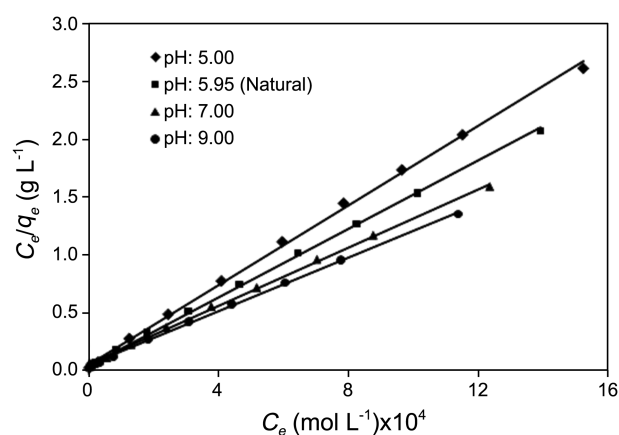
when linearized, Eq. (2) becomes

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \qquad (3)$$

where, q_e is the adsorbed amount at equilibrium (mol g^{-1}), q_m maximum adsorption capacity (mol g^{-1}), K_L. Values of K_L and q_m were calculated from the intercept and slope of the plots of C_e/q_e versus C_e (Eq. 3). The linear plots of C_e/q_e versus C_e (Figs. 2-4) show a good agreement between experimental. The results were illustrated (Table 2).

The shape of the isotherm may also be considered with a view to predicting if an adsorption system is 'favorable' or 'unfavorable'. The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L,[36] which is defined by;

Table 2. Isotherm constants for methylene blue adsorption onto montmorillonite

Parameters			Isotherm Models																
			Langmuir isotherm			Freundlich isotherm			Temkin isotherm			Elovich isotherm			Dubinin-Radushkevich isotherm			
Temperature	pH	Ionic strength (mol L^{-1})	q_m ($\times 10^4$)	K_L	R^2	K_F ($\times 10^3$)	$1/n$	R^2	K_T ($\times 10^{-5}$)	b ($\times 10^{-6}$)	R^2	q_m ($\times 10^5$)	K_E ($\times 10^{-4}$)	R^2	q_m ($\times 10^4$)	B ($\times 10^{10}$)	E	R^2
303	5.95	0	6.766	61.189	0.999	6.181	0.300	0.881	17.240	27.646	0.976	13.571	90.918	0.920	15.755	-24.503	14.285	0.930
313	5.95	0	6.297	92.263	0.999	5.873	0.309	0.873	10.796	29.239	0.982	13.368	57.103	0.919	14.858	-24.317	14.339	0.918
323	5.95	0	5.992	173.576	1.000	8.365	0.372	0.857	3.185	26.777	0.970	17.054	11.911	0.853	17.294	-29.193	13.087	0.902
333	5.95	0	5.362	277.885	0.999	8.653	0.398	0.834	1.945	28.645	0.949	17.988	5.726	0.772	16.878	-30.487	12.806	0.882
303	5.95	**0**	6.766	61.189	0.999	6.181	0.300	0.881	17.240	27.646	0.976	13.571	90.918	0.920	15.755	-24.503	14.285	0.930
303	5.95	**1 × 10^{-3}**	6.274	106.320	0.999	5.901	0.312	0.915	10.381	28.682	0.989	13.012	58.290	0.956	14.436	-25.843	13.910	0.954
303	5.95	**1 × 10^{-2}**	5.721	167.983	0.999	6.349	0.341	0.902	4.844	28.334	0.985	13.881	23.542	0.931	14.475	-29.523	13.014	0.943
303	5.95	**1 × 10^{-1}**	4.953	238.242	1.000	5.855	0.353	0.868	3.159	30.358	0.965	13.742	12.821	0.862	13.357	-31.82	12.535	0.912
303	**5.00**	0	5.804	85.289	0.999	4.277	0.276	0.865	21.692	33.544	0.967	10.984	120.087	0.902	12.473	-22.896	14.778	0.916
303	**5.95**	0	6.766	61.189	0.999	6.181	0.300	0.881	17.240	27.646	0.976	13.571	90.918	0.920	15.755	-24.503	14.285	0.930
303	**7.00**	0	7.911	69.267	0.999	13.031	0.377	0.870	5.446	19.973	0.976	21.187	20.578	0.884	24.259	-31.894	12.521	0.919
303	**9.00**	0	8.554	49.215	0.999	14.593	0.374	0.839	6.860	18.721	0.968	23.053	23.980	0.841	27.130	-31.358	12.627	0.891

$$R_L = \frac{1}{1 + K_L C_e} \qquad (4)$$

The value of R_L indicates the type of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values found in the present study were in the range of 0.999986-1.000000 indicating that adsorption of MB by montmorillonite was favorable ($0 < R_L < 1$).

