



Adsorption of Methyl Violet Dye, A Textile Industry Effluent onto Montmorillonite—Batch Study

Erdoğan Aladağ , Baybars Ali Fil , Recep Boncukcuoğlu , Onur Sözüdoğru & Alper Erdem Yılmaz

To cite this article: Erdoğan Aladağ , Baybars Ali Fil , Recep Boncukcuoğlu , Onur Sözüdoğru & Alper Erdem Yılmaz (2014) Adsorption of Methyl Violet Dye, A Textile Industry Effluent onto Montmorillonite—Batch Study, Journal of Dispersion Science and Technology, 35:12, 1737-1744, DOI: [10.1080/01932691.2013.873865](https://doi.org/10.1080/01932691.2013.873865)

To link to this article: <https://doi.org/10.1080/01932691.2013.873865>



Accepted author version posted online: 19 Dec 2013.
Published online: 25 Aug 2014.



Submit your article to this journal [↗](#)



Article views: 310



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 16 View citing articles [↗](#)

Adsorption of Methyl Violet Dye, A Textile Industry Effluent onto Montmorillonite—Batch Study

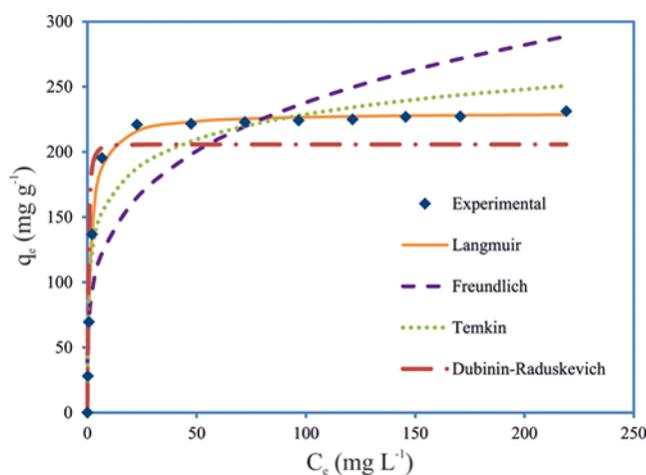
Erdinç Aladağ,¹ Baybars Ali Fil,^{2,3} Recep Boncukcuoğlu,² Onur Sözüdoğru,² and Alper Erdem Yılmaz²

¹Faculty of Engineering and Architecture, Department of Environmental Engineering, Yüzüncü Yıl University, Van, Turkey

²Department of Environmental Engineering, Engineering Faculty, Ataturk University, Erzurum, Turkey

³Department of Environmental Engineering, Engineering Faculty, Balikesir University, Balikesir, Turkey

GRAPHICAL ABSTRACT



In this study, methyl violet (MV) dye adsorption from synthetically prepared solutions onto montmorillonite was investigated. Experimental parameters were selected as stirring speed, adsorbent dosage, initial dyestuff concentration, initial solution pH, ionic strength, and temperature. It was determined that adsorption rate increased with increased stirring speed, initial dye concentration, solution pH, ionic strength, and temperature, but decreased with increased adsorbent dosage. The experimental data were analyzed by Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms, and it was found that the isotherm data were reasonably correlated by Langmuir isotherm. Maximum adsorption capacity of montmorillonite for MV dye was calculated as 230.04 mg g⁻¹. Pseudo-first-order, pseudo-second-order, Elovich, and intraparticle particle diffusion models were used to fit the experimental data. Pseudo-second-order rate equation provided realistic description of adsorption kinetics. Thermodynamic parameters were calculated as 62.14 kJ mol⁻¹, 59.55 kJ mol⁻¹, 51.98 kJ mol⁻¹, and 0.0242 kJ mol⁻¹ K⁻¹ for E_a , ΔH° , ΔG° , and ΔS° at 293 K, respectively. The value of the calculated parameters indicated that the physical adsorption of MV on the clay was dominant and the adsorption process was also endothermic. The positive values of ΔS° suggest the increased randomness. The positive ΔG° value indicated the un-spontaneous nature of the adsorption model.

Keywords Adsorption, isotherm models, kinetic models, methyl violet, montmorillonite

Received 14 October 2013; accepted 7 December 2013.

Address correspondence to Onur Sözüdoğru, Department of Environmental Engineering, Engineering Faculty, Ataturk University, 25240 Erzurum, Turkey. E-mail: cm.onursozudogru@gmail.com

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/ldis.

