



Journal of Dispersion Science and Technology

ISSN: 0193-2691 (Print) 1532-2351 (Online) Journal homepage: http://www.tandfonline.com/loi/ldis20

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To cite this article: Serkan Keleşoğlu , Mürşide Kes , Leman Sütçü & Hürriyet Polat (2012) Adsorption of Methylene Blue from Aqueous Solution on High Lime Fly Ash: Kinetic, Equilibrium, and Thermodynamic Studies, Journal of Dispersion Science and Technology, 33:1, 15-23, DOI: <u>10.1080/01932691.2010.528677</u>

To link to this article: http://dx.doi.org/10.1080/01932691.2010.528677



Accepted author version posted online: 29 Jun 2011. Published online: 29 Jun 2011.

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Adsorption of Methylene Blue from Aqueous Solution on High Lime Fly Ash: Kinetic, Equilibrium, and Thermodynamic Studies

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> Kinetic, equilibrium, and thermodynamic studies were performed for the batch adsorption of methylene blue (MB) on the high lime fly ash as a low cost adsorbent material. The studied operating variables were adsorbent amount, contact time, dye concentration, and temperature. The kinetic data were analyzed using the pseudo-first order and pseudo-second order kinetic models and the adsorption kinetic was followed well by the pseudo-second order kinetic model. The equilibrium data were fitted with the Freundlich, Langmuir, and Dubinin Radushkevich (D–R) isotherms and the equilibrium data were found to be well represented by the Freundlich and D–R isotherms. Based on these two isotherms MB is taken by chemical ion exchange and active sites on the high lime fly ash have different affinities to MB molecules. Various thermodynamic parameters such as enthalpy of adsorption (ΔH°), free energy change (ΔG°), and entropy change (ΔS°) were investigated. The positive value of ΔH° and negative value of ΔG° indicate that the adsorption is endothermic and spontaneous. The positive value of ΔS° shows the increased randomness at the solid–liquid interface during the adsorption. A single-stage batch adsorber was also designed based on the Freundlich isotherm for the removal of MB by the high lime fly ash.

> Keywords Adsorption, equilibrium, high lime fly ash, kinetics, methylene blue, thermodynamic

1. INTRODUCTION

Different synthetic chemical dyes are widely utilized in many industrial processes for various purposes. Paper and pulp manufacturing, dyeing of cloth, leather treatment, and printing are frequent users of these kinds of chemicals. Most of the used solutions containing such dyes drainage as effluents. Some of these dyes are toxic in nature, so their removal from the industrial effluents is a major environmental problem.^[1-4]

Biological oxidation and chemical precipitation are most commonly applied methods to remove color from dye-bearing wastewaters. However, these methods are effective and efficient when the dye concentrations are relatively high. Currently, adsorption is one of the alternative techniques to remove dyes from these kinds of wastewaters and it is basically a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid with physical and/or chemical interaction.^[5–9] In adsorption technology, various adsorbents such as activated carbon and clay are widely utilized to remove dyes from aqueous solutions.^[10,11] Activated carbon has excellent adsorption capacity for dyes but its uses remains limited, because of high cost. Therefore, many investigators have studied to use lower-cost and readily available adsorbents to remove dyes from aqueous solutions such as activated bleaching earth, perlite, seashells, rosewood sawdust, sugar industry pulp, sugar cane dust, tree–fern, peat moss, and natural sediment,^[12–20] as alternatives to activated carbon.

In thermal power plants, fly ash is produced in large amounts from the combustion process. Numerous studies are found in the literature about fly ash as an adsorbent material for the reason that it is abundant, inexpensive, and does not require any additional pretreatment steps.^[21,22] The focus of this research is to examine the adsorption potential of high lime Yeniköy fly ash for methylene blue (MB). In this work, MB was chosen because of its known strong adsorption onto solids and is often serves as a model compound to remove colored bodies and organic contaminants from aqueous solutions. The high lime fly ash was collected from Thermal Power Plant of Yeniköy,

Received 20 August 2010; accepted 10 September 2010.