Freundlich Isotherm: The Freundlich equilibrium isotherm equation[37] was also used to describe experimental adsorption data. This isotherm is an empirical equation which is used for the description of multilayer adsorption with interaction between adsorbed molecules. The Freundlich equation is generally expressed as follows:

$$q_e = K_F C_e^{1/n} \qquad (5)$$

The linear expression takes the following form:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

where, q_e is the adsorbed amount at equilibrium (mol g^{-1}), K_F the Freundlich equilibrium constant (mol g^{-1})/(mol L^{-1})$^{1/n}$, $1/n$ is indicative of the energy or intensity of the reaction and suggests the favorability and capacity of the adsorbent/adsorbate system. To determine the constant K_F and $1/n$, may be used to plot $\ln q_e$ against $\ln C_e$. The results were illustrated (Table 2).

Elovich Isotherm: The equation defining the Elovich model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. It is expressed by the relation:[38]

$$\frac{q_e}{q_m} = K_E C_e \exp\left(-\frac{q_e}{q_m}\right) \qquad (7)$$

when linearized, Eq. (7) becomes

$$\ln\frac{q_e}{C_e} = \ln K_E q_m - \frac{1}{q_m} q_e \qquad (8)$$

where K_E is the Elovich equilibrium constant (L mol^{-1}) and q_m is the Elovich maximum adsorption capacity (mol g^{-1}). If the adsorption obeys Elovich equation, Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the plot $\ln (q_e/C_e)$ versus q_e. The results were illustrated (Table 2).

Temkin Isotherm: Temkin considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms.[39] He suggested that, because of these interactions and ignoring very low and very large values of concentration, the heat of adsorption of all molecules in the layer would decrease linearly with coverage.

$$q_e = \frac{RT}{b} \ln (K_T C_e) \qquad (9)$$

when linearized, Eq. (9) becomes

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \qquad (10)$$

where q_e is the fractional coverage, R the universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), T the temperature (K), $b = (-\Delta H)$ the variation of adsorption energy (kJ mol^{-1}), and K_T is the Temkin equilibrium constant (L mol^{-1}). Values of K_T and b were calculated from the intercept and slope of the plots of q_e versus $\ln C_e$. The results were illustrated (Table 2).

Dubinin-Radushkevich (D-R) Isotherm: The D-R equation[40] is given as:

$$q_e = q_m \exp(B\varepsilon^2) \qquad (11)$$

where q_m the monolayer adsorption capacity (mol g^{-1}) and B the activity coefficient related to mean sorption energy (mol^2 J^{-2}) and ε is the Polanyi potential are the D-R constants and ε can be correlated as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (12)$$

The constant B gives the mean free energy E (kJ mol^{-1}) of sorption per molecule of sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the following relationship:[41]

$$E = \frac{1}{\sqrt{-2B}} \qquad (13)$$

when linearized, Eq. (11) becomes

$$\ln q_e = \ln q_m - B\varepsilon^2 \qquad (14)$$

The adsorption isotherm constant q_m and B, can be determined experimentally by plotting of $\ln q_e$ versus ε^2. The results were illustrated (Table 2).