1. INTRODUCTION

There are more than 100,000 types of dyes commercially available, with over 7×10^5 tons of dyestuff produced annually, which can be classified according to their structure as anionic and cationic. In aqueous solution, anionic dyes carry a net negative charge due to the presence of sulfonate (SO_3^-) groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups.^[1]

Dyes are widely used for dyeing of products in cotton, plastic, textile and in addition to the food and paper-making industries. Wastewaters discharged from the industries such as textile, plastic, paper can cause serious environmental problems. Dyes usually have a synthetic origin and complex chemical structure which makes them very stable to light and oxidation and very difficult to biodegrade.^[2] Most of the dyes are toxic and carcinogenic compounds; they are also recalcitrant and thus stable in the receiving environment, posing a serious threat to human and environmental health.^[3,4] Dyes and pigments cause decay of the soil. When dyes are mixed to the surface waters they reduce photosynthetic activity in the aqueous mediums by impeding the sunlight penetration to the water.^[5,6] Environmental research requires special attention to dye compounds because of the extensive environmental contamination arising from dyeing operations.^[7]

Methyl violet (MV) is a member of the basic dyes, a group with high brilliance and intensity of colors and that inhibits photosynthesis of aquatic plants.^[8] Constant exposure to MV can cause eye and skin irritation and damage. Hence, the MV treatment is of very importance. Many treatment methods are available in the literature in dye removal such as electrocoagulation,^[9,10] electrooxidation,^[11] photo-oxidation,^[12,13] chemical coagulation,^[14] adsorption,^[15,16] etc. Adsorption is widely used in removal of dye effluents from aqueous ambient using clay-type adsorbents such as bentonite,^[17] kaolinite,^[18] montmorillonite,^[19,20] perlite,^[21] sepiolite,^[22] zeolite,^[23] and vermiculite.^[24]

In this study, we aimed to remove cationic dye MV from aqueous solutions by montmorillonite as a function agitation speed, adsorbent dosage, initial dyestuff concentration, initial solution pH, ionic strength, and temperature. Equilibrium data was analyzed by the isotherm models such as Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin. Obtained data of kinetic studies were applied to the kinetic models, viz, pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models. In addition, thermodynamic parameters ΔH^* , ΔG^* , and ΔS^* were also calculated.

2. MATERIALS AND METHODS

2.1. Materials

Montmorillonite sample was obtained from the Süd-Chemie (Balıkesir, Turkey). Chemical composition and

physical properties of montmorillonite were given in Table 1. All reagents used had analytical grade. MV dye was obtained from Dystar (Frankfurt, Germany) ($393.958 \text{ g mol}^{-1}$ molecular weight and molecular formula $\text{C}_{24}\text{H}_{28}\text{N}_3\text{Cl}$).^[25]

2.2. Methods

The effects of variables including pH, stirring speed, temperature, ionic strength, adsorbent dosage, contact time, and initial dye concentration on the adsorptive removal of MV were investigated in batch mode. In each experimental run, 100 mL of MV solutions which have different concentrations changing from 10 to 300 mg L^{-1} were treated with varying amount of montmorillonite in a 250 ml Erlenmeyer flask. In the experiments, the studied stirring speeds changed from 100 to 400 rpm and solution temperatures changed from 293 to 333 K. Ionic strength of aqueous solutions was adjusted with NaCl solutions. The solution pH was adjusted by addition of dilute aqueous solutions of HCl (0.01 M) or NaOH (0.01 M) using a WTW multi 340i pH-meter. Samples were taken at different contact times to determine the time required to reach equilibrium. After centrifugation at 10,000 rpm, the absorbance of the supernatant was measured at 584 nm ^[7] (Spekol-1100 UV-Vis spectrophotometer) and then converted into concentration.

The adsorption equilibrium of MV was calculated using the following relationship:

$$qe = \frac{(C_0 - C_e) \times V}{m} \quad [1]$$

TABLE 1
Chemical composition of montmorillonite a) and physicochemical properties of montmorillonite b)

Component	Weight (%)
SiO ₂	49.90
Al ₂ O ₃	19.70
MgO	0.27
CaO	1.50
Fe ₂ O ₃	0.30
Na ₂ O	1.50
H ₂ O	25.67
Parameters	Value
Color	White
Density (g cm^{-3})	2.3–3
Transparency	Semi-transparent and opaque
Brightness	Matt
Surface area ($\text{m}^2 \text{ g}^{-1}$)	95.36
Reflective index	1–2

TABLE 2
Isotherm models equations a) and kinetic models equations b)

Isotherm	Mathematical equations	Pilots	Equations	References
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$	(C_e/q_e) versus C_e	[3]	[26]
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ versus $\ln C_e$	[4]	[27]
Temkin	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	q_e versus $\ln C_e$	[5]	[28]
Dubinin–Radushkevich	$\ln q_e = \ln q_m - B(RT \ln(1 + 1/C_e C_e))^2$	$\ln q_e$ versus $(RT \ln(1 + 1/C_e))^2$	[6]	[29]

Kinetic model	Mathematical equations	Pilots	Equations	References
Pseudo-first-order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ versus t	[7]	[31]
Pseudo-second-order	$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2} \right] + \frac{1}{q_e} t$	t/q_t versus t	[8]	[32]
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t$	q_t versus $\ln t$	[9]	[33]
Intraparticle diffusion	$q_t = k_{dif} t^{1/2} + C$	q_t versus $t^{1/2}$	[10]	[34]

where C_0 (mg L⁻¹) and C_t (mg L⁻¹) are the dye concentrations at initial and after equilibrium time, respectively. V is the volume of the solution (L) and m is the mass (g) of montmorillonite.

