



Adsorption Study of Methylene Blue Dye on Clay in Aqueous Solution

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ABSTRACT

Removal of Methylene Blue (MB) from aqueous solution by adsorbing it on Montmorillonite was investigated by batch method. The studies were conducted at 25°C and included the effects of pH and initial concentration of Methylene Blue. The adsorption of (MB), whose isotherms are modeled according to Langmuir and Freundlich, were studied at a variety of physical and chemical conditions. The data fitted very well with Freundlich isotherm. The maximum capacity of MB adsorbed on Natural and Activated Clay at equilibrium (Q_e) (78 mg g⁻¹ and 75.7 mg g⁻¹) with a fixed adsorbent dose of 0.5 g L⁻¹ was observed at MB concentration of 30 mg L⁻¹, 293° K, pH 7.5 and 270 min equilibrium time and maximum monolayer adsorption capacity was found to be 36 mg of the dye per gram of clay. The data were also analyzed in terms of their kinetic behavior and was found to obey the pseudo second order equation. In addition, various thermodynamic parameters, such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), standard entropy (ΔS°), and the activation energy (E_a) were calculated. The adsorption process of MB dye onto clay was found to be spontaneous and endothermic process.

Keywords: Methylene blue; Sorption isotherms; Kinetics; thermodynamics; Adsorption.

INTRODUCTION

The removal of coloured and colourless organic pollutants from industrial wastewater is considered an important application of adsorption processes using a suitable adsorbent [1]. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons [2]. Colour or dye being one of the recalcitrant, persist for long distances in flowing water, retards photosynthesis, inhibit growth of aquatic biota by blocking out sunlight and utilizing dissolved oxygen. Some dyes may cause allergic dermatitis, skin irritation, cancer and mutation in man.

On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methaemoglobinemia [3]. Adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the discoloration

process. Commercially activated carbon is a remarkably highly adsorbent material with a large number of applications in the remediation of contaminated groundwater and industrial wastes such as colored effluents. However, activated carbon is an expensive adsorbent due to its high costs of manufacturing and regeneration.

For the purpose of removing unwanted hazardous compounds from contaminated water at a low cost, much attention has been focused on various naturally occurring adsorbents such as chitosan, zeolites, fly ash, coal, paper mill sludge, and various clay minerals [4]. Among these adsorbents, clay minerals have been shown to be the most promising alternatives due to their local availability, technical feasibility, easy engineering applications, highly specific surface area, and cost effectiveness [5,6,7].

The present study undertaken to evaluate the efficiency of teak tree bark powder as an adsorbent for the removal of MB dye from aqueous solutions. The kinetic, equilibrium and thermodynamic data on batch adsorption studies were carried out to understand the process of adsorption. The effect of adsorption parameters such as initial dye concentration, temperature, pH, adsorbent dose, contact time, agitation time has been studied.

MATERIALS AND METHODS

The structure of a cationic MB dye, $C_{16}H_{18}N_3SCl \cdot 3H_2O$, supplied from (NICE CHEMICALS Pvt. Ltd., COCHIN) is shown in figure.1. The stock dye solution was prepared by dissolving 1g of methylene blue in 1000 ml distilled water to obtain $1000mg L^{-1}$ dye used for preparing different initial dye concentrations. For hydrolyzed sawdust throughout the experiment, a sodium hydroxide solution was used. For pH adjustment throughout the experiment, hydrochloric acid and/or sodium hydroxide solutions were used as necessary. The clay used in this study was an Algerian montmorillonite.