The capacity of montmorillonite for MB can be determined by measuring equilibrium isotherms. Basically, adsorption isotherm is important to describe how adsorbate interacts with adsorbents. The relationship between the amount of adsorbate adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at the equilibrium can be given by the adsorption isotherms. The equilibrium adsorption isotherm of MB on the montmorillonite was showed (Figs. 2-4). It exhibits a steep increased at low concentrations, indicating high affinity towards the solute. At high MB concentrations, the adsorbed amounts increased slightly, showing almost horizontal plateaus. Adsorption isotherm study was carried out on five isotherm models: the Langmuir, Freundlich, Temkin, Elovich and Dubinin-Radushkevich isotherm models. The applicability of the isotherm equation to describe the adsorption process was judged by the correlation coefficients, R^2 values. The correlation coefficient, R^2 between 0.999-1.000 indicated that the adsorption data of MB on the montmorillonite was well fitted to the Langmuir isotherm. The Langmuir constants K_L and q_m were calculated from Eq. (3) (Table 2). The fitness of experimental data to Langmuir isotherm equation indicated the homogeneous nature of montmorillonite surface, *i.e.*,
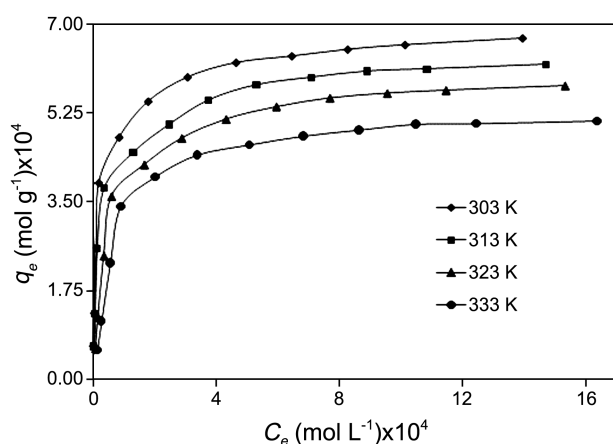
Figure 5. The effect of temperature on the adsorption of methylene blue on montmorillonite (natural pH, ionic strength 0 mol/L NaCl, 150 rpm of stirrer speed, adsorbent dosage 0.075 g/50 mL and contact time 24 h.)

Figure 6. The effect of ionic strength on the adsorption of methylene blue on montmorillonite (temperature at 303 K, natural pH, 150 rpm of stirrer speed, adsorbent dosage 0.075 g/50 mL and contact time 24 h.)

Figure 7. The effect of pH on the adsorption of methylene blue on montmorillonite (temperature at 303 K, ionic strength 0 mol/L NaCl, 150 rpm of stirrer speed, adsorbent dosage 0.075 g/50 mL and contact time 24 h.)

each dye molecule/montmorillonite adsorption had equal adsorption activation energy. The results also demonstrated the formation of monolayer coverage of dye molecule at the outer surface of montmorillonite. Similar observations were reported by the adsorption of MB on fibrous clay minerals,[42] methyl violet on perlite[43] and methylene blue on chitosan-*g*-poly (acrylic acid)/vermiculite hydrogel composites.[21]

Adsorption Equilibrium.

Effect of Temperature: In this section of study, a series of experiments were conducted at 303, 313, 323 and 333 K to study the effect of temperature to the adsorption of MB dye on montmorillonite. The adsorption of MB dye has decreased with increasing temperature (Fig. 5). Similar observations have been reported in the literature.[7,44] When temperature increased, the physical bonding between the organic compounds (including dyes) and the active sites of the adsorbent weakened. Besides, the solubility of MB also increased with increase in temperature and, therefore the dye was more difficult to adsorb. The result may be attributed to that changing temperature could change the equilibrium capacity of the adsorbent for a particular adsorbate.[33,45]