The adsorption capacity of MV was calculated for kinetic studies by the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad [2]$$

where C_0 (mg L⁻¹) and C_t (mg L⁻¹) are the dye concentrations at initial and after time t , respectively. V is the volume of the solution (L) and m is the mass (g) of montmorillonite.

3. RESULTS AND DISCUSSIONS

3.1. Adsorption Isotherm Models

The results obtained for the adsorption of MV were analyzed by the well-known models such as Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich model. The mathematical equations for these models were given in Table 2.^[26–29] The isotherm parameters related to the isotherms defined above were given in Table 3. 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 purposes.^[30] The fitness of experimental data to the isotherm models were shown in Figure 1. The best fitted model was selected based on the coefficient of determination values (R^2 Table 3). The R^2 values of the Langmuir isotherm model for the tested temperature was higher than the other fitted models, showing

that the equilibrium experimental data was better explained by the Langmuir equation.^[19]

3.2. Adsorption Kinetic Models

Several steps can be used to examine the controlling mechanism of adsorption process such as chemical reaction, diffusion control, and mass transfer. Kinetic models were used to test experimental data from the adsorption of MV onto montmorillonite clay. The kinetics of dyes adsorption onto montmorillonite is required for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes. Thus, the kinetics of MV adsorption onto montmorillonite was analyzed using pseudo-first-order, pseudo-second-order, Elovich kinetic models, and intraparticle diffusion models. Kinetic model equations were given in Table 2.^[31–34]

The results of kinetic analysis were shown in Table 4. The fitness of kinetic data to the pseudo-second-order model

TABLE 3
Isotherm constants for MV adsorption onto montmorillonite

Langmuir isotherm		Freundlich isotherm	
K_L	0.668	K_F	76.29
q_m	230.04	n	4.05
R^2	0.9998	R^2	0.7977
Temkin isotherm		Dubinin–Radushkevich isotherm	
K_T	36.76	q_m	205.69
b	87.44	B	1.109×10^{-7}
R^2	0.8999	R^2	0.9044

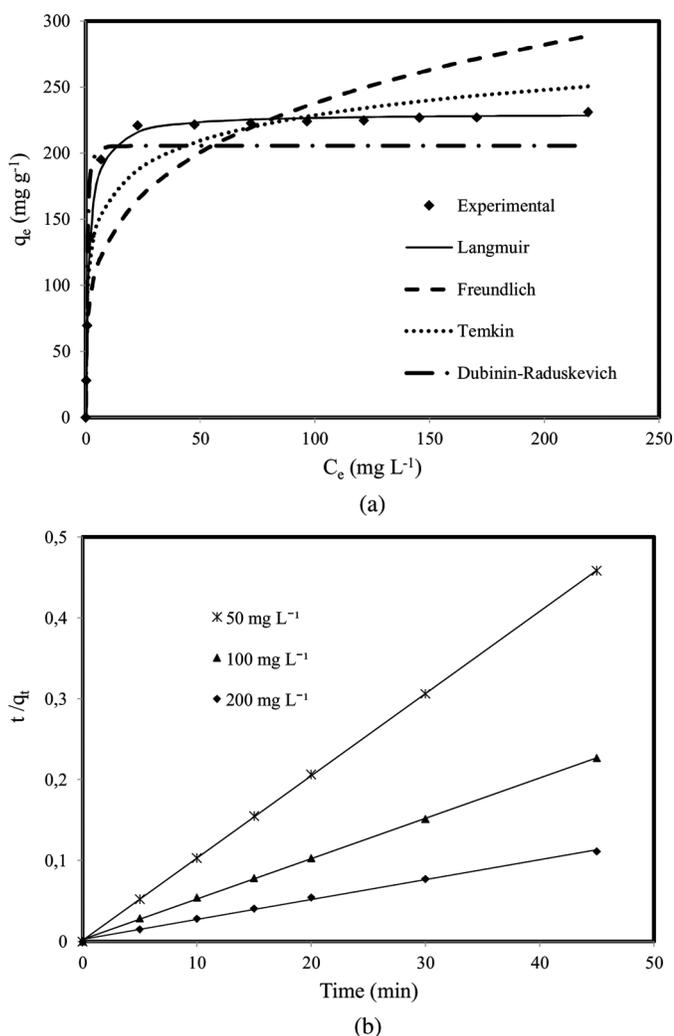


FIG. 1. Comparison of isotherm models a) and pseudo-second-order kinetic equation for adsorption of MV on montmorillonite at different initial dyestuff concentrations b).

was given in Figure 1. It was seen that the data were fitted with the pseudo-second-order kinetic model. As seen in Table 4, the correlation coefficients for the Elovich equation have changed in the range of 0.642–0.988, the pseudo-first-order have changed in the range of 0.549–0.913, and the intra-particle have changed in the range of 0.497–0.962. These results have shown that the experimental data did not fit the Elovich equation, pseudo-first-order, and intraparticle.