The authors would like to acknowledge Centre of Material's Research at İzmir Institute of Technology for the facilities (SEM/EDS and x-ray).

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Turkey. According to our literature survey, high lime Yeniköy fly ash has not been used as an adsorbent material for the removal of dyes from water and wastewater.

In the present study, the influence of fly ash amount, initial MB concentration, contact time, and temperature on the amount of MB uptake from the aqueous solutions have been investigated. Kinetics and the mechanistic steps involved in the adsorption process were also evaluated for different MB concentrations. In addition, the adsorption of MB at solid liquid interfaces has been studied extensively at equilibrium and various thermodynamic parameters have been investigated.

2. MATERIALS AND METHODS

The fly ash sample used in this study was obtained from Thermal Power Plant of Yeniköy, Turkey. Representative ash sample were placed into a size screen analyzer (Retsch S1000) to determine size distributions of particles. The nominal particle size of the ash sample was found 100 μ m. Particle size of the fly ash sample used in the adsorption experiments was smaller than 500 μ m and it was dried at 105°C for 2 hours before each set of experiments.

Scanning electron microscope (SEM)/energy dispersive spectroscopy (EDS) characterization of the fly ash sample was performed using a Philips XL-30S FEG type instrument. Prior to analysis, the ash sample was sprinkled onto carbon tape which is adhesive and supported on metallic disk. Images of the sample surface were recorded at different magnifications. EDS analysis was performed randomly at several different points of the surface to minimize any possible anomalies arising from the heterogeneous nature of the analyzed fly ash sample.

X-ray diffraction pattern of the fly ash sample was collected on a Philips X'Pert Pro diffractometer (Philips, Holland) using Cu K α radiation ($\lambda = 0.154$ nm). Sample was prepared by compressing in the cassette sample holder without any adhesive substance.

Methylene blue (MB) with a labeled purity of more than 98% and molecular weight 373.9 g/mol was purchased from Fluka (Germany). MB solutions were prepared by dissolving a known amount of MB in water at room temperature and stirred for 1 hour prior to adsorption studies. Double distilled water, which was passed through a Barnstead Easypure UV-Compact ultrapure water system (ThermoScientific, USA, 18.3 M $\Omega \cdot$ cm) was used to prepare all solutions.

The effect of fly ash concentration on the amount of MB uptake was investigated by contacting 50 mL of MB solution of 250 mg/L initial concentration with different weighted amount of fly ash ranging from 0.1 to 2 g using GFL 1083 (Germany) water bath shaker equipped with a microprocessor thermostat at 20°C for 2 hours, which is more sufficient time to reach equilibrium at a constant agitation speed of 250 rpm. After equilibrium, the samples

were centrifuged and the concentrations of MB in the supernatant solutions were analyzed using Cary 50 ultraviolet-visible (UV-vis) spectrophotometer, using a 1 cm glass cell by monitoring the changes at a wavelength of maximum absorbance (663 nm).

Adsorption kinetic experiments were performed agitating the 50, 150, and 250 mg/L of MB concentrations with 0.25 g fly ash in 50 mL polyethylene tubes at 20, 35, and 50° C using water bath at a constant agitation speed of 250 rpm. The agitation times were changed from 5 to 120 minutes. The collected samples were then centrifuged and the concentration in the supernatant solution was analyzed using UV-vis spectrophotometer.

Adsorption equilibrium experiments were performed by contacting 0.25 g of fly ash with 50 mL of MB solution of different amounts, 25, 50, 100, 150, 200, and 250 mg/L in polyethylene tubes at 20, 35, and 50° C using water bath at a constant agitation speed of 250 rpm. The agitation was made for 2 hours, which is more sufficient time to reach equilibrium. The collected samples were centrifuged and analyzed as before.

In this study, all adsorption experiments were performed in duplicate and average values are reported for each condition.