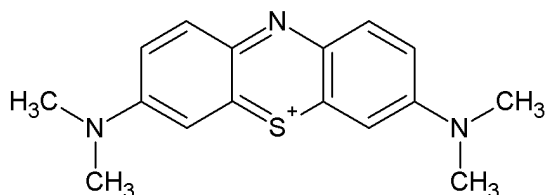


Figure 1. Molecular Structure of Methylene Blue

Treatment and purification procedure: The natural clays were washed several times with distilled and deionized water and were completely dispersed in water. After 7 h at rest, the dispersion was centrifuged for 1 h at 2 400 rpm. The size of the clay particles obtained was 2 μm . Preparation of Na-montmorillonite These clay particles were dispersed in water and heated at $75^{\circ}C$ in the presence of a solution composed of the sodium salts of bicarbonate (1 M), citrate (0.3 M), and chloride (2 M) [8]. The purpose of this operation was to eliminate inorganic and organic compounds, aluminium found in the inter-layer spaces and various free cations. Carbonates were removed by treatment with HCl (0.5 M) and chloride was eliminated after several washings. The organic matter was eliminated completely by treatment with H_2O_2 (30% v/v) at $70^{\circ}C$. The purified clay was dried at $110^{\circ}C$, and then saturated with sodium (Na^+). To ensure complete transformation into the sodium form, all samples were washed several times with a NaOH solution (1 M), 40 g of Na-montmorillonite was treated with 400 mL of 5 N sulphuric acid (analytical grade) at $90^{\circ}C$ for 3.5 h [9] in a stirred glass reaction vessel with reflux. After the acid treatment, the sample was filtered and washed with distilled water until free of SO_4^{2-} . The samples were dried at $60^{\circ}C$ for 12 h and ground to pass through a 0.074 mm sieve. Activated clay acid was characterized using FTIR, DRX and DTA/TG techniques.

Adsorption studies: Adsorption experiments were carried out by adding a fixed amount of gypsum (0.5 g) to a series of 100 mL conical flasks filled with 30 mL of Methylene Blue dye. The conical flasks were then sealed and placed in a water-bath shaker and shaken at 100 rpm with a required time at 293 $^{\circ}K$. After

regular time intervals, the flasks were then removed from the shaker, and the final concentration of dye in the solution was measured at maximum wavelength of the dye solution (668 nm) by a CARY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell. The amount of dye adsorption at equilibrium Q_e (mg/g) was calculated from the following equation:

$$Q_e = (C_0 - C_e) \times \frac{V}{W} \quad (1)$$

where, C_0 and C_e (mg L^{-1}) are the liquid phase concentrations of dye at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used. The procedure of kinetic tests was basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentration of dye solution was similarly measured. The amount of adsorption at time t , Q_t (mg/g), was calculated by

$$Q_t = (C_0 - C_t) \times \frac{V}{W} \quad (2)$$

Since the solution pH has a considerable effect on dye removal, the pH of the solution was also changed to monitor the adsorption behavior of dyes on Na-montmorillonite samples. The pH was changed by adding incremental amounts of either dilute HCl or NaOH (0.1 M each) to the solution. Changes in absorption was then used to calculate the concentration and adsorption for the dye used in this study.

RESULTS AND DISCUSSION

Characterization of adsorbing material

Thermogravimetric analysis TGA/ATD: The thermal analysis diagrams for *Natural* and *Na-montmorillonite* clay are shown in figures 2 and 3. The corresponding weight loss for *Natural* and *Na-montmorillonite* were 8.69% and 2.04% respectively.