3.3. Effect of Agitation Speed

The stirring speed experiments were carried out at 293 K temperature, pH: 4.87 (natural), 0.75 g L⁻¹ the amount of adsorbent, 100 mg L⁻¹ the initial dyestuff concentration, and stirring speed at 100, 200, 300, and 400 rpm for different time intervals (5, 10, 15, 20, 30, 45 minutes). Stirring speed

affects solution distribution on solid–liquid system so this parameter is very important for adsorption phenomenon. In the batch adsorption systems, agitation speed plays a significant role in affecting the external boundary film and the distribution of the solute in the bulk solution.^[35] Adsorption capacity increased with the increase in agitation speed as shown in Figure 2a. When the stirring speed increased from 100 to 300 rpm maximum adsorption capacity increased as 19.78 mg g⁻¹. In addition, when stirring speed was increased from 300 to 400 rpm, the adsorption capacity increased only 0.29 mg g⁻¹ at 45 minutes.^[36]

3.4. Effect of Adsorbent Dosage

The adsorption of MV was studied by changing the quantity of adsorbent and the parameters were as follows: 0.05, 0.075, 0.1, and 0.15 g/100 mL at 293 K temperature, pH: 4.87 (natural), 100 mg L⁻¹ the initial dyestuff concentration, and 300 rpm stirring speed. As can be seen in Figure 2b, the adsorbent capacity decreased from 182.32 to 66.47 mg g⁻¹ while the adsorbent dosage increased from 0.05 to 0.15 g/100 mL. It is readily understood that the number of available sorption sites increases by increasing the adsorbent dosage, and therefore results in the increase of removal efficiency for MV. The decrease in sorption density can be attributed to the fact that some of the sorption sites remain unsaturated during the sorption process.^[37]

3.5. Effect of Initial Dyestuff Concentration

To study the effect of initial dye concentrations on MV adsorption in aqueous solutions on montmorillonite, the experiments were carried out by 50, 100, and 200 mg L⁻¹ initial dye concentration at 293 K temperature, pH: 4.87 (natural), 0.075 g/100 mL the amount of adsorbent, and 300 rpm stirring speed. When the MV concentration increased from 50 to 200 mg L⁻¹, the amount of adsorbed MV increased from 65.474 to 215.825 mg g⁻¹ as shown in Figure 2c. Apparently, the initial MV concentration plays an important role in affecting the capacity of MV to adsorb onto montmorillonite. The higher the MV concentration is, the stronger the driving forces of the concentration gradient, and therefore the higher the adsorption capacity.^[38]

3.6. Effect of Ionic Strength

The effect of electrolyte concentrations was investigated in 0 M, 1 × 10⁻¹ M, 1 × 10⁻² M, and 1 × 10⁻³ M NaCl solutions with 293 K temperature, pH: 4.87 (natural), 0.75 g L⁻¹ the amount of adsorbent, 100 mg L⁻¹ the initial dyestuff concentration, and 300 rpm stirring speed. As seen in Figure 2d, the presence of NaCl significantly affects the adsorption rate of dye. The salt caused an increase in the degree of dissociation of the dye molecules by facilitating the protonation.^[39] The presence of NaCl in the solution may have two opposite effects. On the one hand, since the salt screens the electrostatic interaction of opposite