3. RESULTS AND DISCUSSION

3.1. Characterization of Fly Ash

The fly ash sample was characterized to investigate its mineralogical and elemental constituents using x-ray diffraction and SEM/EDS techniques. The x-ray diffraction studies revealed the presence of portlandite, anhydrite, larnite, lime, and quartz minerals in the fly ash sample.

EDS results of the atomic percentages of N, O, Mg, Al, Si, S, Ca, Ti, Fe, and molecular percentages of their oxides in the ash sample were obtained by spot analysis. Many points were randomly selected on the surface of the ash sample and mean value was calculated for each element and compound. A summary of the EDS results of the fly ash sample was given in Table 1. Surface area of the fly ash sample was also investigated by Micromeritics ASAP 2010 volumetric adsorption device employing nitrogen at a temperature of 77 K was also given in Table 1.

Fly ash is divided into two types namely C and F type according to ASTM C 618 standard. F type fly ash is named low lime fly ash since the quantity of CaO is below 10%. However, C type fly ash is named high lime fly ash because the quantity of CaO is more than 10%.^[23] EDS results showed that the quantity of lime in the ash sample was found 55.42%; this result indicates that Yeniköy fly ash is high lime (C type) fly ash.

The SEM images of the high lime fly ash sample were also given in Figure 1. The microscopic images showed that

Mineralogical constituents	Elements	Mass (%)	Oxides	Mass (%)	Physical properties		
Larnite	Ν	10.91	N_2O_5	14.07	BET surface area (m^2/g)	25.2	
Portlandite	Ο	57.03	MgO	2.18	Average pore diameter (Å)	30.1	
Anhydrite	Mg	0.78	Al_2O_3	2.13	Pore volume (cm^3/g)	0.006	
Lime	Al	1.51	SiO_2	5.11	Nominal particle size (µm)	100	
Quartz	Si	1.81	SO_3	20.26	Micropore area (m^2/g)	11.1	
	S	7.27	CaO	55.42			
	Ca	20.11	TiO_2	0.06			
	Ti	0.02	Fe_2O_3	0.81			
	Fe	0.58	-				

 TABLE 1

 Characteristic properties of the high lime fly ash sample

the high lime fly ash contains porous and agglomerated particles of irregular size and shape.

3.2. Effect of Adsorbent Amount

The plots between amount of MB adsorbed q_e (mg/g) and percent MB removal against amount of fly ash mass





FIG. 1. SEM images of the high lime fly ash sample (a) $\times 8000$ (b) $\times 25000.$

(b)

(g) were given in Figure 2, where q_e and the percentage of MB removal were obtained by

$$q_e = \frac{(C_0 - C_e)V}{M},\qquad [1]$$

Percent MB removal =
$$\left(\frac{C_0 - C_e}{C_0}\right) \times 100,$$
 [2]

where $C_0 \text{ (mg/L)}$ and $C_e \text{ (mg/L)}$ are, respectively, the concentration of MB in the solution at time = 0 and at equilibrium time *t*, *V* is the volume of MB solution (L), and *M* is the amount of fly ash (g). From the Figure 2 the uptake amount of MB is varied with varying fly ash mass and it decreased with increasing in fly ash mass. The uptake amount of MB decreases from 25.83 to 6.06 mg/g for an increase in fly ash mass from 0.1 to 2 g, whereas the percent MB removal increased from 20.66 to 96.99. This indicates that only fixed amount of MB can be adsorbed by certain amount of fly ash. In this study the relation between the amount of MB adsorbed, q_e and fly ash mass fits the



FIG. 2. Effect of the high lime fly ash amount on MB removal $(C_0 = 250 \text{ mg/L}, V = 50 \text{ mL}, T = 20^{\circ}\text{C}, \text{pH} = 9-10, \text{agitation rate} = 250 \text{ rpm}).$

Equation (3) with a correlation coefficient; R^2 of 0.988.

$$M = \frac{17.843 - 0.597q_e}{q_e}.$$
 [3]