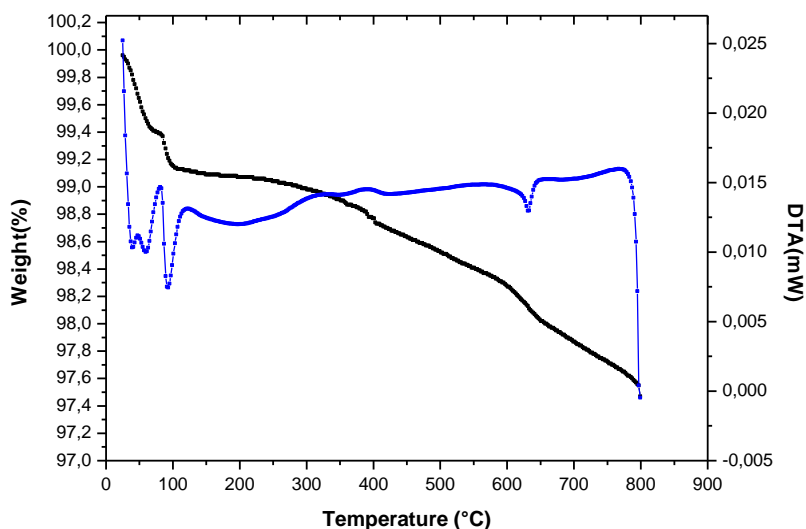


Figure.2. DTA and TG curve of Natural clay

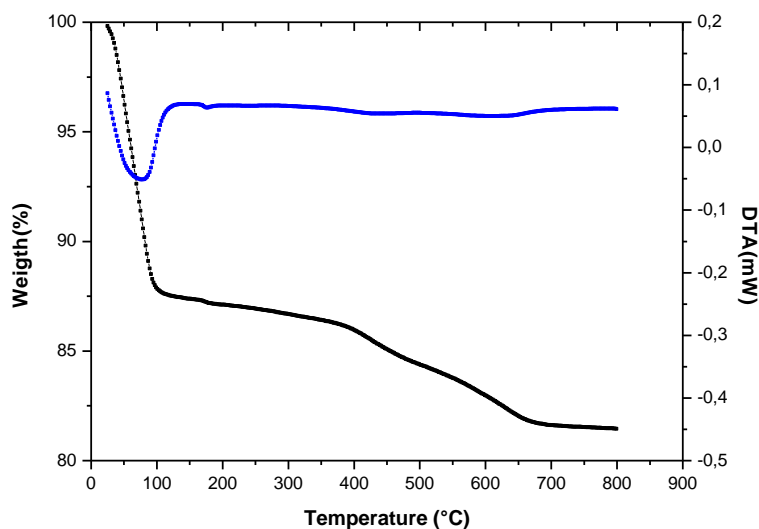


Figure.3. DTA and TG curve of Activated clay

Results showed an endothermic peak in the DTA curve of *Natural* (figure 2) in the range of 25 °C to 130 °C due to the dehydration of clay minerals. The second endothermic phenomenon took place between 350 and 600 °C, this peak is referring to the loss of hydroxyl in the structure [3]. The corresponding loss of bicarbonates and carbonates are related to the endothermic peak around 283 °C and 702 °C, respectively. The thermogravimetric results for *Na-montmorillonite* clay (figure 3) revealed a weight loss corresponding to free and absorbed water on the outer surface of Montmorillonite and organic materials [10], due to acid treatment in the range of 34 to 133 °C. The second peak occurring between 397 to 536 °C refers to the loss of hydroxyl in the structure [10].

SEM observations: SEM was used to probe the change in morphological features of natural clay and activated samples using conventional heating or microwave irradiation. SEM images of natural clay and

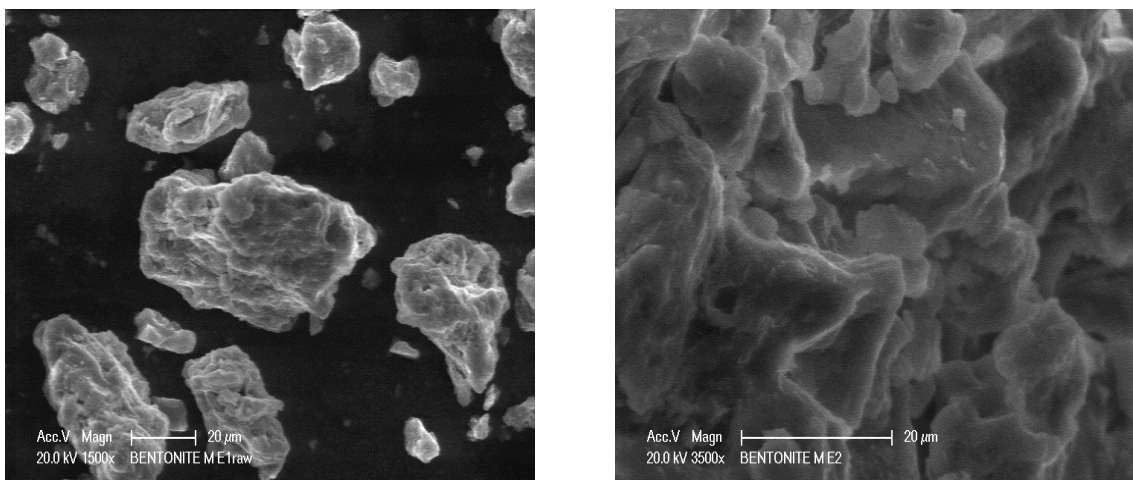


Figure.4. SEM micrographs of: 1) natural clay and 2) activated clay.