TABLE 4
Kinetic constants for MV adsorption onto montmorillonite

Parameters	Kinetic models											
	Adsorbent dosage (g/100 ml)	Temperature (K)	Initial dye concentration (mg L ⁻¹)	Ionic strength (mol L ⁻¹ NaCl)	pH	Agitation speed (rpm)	The Elovich equation	Pseudo-first-order	Pseudo-second-order		Intraparticle	
									$h = k_2 \times q_e^2$ (mg g ⁻¹ min ⁻¹)	$k_2 \times 10^3$ (g mg ⁻¹ min ⁻¹)		R^2
0.075	293	100	0.000	0.000	4.87	300	0.971	0.897	375.657	0.009358	1.000	0.889
0.075	303	100	0.000	0.000	4.87	300	0.904	0.913	668.003	0.016713	1.000	0.780
0.075	313	100	0.000	0.000	4.87	300	0.756	0.5490	1221.001	0.030598	1.000	0.612
0.075	323	100	0.000	0.000	4.87	300	0.793	0.549	2392.344	0.060072	1.000	0.661
0.075	333	100	0.000	0.000	4.87	300	0.642	0.6558	9327.488	0.234086	1.000	0.497
0.075	293	50	0.000	0.000	4.87	300	0.919	0.558	628.536	0.063105	1.000	0.837
0.075	293	100	0.000	0.000	4.87	300	0.971	0.897	375.657	0.009358	1.000	0.889
0.075	293	200	0.000	0.000	4.87	300	0.930	0.719	276.472	0.002604	0.997	0.962
0.050	293	100	0.000	0.000	4.87	300	0.883	0.719	179.630	0.001338	0.991	0.966
0.075	293	100	0.000	0.000	4.87	300	0.971	0.897	375.657	0.009358	1.000	0.889
0.100	293	100	0.000	0.000	4.87	300	0.946	0.795	2277.904	0.129022	1.000	0.883
0.150	293	100	0.000	0.000	4.87	300	0.786	0.744	3472.222	0.348821	1.000	0.646
0.075	293	100	0.000	0.000	4.87	100	0.965	0.865	120.977	0.004091	0.998	0.885
0.075	293	100	0.000	0.000	4.87	200	0.981	0.8851	216.638	0.005512	0.999	0.936
0.075	293	100	0.000	0.000	4.87	300	0.983	0.8650	419.287	0.010457	1.000	0.931
0.075	293	100	0.000	0.000	4.87	400	0.988	0.7632	757.576	0.018977	0.999	0.940
0.075	293	100	0.000	0.000	4.87	300	0.971	0.8969	375.657	0.009358	1.000	0.889
0.075	293	100	0.001	0.001	4.87	300	0.968	0.9008	575.374	0.014402	1.000	0.880
0.075	293	100	0.010	0.010	4.87	300	0.918	0.8794	754.717	0.018898	1.000	0.802
0.075	293	100	0.100	0.100	4.87	300	0.831	0.7838	1078.749	0.027023	1.000	0.705
0.075	293	100	0.000	0.000	3.00	300	0.958	0.814	262.398	0.006700	0.999	0.953
0.075	293	100	0.000	0.000	4.87	300	0.971	0.897	375.657	0.009358	1.000	0.889
0.075	293	100	0.000	0.000	7.00	300	0.966	0.6825	507.357	0.012537	1.000	0.881
0.075	293	100	0.000	0.000	9.00	300	0.855	0.754	1114.827	0.027859	0.999	0.855
0.075	293	100	0.000	0.000	11.00	300	0.786	0.7444	6944.444	0.174445	1.000	0.646

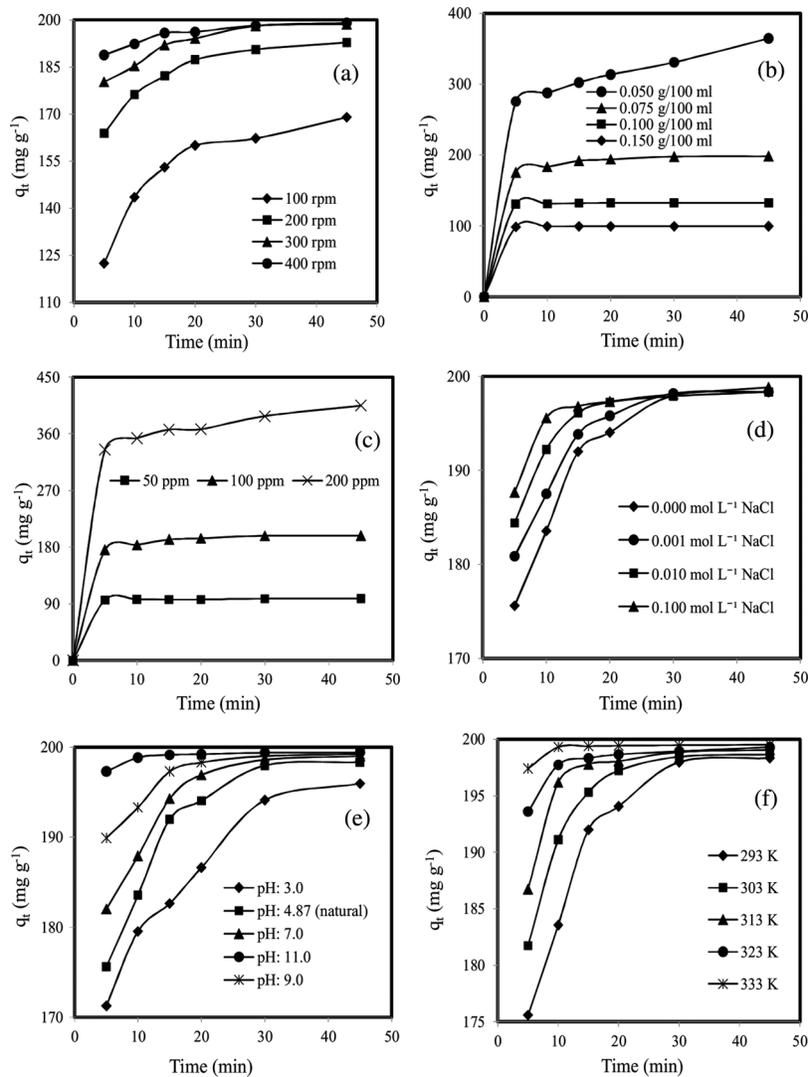


FIG. 2. Effect of all studied parameters on MV adsorption onto montmorillonite: a) agitation speed, b) adsorbent dosage, c) initial dyestuff concentration, d) ionic strength, e) solution pH, and f) temperature.