Effect of Ionic Strength: To observe the effect of ionic strength on adsorption capacity, 0-0.1 mol L^{−1} NaCl concentration was studied by keeping parameters constant temperature at 303 K, natural pH, 150 rpm of stirrer speed and contact time 24 h. Ionic strength is the most important variable in dye-clay interaction.[46] In the present study, ionic strength of the solution exhibited some effect on adsorption of montmorillonite. The amount of MB adsorbed onto montmorillonite was decreased with increasing concentration of NaCl in solution (Figure 6). This result was similar to the investigation of Narine and Guy[46] and Yu-Long Ma *et al.*,[47] who studied the variation in adsorption of MB on bentonite as a function of ionic strength. The reason for this is that, hydrated cations in the aqueous phase compete effectively for the adsorption sites on the clay. On the other hand, "ionic atmosphere may be progressively formed around MB molecules with increased NaCl concentration and results
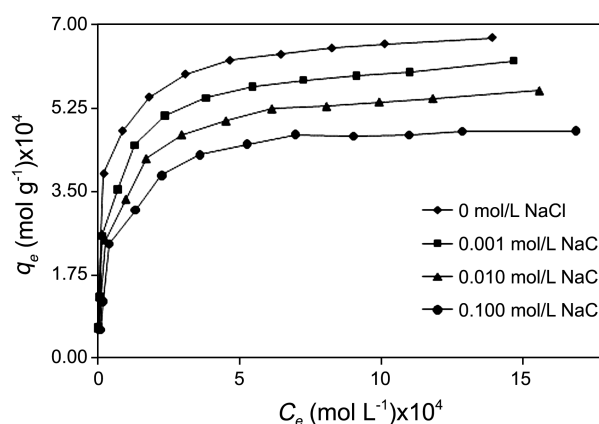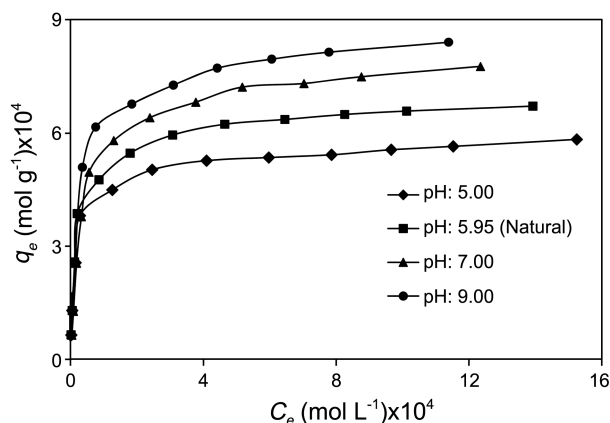
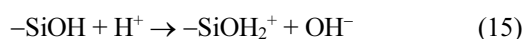in the reduction of MB adsorption onto montmorillonite.

Effect of pH: The pH is one of the most important factors controlling the adsorption of dye onto adsorbent. Adsorption of MB onto montmorillonite was carried out for the examination of the effect of pH at a range of 5.00-9.00 and it was found that the adsorption capacity increased with increase in pH (Figure 7). Figure showed that at low pH value, the adsorption was decreased. When solution pH increased from 5.00 to 9.00, the adsorption increased. The maximum dye uptake was observed in the pH range of 9.00. The basic dyes give positively charged ions when dissolved in water. Thus, in acidic medium positively charged surface of sorbent tends to oppose the adsorption of cationic sorbate species. When the pH of dye solution is increased the surface tends to acquire negative charge, thereby resulting in an increased adsorption of dyes due to increasing electrostatic attraction between positively charged sorbate and negatively charged sorbent.[48]

As the pH of the aqueous phase is lowered, a solid surface will usually become more positive, or less negative, because
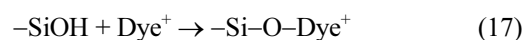
Table 3. Thermodynamic parameters for the adsorption of methylene blue onto montmorillonite at different temperatures

Dye concentration ($\times 10^{-4}$ mol L^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (kJ mol^{-1} K^{-1})	ΔG^0 (kJ mol^{-1})			
			303 K	313 K	323 K	333 K
8.00	-28.788	-0.081	-4.203	-3.392	-2.580	-1.769
12.00	-20.806	-0.063	-1.662	-1.030	-0.398	0.234
16.00	-15.115	-0.050	-0.013	0.486	0.984	1.482
20.00	-12.992	-0.046	1.045	1.508	1.972	2.435
24.00	-11.966	-0.045	1.803	2.257	2.712	3.166

of adsorption onto charged sites of protons from the solution, with consequent increase in the adsorption of anionic surfactants and decrease in the adsorption of cationics. At acidic media, electrostatic repulsion occurred between the dye ions and the edge groups with positive charge (Si-OH^{2+}) on the surface as follows:

$$-SiOH + H^+ \rightarrow -SiOH_2^+ + OH^- \qquad (15)$$

In an alkaline medium (pH > 7), the surface of montmorillonite clay becomes negatively charged and electrostatic repulsion decreases with raising pH due to reduction of positive charge density on the sorption edges thus resulting in an increase dye adsorption. This mechanism can be shown as follows:

$$-SiOH + OH^- \Leftrightarrow -SiO^- + H_2O \qquad (16)$$

$$-SiOH + Dye^+ \rightarrow -Si-O-Dye^+ \qquad (17)$$

The pH value of the solution is an important parameter for the adsorption processes, and the initial pH value of the solution has significant influence compared to than the final pH. In general, initial pH value may enhance or depress the uptake. This is attributed to the charge of the adsorbent surface with the change in pH value. Figure 7 showed the relationship between the pH value and the removal of methylene blue. It could be seen from the figure that as the solution pH increases, the adsorption capacity increases. Increasing solution pH increases the number of hydroxyl groups thus, increases the number of negatively charge sites and enlarges the attraction between dye and adsorbent surface. Generally, the net positive charge decreases with increasing pH value lead in the decrease in the repulsion between the adsorbent surface and the dye thus, improving the adsorption capacity.[46]