3.3. Effect of Contact Time and Temperature

The plots of the percent MB removal versus contact time for different initial MB concentrations of 50, 150, and 250 mg/L at 20, 35, and 50°C on the high lime fly ash were indicated in Figures 3a–3c. From these figures it was observed that percent MB removal is increased with



FIG. 3. Effect of contact time and temperature for the MB adsorption on the high lime fly ash. (V = 50 mL, M = 0.25 g, pH = 9–10, agitation rate = 250 rpm) (a) 20°C (b) 35°C (c) 50°C.

contact time and temperature for all initial MB concentrations and uptake is very rapid for the first 30 minutes for all experiments. Thereafter a gradual increase in the adsorption is seen with increasing contact time up to 60 minutes and adsorption rates were nearly stable up to 120 minutes. The higher adsorption rate at the first 30 minutes may be because of an increased number of vacant sites available at the initial stage. In addition, initial MB concentration has no effect on the equilibrium time for the MB adsorption on the high lime fly ash, so the period of 2 hours was fixed as the contact time for the equilibrium studies.

3.4. Effect of Initial Dye Concentration

The plots between amounts of MB adsorbed, q_e and percent MB removal by high lime fly ash against initial MB concentration were given in Figure 4. From this figure it was observed that the adsorbed amount of MB increased from 2.33 to 14.01 mg/g for an increase in initial MB concentration from 25 to 250 mg/L, whereas the percentage of MB removal decreases from 46.65 to 28.03%. In this study the relation between amount of MB adsorbed, q_e and initial MB concentration fits the Equation (4) with a correlation coefficient; R^2 of 0.990 as follows:

$$q_e = \frac{37.43C_0}{402.71 + C_0}.$$
 [4]

3.5. Adsorption Kinetics

3.5.1. The Pseudo-First Order Model

The pseudo-first order rate equation was proposed by Lagergren^[24] and linearized form of this equation is given by

$$\ln(q_e - q_t) = \ln q_e - k_1 t,$$
 [5]



FIG. 4. Effect of initial MB concentration for the adsorption on the high lime fly ash (V = 50 mL, M = 0.25 g, $T = 20^{\circ}\text{C}$, pH = 9–10, agitation speed = 250 rpm).

where q_t and q_e are the adsorbed amount of dye (mg/g) at time t and at equilibrium time, respectively, k_1 is the pseudo-first order rate constant (min⁻¹). The adsorption rate constant, k_1 can be obtained by plotting of $\ln(q_e - q_t)$ versus t.

The plots of $\ln(q_e - q_t)$ versus t for the pseudo-first order model for the MB adsorption on the high lime fly ash were not indicated as figure because the calculated correlation coefficient; R^2 values of this model is low and ranged from 0.891 to 0.936 as seen in Table 2. It indicates that the adsorption of MB on the high lime fly ash does not fit the pseudo-first order kinetic model.

3.5.2. The Pseudo-Second Order Model

The pseudo-second order kinetic model was also applied to experimental data of the MB adsorption on the high lime fly ash. The linearized form of this model is given $by^{[25]}$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t,$$
[6]

where k_2 (g/mgmin) is the pseudo-second order rate constant, q_t (mg/g) is the amount of adsorption time, t (min) and q_e is the amount of adsorption equilibrium (mg/g).

This model is more likely to predict kinetic behaviour of adsorption with chemical adsorption being the rate controlling step.^[25,26] The linear plots of t/q_t versus t for 50, 150, and 250 mg/L of MB adsorption on the high lime fly ash at 20, 35, and 50°C were given in Figures 5a–5c, respectively. The calculated correlation coefficients; R^2 of the pseudo-second order for the adsorption of MB on the high lime fly ash are very high and ranging from 0.988 to 0.999. The rate constants k_2 , R^2 , and q_e values were also given in Table 2. These results indicate that the adsorption of MB on the high lime fly ash follows well the pseudo-second order kinetic model. These results

strongly suggesting a chemical reaction mechanism of MB adsorption which could occur due to the chemical character of high lime fly ash.^[27,28]

3.6. Adsorption Isotherms

Adsorption isotherms are mathematical models, which are used to describe the distribution of the adsorbate species among solid and liquid phases. The adsorption data of MB on the high lime fly ash were investigated by using three types of the most common isotherms; Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) models.