changes of the oxide surface and the dye molecules, the adsorbed amount should decrease with increase of NaCl concentration. On the other hand, the salt causes an increase in the degree of dissociation of the dye molecules by facilitating the protonation. The adsorbed amount increases as the dissociated dye ions free for binding electrostatically onto the solid surface of oppositely charged increase.^[40]

3.7. Effect of Initial Solution pH

The effect of pH on the removal of MV from aqueous solutions on montmorillonite was observed at pH: 3, 4.87 (natural), 7, 9, and 11 with 293 K temperature, 0.75 g L⁻¹ the amount of adsorbent, 100 mg L⁻¹ the initial dyestuff concentration, and 300 rpm stirring speed. The results were given in Figure 2e. Results showed that the adsorption

capacity increased significantly with an increase in the pH. This could be explained by the adsorption mechanism. At basic pH, the negatively charged species started to dominate on the montmorillonite surface and the surface acquired negative charge, but the adsorbate species still had positive charge. As the negatively charged adsorbent surface increased the electrostatic attraction of positively charged adsorbate species on the adsorbent particles, adsorption of the MV ions increased.^[41] With increase in pH from 3 to 11, the adsorption capacity increased from 195.97 to 199.42 mg g⁻¹.^[40]

3.8. Effect of Temperature

The temperature experiments were carried out at 293, 303, 313, 323, and 333 K with pH: 4.87 (natural), 0.75 g L⁻¹ the amount of adsorbent, 100 mg L⁻¹ the initial dyestuff

concentration, and 300 rpm stirring speed. The results were given in Figure 2f. From this figure, it has been observed that when solution temperature increased from 293 to 333 K, adsorption capacity of MV onto montmorillonite increased from 198.34 to 199.52 mg g⁻¹. The kinetic energy between the dye molecules and the montmorillonite particles increased with increasing the temperature of the solution. When the collision frequency between adsorbent and the dye molecules increased then the dye molecules electrostatically adsorbed onto the surface of the adsorbent particles.^[37]

3.9. Activation Energy and Thermodynamic Parameters

3.9.1. Activation Energy

Temperature dependence of the adsorption rate constant can be given as follows^[43]:

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g} \times \frac{1}{T} \quad [11]$$

where E_a , activation energy (kJ mol⁻¹); k_0 , Arrhenius constant; R_g , universal gas constant (8.314 J mol⁻¹ K⁻¹). For calculate k_0 and E_a value at different temperatures, pseudo-second-order rate constants piloted for $\ln k_2$ against to $1/T$ and k_0 and E_a values were calculated from this graphs (Equation (11)). Figure 3a showed pilot of $\ln k_2$ against to $1/T$ giving a straight line. In aqueous solution activation energy was found to be 62.14 kJ mol⁻¹ for MV adsorption onto montmorillonite surface. Activation energy basically gives an idea about whether adsorption is physical or chemical. If adsorption process occurred with low activation energy (0–88 kJ mol⁻¹) it means that adsorption has physical nature and if adsorption occurred with high activation energy (88–400 kJ mol⁻¹) it means that adsorption has chemical nature.^[42]

3.9.2. Thermodynamics Parameters

Thermodynamic activation parameters Gibbs free energy (ΔG^*), enthalpy (ΔH^*), and entropy (ΔS^*) changes were calculated using Eyring equation^[43]:

$$\ln\left(\frac{k_2}{T}\right) = \left[\ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^*}{R_g} \right] - \frac{\Delta H^*}{R_g} \times \frac{1}{T} \quad [12]$$

where, respectively, k_b and h is the Boltzmann (R_g/N , 1.38.10⁻²³ J mol⁻¹ K⁻¹) and Planck (6.62.10⁻³⁴ J s) constant. The pilot $\ln(k_2/T)$ against $1/T$ gives a straight line with the slope $-(\Delta H^*/R_g)$ and intercept $[\ln(k_b/h)+(\Delta S^*/R_g)]$ (Figure 3b). The relationship between activation Gibbs free energy, enthalpy, and entropy can be found with the following equation:

$$\Delta G^* = \Delta H^* - T \times \Delta S^* \quad [13]$$

from Equation (12); enthalpy (ΔH^*) and entropy (ΔS^*) values were found, respectively, to be 59.55 and