Heat of Adsorption. The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic van't Hoff equation

$$\Delta G^0 = -RT \ln K \qquad (18)$$

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (19)$$

Combining above two equations, we get

$$\ln K = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \cdot \frac{1}{T} \qquad (20)$$

Where ΔG^0 the free energy change (kJ mol^{-1}) is, ΔH^0 is the change enthalpy (kJ mol^{-1}), ΔS^0 is entropy change (kJ mol^{-1} K^{-1}), $K = (q_e/C_e)$ is constant (L g^{-1}), is absolute temperature (K) and Rg is the universal gas constant (8.314 J mol^{-1} K^{-1}). Thus ΔH^0 can be determined by slope of the linear van't Hoff plot *i.e.* as $\ln K$ *vs.* $(1/T)$, using equation:[49]

$$-\frac{\Delta H^0}{Rg} = \left[\frac{\partial(\ln K)}{\partial(1/T)}\right] \qquad (21)$$

The values of ΔH^0, ΔS^0 and ΔG^0 for the initial dye concentrations of 8×10^{-4} - 24×10^{-4} were shown (Table 3). The exothermic nature is also indicated by the decrease in the amount of adsorption with temperature (Fig. 8). The value of the enthalpy change indicates that the adsorption is physical in nature involving weak forces of attraction.[36] In general, the adsorption process was exothermic with heats of adsorption for the concentration range of the dye solution. These values did not indicate strong chemisorptive bond formation between the dye molecules and the adsorbent surface.[50] Similar result was also found for the adsorption of MB on coconut husk.[7] ΔG^0 values for 8×10^{-4} and 12×10^{-4} mol L^{-1} at 303, 313 and 323 K were negatives but other values were positives (Table 3). The negative values of ΔG^0 indicated that dye adsorption by montmorillonite was spon-
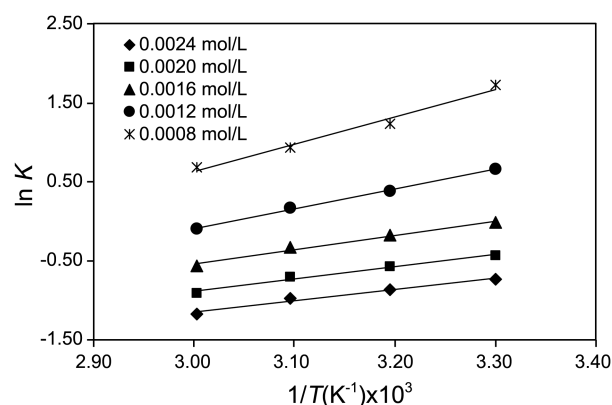

Figure 8. Plots of $\ln K$ *versus* $1/T$ for adsorption of methylene blue on montmorillonite (natural pH, ionic strength 0 mol/L NaCl, 150 rpm of stirrer speed, adsorbent dosage 0.075 g/50 mL and contact time 24 h.)

taneous at lower temperatures and lower concentrations. Increasing of temperatures and concentrations caused the decreasing of feasibility of dye uptake. Similar thermodynamics values for cationic dyes removal was found in literature.[51] Negative values of ΔS^0 reveal the decreased randomness at the solid-solution interface during dye removal.[52]

Conclusions

The present study showed that montmorillonite was an effective adsorbent for the removal of methylene blue from aqueous solution. The results suggested that the adsorption capacity of methylene blue on montmorillonite adsorbent increased with increasing pH, but decreased with increased ionic strength and temperature. Equilibrium data were fitted to Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Elovich isotherms and the equilibrium data were best described by the Langmuir isotherm model. The negative ΔH^0 value confirmed the exothermic nature of the adsorption interaction. Negative values of ΔS^0 reveal the decreased randomness at the solid-solution interface during dye removal. The negative values of ΔG^0 indicate that dye adsorption by montmorillonite was spontaneous at lower temperatures and lower concentrations. Increasing of temperatures and concentrations caused the decreasing of feasibility of dye uptake.

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