The Freundlich model can be applied to describe for non-ideal adsorption on heterogeneous surfaces and multilayer adsorption. The Freundlich model^[29] is given by

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e, \qquad [7]$$

where $K_{\rm F}$ is the constant relating the adsorption capacity and 1/n is an empirical parameter relating the adsorption intensity, which depends on heterogeneity of the material.

The Langmuir model assumes that adsorptions occur at specific homogeneous sites on the adsorbent and it is used successfully in numerous monolayer adsorption processes. The linear form of the Langmuir model^[30] is represented by

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m},\tag{8}$$

where q_m is the monolayer adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir constant (L/mg) relating the free energy of adsorption.

The equilibrium data were also analyzed with the Dubinin-Radushkevich (D-R) isotherm model to investigate the nature of adsorption process as physical or

TABLE 2

Pseudo-first order and pseudo-second order parameters for the adsorption of MB on the high lime fly ash

	<i>T</i> (°C)	$q_{e, \exp}$ (mg/g)	Pseudo-first order			Pseudo-second order			
$C_0 \ (\mathrm{mg}/\mathrm{L})$			$q_{\rm e, \ calc.} \ ({\rm mg}/{\rm g})$	$k_1 (\min^{-1})$	R^2	$q_{\rm e, \ calc.} \ ({\rm mg}/{\rm g})$	k_2 (g/mg min)	R^2	
50	20	4.84	4.90	9.1×10^{-2}	0.919	5.34	21.1×10^{-3}	0.991	
	35	5.35	1.33	$7.4 imes 10^{-2}$	0.906	5.43	12.6×10^{-2}	0.999	
	50	5.98	2.68	5.7×10^{-2}	0.914	6.23	39.9×10^{-3}	0.994	
150	20	12.56	14.60	7.2×10^{-2}	0.927	14.21	5.9×10^{-3}	0.994	
	35	15.04	8.10	6.3×10^{-2}	0.891	15.67	15.4×10^{-3}	0.999	
	50	16.59	15.83	9.8×10^{-2}	0.936	17.61	10.7×10^{-3}	0.998	
250	20	20.25	17.91	4.9×10^{-2}	0.912	23.87	26.1×10^{-3}	0.988	
	35	23.06	23.65	$6.8 imes 10^{-2}$	0.926	26.04	3.3×10^{-3}	0.990	
	50	24.98	21.83	$8.5 imes 10^{-2}$	0.919	26.95	5.5×10^{-3}	0.997	



FIG. 5. Pseudo-second order kinetic plots for the MB adsorption on the high lime fly ash (V=50 mL, M=0.25 g, pH=9-10, agitation rate=250 rpm) (a) 20°C (b) 35°C (c) 50°C.

chemical. The linearized form of the D–R isotherm equation $^{[31]}$ is given by

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \qquad [9]$$

where q_e is the amount of adsorbate on per unit weight of adsorbent (mol/g), q_m is the maximum adsorption capacity (mol/g), β is the activity coefficient related to mean adsorption energy (mol²/J²), and ε is the Polanyi potential that is defined as

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right).$$
^[10]

The Freundlich, Langmuir, and D–R isotherms for the adsorption of MB on the high lime fly ash were obtained by using the linear fitting of (i) $\ln q_e$ versus $\ln C_e$ (ii) C_e/q_e versus C_e and (iii) $\ln q_e$ versus ϵ^2 , respectively. Figure 6a–c shows the Freundlich, Langmuir, and D–R isotherms for the MB adsorption on the high lime fly ash. From these figures it was observed that the equilibrium data were very well represented by the Freundlich and D–R isotherm equations when compared to Langmuir equation. The adsorption equilibrium data fit the



FIG. 6. Equilibrium isotherms for the adsorption of MB on the high lime fly ash (V = 50 mL, M = 0.25 g, pH = 9–10, agitation rate = 250 rpm) (a) Freundlich (b) Langmuir (c) D–R.