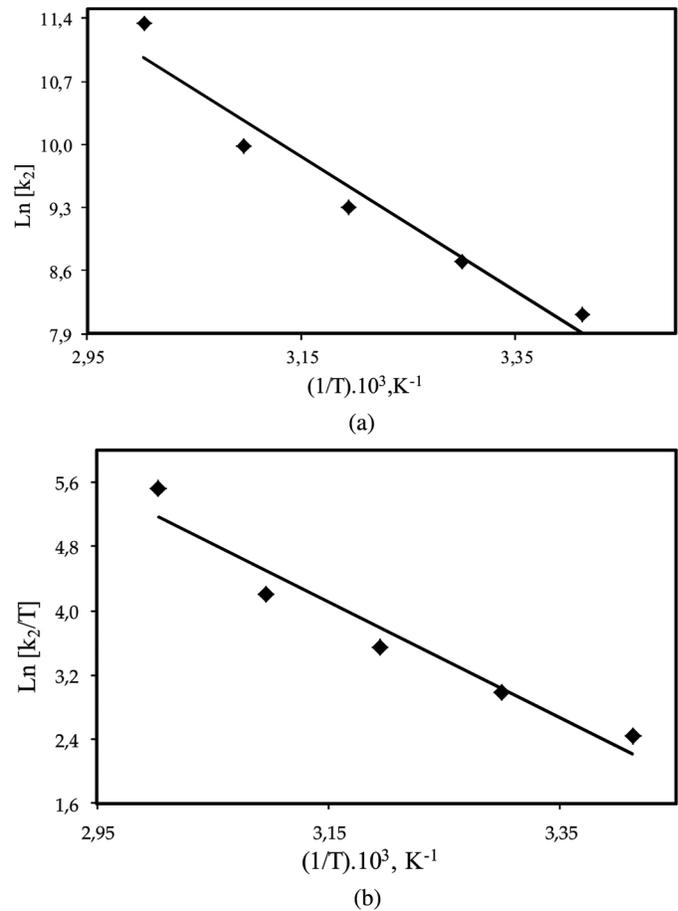


FIG. 3. Arrhenius plots for adsorption of dye on montmorillonite a) and plots of $\ln(k_2/T)$ versus $1/T$ for adsorption of dye on montmorillonite b).

0.0242 kJ mol⁻¹ K⁻¹ and Gibbs free energy (ΔG^*) for MV calculated from Equation (13) at 293 K is 52.46 kJ mol⁻¹. Thermodynamic coefficients were given in Table 5. The positive values of ΔG^* indicated that dye adsorption by montmorillonite was un-spontaneous at lower temperatures and lower concentrations. Increasing of temperatures and concentrations caused the increasing of feasibility of dye uptake. Positive values of ΔS^* reveal the increased randomness at the solid-solution interface during dye removal.

TABLE 5
Thermodynamic parameters of MV adsorption onto montmorillonite

	T (K)				
	293	303	313	323	333
ΔG^* (kJ mol ⁻¹)	52.46	52.22	51.98	51.74	51.50
ΔH^* (kJ mol ⁻¹)	59.55				
ΔS^* (kJ mol ⁻¹ K ⁻¹)	0.0242				

4. CONCLUSIONS

In this study, the MV adsorption by montmorillonite was studied and the main results were as follows:

- The adsorption capacity of the used montmorillonite increased with stirring speed, initial dyestuff concentration, pH, ionic strength, and temperature rise.
- The adsorption capacity of the used montmorillonite decreased with adsorbent dosage increase.
- The experimental results were fitted well to the Langmuir isotherm model. The kinetic analysis indicated that the adsorption data followed the pseudo-second-order rate.
- Activation energy for adsorption of MV onto montmorillonite surface in aqueous solution was calculated as $62.14 \text{ kJ mol}^{-1}$.
- Enthalpy (ΔH^*) value was calculated as $59.55 \text{ kJ mol}^{-1}$ and according to this value process was determined as endothermic.
- Entropy (ΔS^*) value was calculated as $0.0242 \text{ kJ mol}^{-1} \text{ K}^{-1}$ and according to this value adsorption process irregularity decreases.
- Gibbs free energy (ΔG^*) value was calculated for 293 K as $52.46 \text{ kJ mol}^{-1}$ and according to this value adsorption system was un-spontaneous.
- Montmorillonite can be used for the removal of cationic dyes from aqueous solutions.

Results can be concluded.