activated clay) exhibited the structure typical of smectite clays. Figure.4 shows the SEM micrographs of natural and treated clay. The surface morphology of natural clay is different from that of the treated samples.

Activated clay (figure 4.2) has larger pores between particles than natural clay (figure.4.1). Also, natural clay appears to be highly compact, so it is seen that the inter-particle pores are smaller in the natural clay, compared to the activated clay (Figure. 4.2) [11].

X-ray diffraction: Results of the X-ray diffraction analysis for natural and activated clay are shown in figure 5 clearly shows that the d-spacing of clay increased from 10.27 Å a) Natural Clay to 12.11 Å, which could be attributed to the b) activated clay. Quartz (reflection at $d = 2.89 \text{ \AA}$, $2\Theta = 35.97^\circ$) and calcite (reflection at $d = 2.89 \text{ \AA}$, $2\Theta = 35.97^\circ$) are the major impurities. The purified sample with Na-exchange shows the position of the 001 (reflection at 12.11 Å, $2\Theta = 5.37^\circ$) characteristics of sodium and kaolinite (reflection at $d = 5.41 \text{ \AA}$, $2\Theta = 19.03^\circ$).

The chemical compositions of the natural clay were comparable but activated clay had a distinctly higher content of iron (table 1). Activation decreased the iron, calcium and magnesium content and increased the silica and alumina content. Montmorillonite and Kaolinite as major clay minerals were identified by XRD (figure 5).

Table 1. Chemical analyses of material clays of Roussel from Maghnia, N. W. Algeria

Samples	Clay (%)	Clay (%)	Montmorillonite family
SiO ₂	54.10–54.98	55	50.04–57.49
Al ₂ O ₃	18.04–19.02	24.3	17.15–20.27
TiO ₂	0.14–0.16	0.10	0.12–0.48
P ₂ O ₅	<0.05	0.02	–
Fe ₂ O ₃	1.98–2.94	2	0.5–5.65
CaO	1.05–2.95	0.98	0.23–4.9
MgO	0.11–2.65	3.58	0.23–7.2
MnO	2.49	–	–
Na ₂ O	0.86–2.40	0.70	1.32
SO ₃	0.1	0.10	–
K ₂ O	1.14–1.21	1.06	0.28–1.27

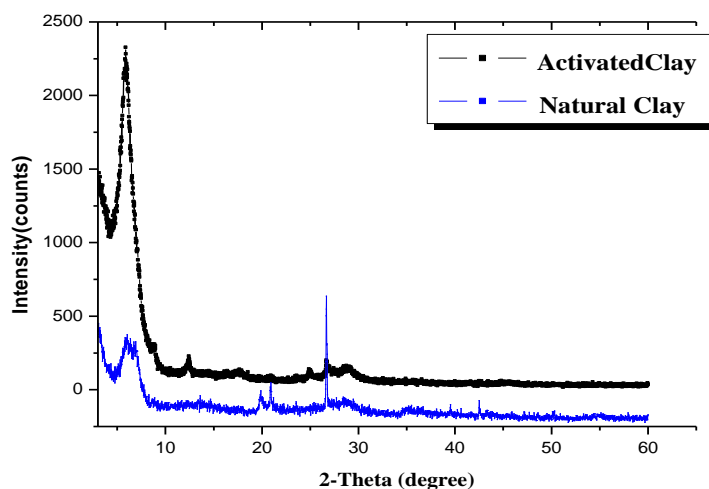


Figure.5 XRD pattern for a) Natural Clay and b) Activated Clay.