Freundlich, Langmuir, and D–R isotherms with correlation coefficients; R^2 values ranging from 0.990 to 0.995, 0.887–0.915, and 0.990–0.994, respectively. The calculated Freundlich, Langmuir and D–R constants and their calculated correlation coefficients at different temperatures were also given in Table 3.

The Freundlich isotherm model is suitable to investigate the adsorption process of MB on the high lime fly ash in this study. The constants of Freundlich model, K_F and 1/nwere ranging from 0.348 to 0.538 and from 0.720 to 0.792, respectively. The 1/n values between 0 and 1 indicating that the adsorption of MB on the high lime fly ash was favourable at studied conditions. The high correlation coefficients values of this model indicate that the high affinity between the high lime fly ash surface and MB plays the role in the adsorption mechanism in the Freundlich model. This indicates that some heterogeneity in the surface of the high lime fly ash plays a role in adsorption process.^[32]

The D-R isotherm model also well fitted the equilibrium data because of the high correlation coefficient values. The q_m values were found to be ranging from 3.4×10^{-4} to 9.7×10^{-4} mol/g for the adsorption of MB on the high lime fly ash from the intercepts of the plots. The mean adsorption energy (*E*; kj/mol) can be calculated as follows:

$$E = \frac{1}{\sqrt{-2\beta}}.$$
 [11]

This adsorption potential is independent of temperature, but it varies depending on the nature of adsorbent and adsorbate. The mean free energy of adsorption gives information about adsorption mechanism as chemical ion-exchange. If *E* value is between 8 and 16 kj/mol, the adsorption process follows by chemical ion exchange and if E < 8 kj/mol, the adsorption process is a physical nature [^{33,34]} The mean energy of the MB adsorption was calculated as 9.13 kj/mol. This result indicates that the adsorption of MB on the high lime fly ash may be carried out via chemical ion-exchange mechanism.

3.7. Adsorption Thermodynamics

To describe the thermodynamic behaviour of the MB adsorption from aqueous solution by the high lime fly

ash, the thermodynamic parameters enthalpy change (ΔH°) , entropy change (ΔS°) , and free energy change (ΔG°) were calculated using the following equations:^[35,36]

$$\Delta G^{\circ} = -RT \ln K_d, \qquad [12]$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT},$$
[13]

$$K_d = \frac{q_e}{C_e},\tag{14}$$

where *R* is universal gas constant and equals to 8.314 J/mol K, *T* is the absolute temperature, and K_d (mL/g) is the distribution coefficient. The distribution coefficient is an empirical equilibrium constant and it is valid at particular initial concentration and reaction conditions.^[37] The calculated values of ΔH° , ΔS° , and ΔG° at different concentration of the MB adsorption on the high lime fly ash were given in Table 4. The positive value of ΔH° indicates the endothermic nature of the adsorption process of MB on the high lime fly ash. The positive value of ΔS° shows the affinity of the high lime fly ash for MB and the increasing the randomness at the solid–liquid interface during the adsorption. The negative value of ΔG° confirms the feasibility of the adsorption with a high preference of MB on the high lime fly ash.