REFERENCES

- [1] Al-Degs, Y.S., El-Barghouthi, M.I., El-Sheikh, A.H., and Walker, G.M. (2008) *Dyes Pigm.*, 77: 16–23.
- [2] Ofomaja, A.E. and Ho, Y.-S. (2008) *Int. J. Environ. Pollut.*, 34: 466–476.
- [3] Hejazifar, M. and Azizian, S. (2011) *J. Dispersion Sci. Technol.*, 33: 846–853.
- [4] Chen, S., Zhang, J., Zhang, C., Yue, Q., Li, Y., and Li, C. (2010) *Desalination*, 252: 149–156.
- [5] Bayrak, Y. and Uzgör, R. (2012) *J. Dispersion Sci. Technol.*, 34: 828–833.
- [6] Baskaralingam, P., Pulikesi, M., Ramamurthi, V., and Sivanesan, S. (2007) *Appl. Clay Sci.*, 37: 207–214.
- [7] Doğan, M. and Alkan, M. (2003) *Chemosphere*, 50: 517–528.
- [8] Hameed, B.H. (2008) *J. Hazard. Mater.*, 154: 204–212.
- [9] Yilmaz, A.E. (2012) *Fresenius Environ. Bull.*, 21: 1052–1059.
- [10] Nandi, B.K. and Patel, S. (2013) *J. Dispersion Sci. Technol.*, 34: 1713–1724.
- [11] Gaber, M., Abu Ghalwa, N., Khedr, A.M., and Salem, M.F. (2013) *J. Chem.*, 2013: 9.
- [12] Genç, N. and Can-Doğan, E. (2006) *Pol. J. Environ. Stud.*, 15: 73–79.
- [13] Jain, R. and Sikarwar, S. (2011) *J. Dispersion Sci. Technol.*, 32: 1345–1352.
- [14] Merzouk, B., Yakoubi, M., Zongo, I., Leclerc, J.P., Paternotte, G., Pontvianne, S., and Lopicque, F. (2011) *Desalination*, 275: 181–186.
- [15] Karim, A.B., Mounir, B., Hachkar, M., Bakasse, M., and Yaacoubi, A. (2009) *J. Hazard. Mater.*, 168: 304–309.
- [16] Keleşoğlu, S., Kes, M., Sütçü, L., and Polat, H. (2011) *J. Dispersion Sci. Technol.*, 33: 15–23.
- [17] Hu, Q.H., Qiao, S.Z., Haghseresht, F., Wilson, M.A., and Lu, G.Q. (2006) *Ind. Eng. Chem. Res.*, 45: 733–738.
- [18] Karaoğlu, M.H., Doğan, M., and Alkan, M. (2009) *Micropor. Mesopor. Mater.*, 122: 20–27.
- [19] Fil, B.A., Özmetin, C., and Korkmaz, M. (2012) *Bull. Korean Chem. Soc.*, 33: 3184–3190.
- [20] Kaur, M. and Datta, M. (2012) *Sep. Sci. Technol.*, 48: 1370–1381.
- [21] Vijayakumar, G., Dharmendirakumar, M., Renganathan, S., Sivanesan, S., Baskar, G., and Elango, K.P. (2009) *CLEAN Soil Air Water*, 37: 355–364.
- [22] Rodríguez, A., Ovejero, G., Mestanza, M.A. and García, J. (2010) *Ind. Eng. Chem. Res.*, 49: 3207–3216.
- [23] Karadağ, D., Akgül, E., Tok, S., Ertürk, F., Kaya, M.A., and Turan, M. (2007) *J. Chem. Eng. Data*, 52: 2436–2441.
- [24] Choi, Y.S. and Cho, J.H. (1996) *Environ. Technol.*, 17: 1169–1180.
- [25] Korkmaz, M., Özmetin, C., Fil, B.A., Özmetin, E., and Yaşar, Y. (2013) *Environ. Bull.*, 22: 1524–1533.
- [26] Langmuir, I. (1918) *J. Am. Chem. Soc.*, 40: 1361–1403.
- [27] Freundlich, H.M.F. (1906) *J. Phys. Chem.*, 57: 385–471.
- [28] Temkin, M.I. (1941) *Zh. Fiz. Khim.*, 15: 296–332.
- [29] Dubinin, M.M. and Radushkevich, L.V. (1947) *Chem. Zentr.*, 55: 331–333.
- [30] Liu, Y., Zheng, Y., and Wang, A. (2010) *J. Environ. Sci. (China)*, 22: 486–493.
- [31] Ho, Y.S. and McKay, G. (1998) *Trans. Inst. Chem. Eng.*, 76B: 332–340.
- [32] Ho, Y.S., Wase, D.A.J., and Forster, C.F. (1996) *Water SA*, 22: 219–224.
- [33] McKay, G., Ho, Y.S., and Ng, J.C.Y. (1999) *Sep. Purif. Methods*, 28: 87–125.
- [34] Furusawa, T. and Smith, J.M. (1974) *AIChE J.*, 20: 88–93.
- [35] Crini, G., Peindy, H.N., Gimbert, F., and Robert, C. (2007) *Sep. Purif. Technol.*, 53: 97–110.
- [36] Shiau, C.-Y. and Pan, C.-C. (2004) *Sep. Sci. Technol.*, 39: 1733–1750.
- [37] Fil, B.A. and Özmetin, C. (2012) *J. Chem. Soc. Pak.*, 34: 896–906.
- [38] Karaca, S., Gürses, A., Açıkyıldız, M., and Ejder, M. (2008) *Micropor. Mesopor. Mater.*, 115: 376–382.
- [39] Gil, A., Assis, F.C.C., Albeniz, S., and Korili, S.A. (2011) *Chem. Eng. J.*, 168: 1032–1040.
- [40] Doğan, M., Özdemir, Y., and Alkan, M. (2007) *Dyes Pigm.*, 75: 701–713.
- [41] Doğan, M. and Alkan, M. (2003) *J. Colloid Interface Sci.*, 267: 32–41.
- [42] Nollet, H., Roels, M., Lutgen, P., Van der Meeren, P., and Verstraete, W. (2003) *Chemosphere*, 53: 655–665.
- [43] Laidler, K. and Meiser, J.H. (1999) *Physical Chemistry*; New York: Houghton Mifflin; 852 p.