Infrared spectroscopy study: The IR spectra of the clay samples were recorded over the spectral range 400–4 000 cm^{-1} . In fact, IR techniques have been used by many researchers for identification of natural clay minerals [12]. The obtained characteristic bands of kaolinite appeared at 1 037, 912, 882, 590 and 420 cm^{-1} [13] are shown in figure 6. The high intensity of the peak appearing at 1037 cm^{-1} is an indication of the large amount of this mineral in the sample. The band at 1037 cm^{-1} is attributed to Si–O stretching. The bands at 882 cm^{-1} and 590 and 882 cm^{-1} are assigned to Si–O–Al and Si–O–Mg, Si–O–Fe and bending vibrations, respectively. This indicated that most part of the layer charge resulted from trivalent (Al^{3+} , Fe^{3+}) to bivalent (Mg^{2+}) ion substitution in the octahedral sheet. These functional groups are present in silicate minerals such as kaolinite and montmorillonite are shown in figure 6. The band observed at 3437 cm^{-1} is assigned to stretching vibrations of adsorbed water molecules. Another characteristic band for bending vibrations of adsorbed water usually appears at 1650–1600 cm^{-1} as a medium band.

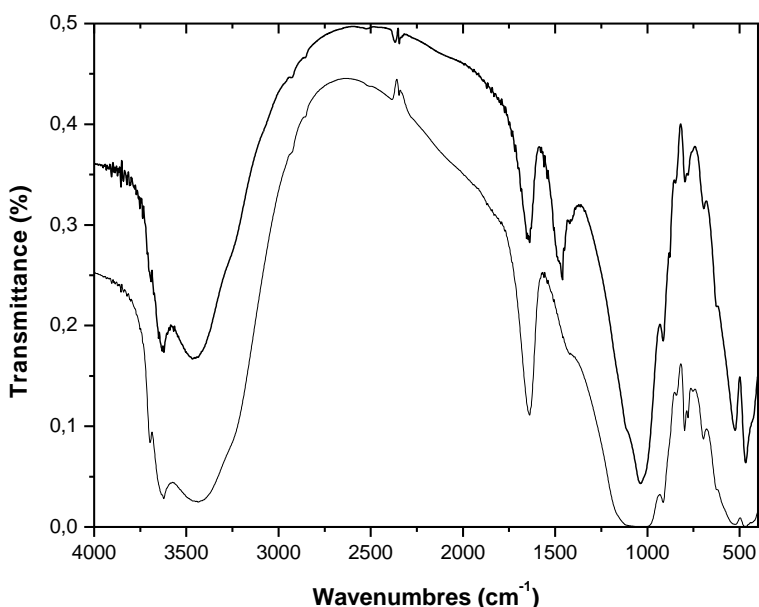


Figure.6 FTIR spectra of b) Activated and a) Natural clay

Investigation of adsorption parameters: The adsorption process of MB on clay Characterization has been discussed considering the effect of different factors.

Effect of Initial Concentration and Contact Time: A 0.5 g sample of Na-montmorillonite was added to each 30 mL volume of MB solution. The initial concentrations of dye solution tested were 10, 30, 50 and 70 mg L^{-1} and the experiments were carried out at 293° K for 270 min.

Effect of initial solution pH: Adsorption increased with pH (figure.7). All samples showed similar adsorption at $\text{pH} > 9$. The increase may be related to the formation of negative surface charges at higher pH. Since the zero point of charge of clay was at $\text{pH} = 2.3$ [14], the clay surface in water had a negative surface charge. The surface charge became more negative as the pH increased favoring the adsorption of MB cations.