3.8. Single-Stage Batch Adsorber

To predict the design of single-stage batch adsorption system, adsorption isotherms can be used.^[38] The schematic illustration of the single-stage batch adsorption process is indicated in Figure 7. The treated solution contains V(L of water) and the dye concentration is reduced from C_0 to C_e during the adsorption. M (dye free, g adsorbent) added and the dye concentration on the high lime fly ash from $q_0 = 0$ to q_e in the treatment stage. The mass balance that requires the dye removed from the liquid effluent to the accumulated by high lime fly ash is

$$V(C_0 - C_e) = M(q_e - q_0) = Mq_e.$$
 [15]

In the case of the adsorption of MB on the high lime fly ash, the Freundlich isotherm gave the best fit to the experi-

Freundlich isotherm parameters Langmuir isotherm parameters D-R isotherm parameters R^2 R^2 R^2 Temp. (°C) K_F 1/n K_L (L/mg) $q_m \,(\mathrm{mg/g})$ $q_m \,(\mathrm{mol/g})$ E (kj/mol) 5.7×10^{-3} 3.4×10^{-4} 20 0.348 0.720 0.993 27.624 0.877 9.128 0.990 8.2×10^{-4} 6.3×10^{-3} 0.915 35 0.470 0.781 0.990 44.248 9.128 0.992 5.8×10^{-3} 0.899 9.7×10^{-4} 0.994 50 0.538 0.792 0.995 56.497 9.128

 TABLE 3

 Equilibrium isotherm parameters for the adsorption of MB on the high lime fly ash

TABLE 4Thermodynamic parameters for the adsorption of MB on
the high lime fly ash

C	۸ <i>LI</i> o	۸ S°	$-\Delta G^{\circ}$ (kj/mol)				
(mg/L)	(kj/mol)	(j/mol K)	20°C	35°C	50°C		
25	16.107	97.931	12.583	13.426	14.076		
50	11.967	84.227	12.765	13.276	13.878		
100	14.413	91.121	12.266	13.074	13.600		
150	14.244	90.049	12.115	12.929	13.433		
200	13.361	86.349	11.949	12.584	13.191		
250	10.108	75.433	11.976	12.560	12.911		



FIG. 7. A single-stage batch adsorber.



FIG. 8. Adsorbent mass (*M*) against volume of solution (*L*) for different percentage of MB removals by high lime fly ash ($C_0 = 100 \text{ mg/L}$, pH = 9–10, T = 20°C).

mental data. The Freundlich data can be applied to Equation (15) and rearrangement gives

$$\frac{M}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{K_F C_e^{1/n}}.$$
[16]

Analytical calculation of the adsorbent solution ratio for a given change in solution concentration from C_0 to C_e is obtained using the Equation (16). A series of plots obtained from the Equation (16) for the adsorption of MB on the high lime fly ash was represented in Figure 8. An initial MB concentration of 100 mg/L is assumed and the figure shows the amount of effluent which can be treated to reduce the MB content by 90%, 80%, 70%, 60%, and 50% using various mass of the high lime fly ash. For example, the amount of high lime fly ash required to remove 90% of MB solution concentration 100 mg/L was 10.13, 20.26, 30.39, and 40.52 g for MB solution of 1, 2, 3, and 4 L, respectively.

4. CONCLUSIONS

In the present study the high lime fly ash as a low cost adsorbent material was used to remove methylene blue (MB) from aqueous solution. Adsorption experiments show that high lime fly ash can be used as an alternative adsorbent for the removal of MB from its aqueous solutions. The amount of adsorbed MB was found varying with temperature, concentration, mass of fly ash, and contact time. The amount of MB uptake (mg/g) was found as increasing in contact time, concentration, and temperature and decreasing with an increase in fly ash amount. The adsorption data of MB on the high lime fly ash well represents the pseudo-second order kinetic model and equilibrium data fitted very well with the Freundlich and Dubinin Radushkevich (D-R) isotherms. The MB uptake process was found to be controlled by chemical ion exchange and some heterogeneity in the surface of high lime fly ash plays role during the adsorption. Investigation of the thermodynamic parameters for the adsorption of MB on the high lime fly ash shows that adsorption process is endothermic, feasible, and spontaneous. The positive value of entropy ΔS° indicates the increased randomness at the solid-liquid interface during the adsorption of MB on the high lime fly ash.

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