Initial dye concentration and contact time: The effect of contact time on the adsorption of MB dye was investigated at different initial dye concentration (10–100 mg L^{-1}) onto natural and activated clay adsorbents. It can be noticed from figures.8 and 9 that the removal of dye by adsorption on onto natural clay and activated was found to be rapid at the initial period of contact time and then to slow down with

time. The reason for this from my opinion is the attractive forces between the dye molecule and the adsorbent such as Vander Waals forces and electrostatic attractions; fast diffusion onto the external surface was followed by fast pore diffusion into the intraparticle matrix to attain equilibrium at 270 min. Also it can be seen from Figures 8 and 9 that the amount of dye adsorbed (mg g^{-1}) increased with increased initial dye concentration and remained constant after equilibrium time (270 min). The concentration provides an important driving force to overcome all mass transfer resistance of the dye between the aqueous and solid phases. Hence a higher initial concentration of dye will enhance the adsorption process. The equilibrium sorption capacity of the natural and activated clay increased with the increase of the initial dye concentration, while the effect of contact time and initial dye concentration showed the opposite trend (figures 8 and 9). When the initial dye concentration increased from 10 to 100 mg L^{-1} , the actual amount of dye adsorbed per unit mass of Natural clay increased from 55.6 to 95.25 mg g^{-1} and Activated Clay increased from 57.3 to 98.7 mg g^{-1} .

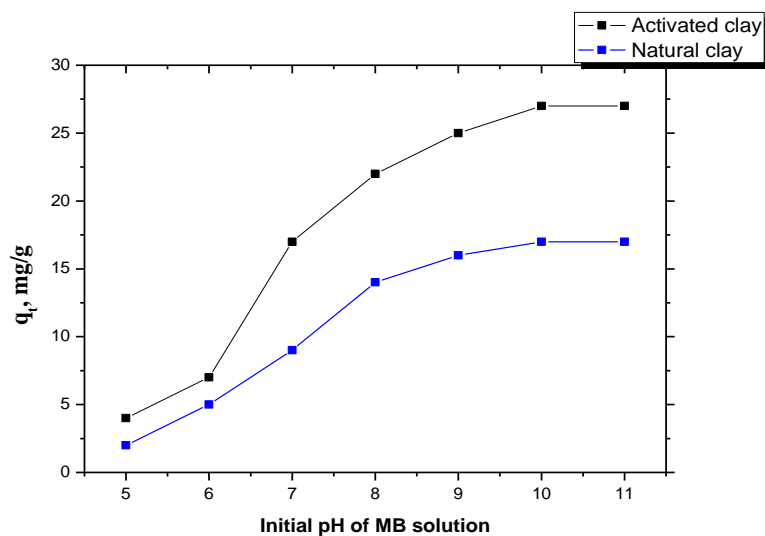


Figure.7 Effect of pH on MB adsorption (initial MB concentration: 30 mg L^{-1} adsorbent content: 0.5 g 30 mL^{-1} ; equilibrium time: 270min).

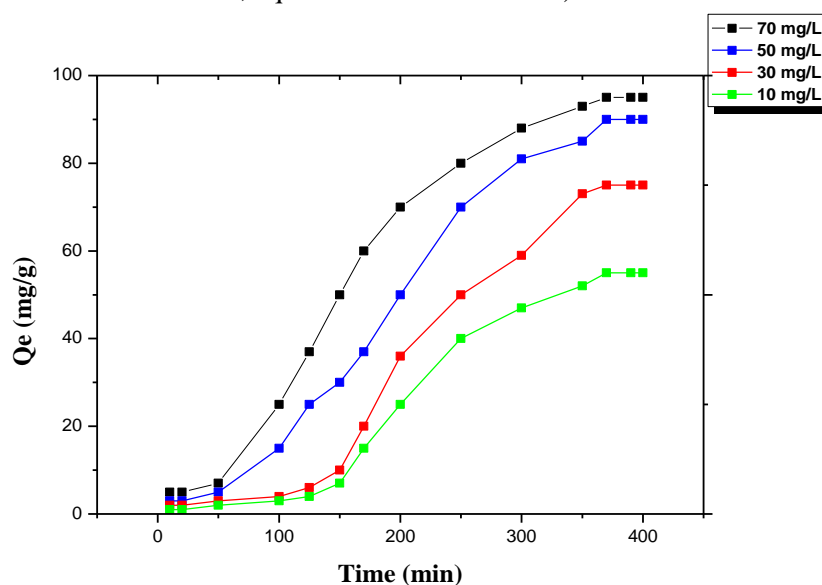


Figure.8 Effect of contact time and initial dye concentration on the removal of MB dye onto Natural Clay (pH= 7.5, solution temp. = 293°K).

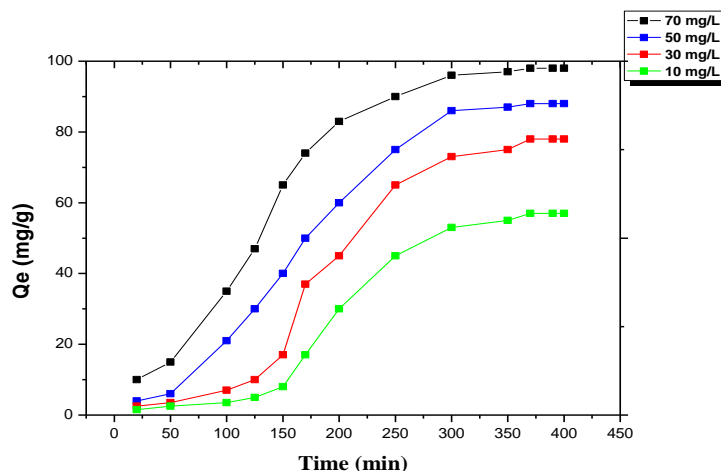


Figure.9 Effect of contact time and initial dye concentration on the removal of MB dye onto Activated clay (pH= 7.5, solution temp = 293°K).

Effect of temperature and the calculation of thermodynamic parameters: Temperature is a highly significant parameter in the adsorption process. Figures 10 and 11 displays the adsorption curves under different isothermal conditions. The amount of methyl orange adsorption increases with temperature and the time taken to reach equilibrium decreases with increasing temperature. This suggests that the interaction of adsorbate and adsorbent is endothermic in nature. Isotherms for MB adsorption by natural and activated clay can be modeled using two commonly used isotherms of Langmuir (Eq. (3)) and Freundlich (Eq. (4)) [15].

$$\frac{1}{Q_e} = \frac{1}{(K_L \times Q_m \times C_e)} + \frac{1}{Q_m} \quad (3)$$

$$Q_e = K_f \times C_e^n$$

$$\log Q_e = \log K_f + (n \times \log C_e) \quad (4)$$

Where Q_e (mg g^{-1}) is the amount of MB adsorbed at equilibrium, Q_m (mg g^{-1}) the theoretical maximum monolayer adsorption capacity, C_e (mg L^{-1}) the equilibrium concentration of MO in solution, and K_f , n and K_L are empirical constants.

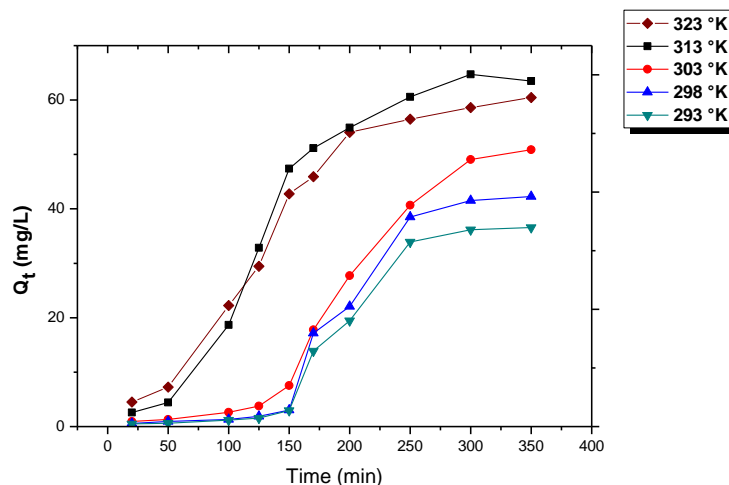


Figure.10 Effect of temperature on the adsorption of MB dye onto Natural clay ([MO] = 30 mg L^{-1} , pH 7,5, [clay natural] = 0.5 g L^{-1}).

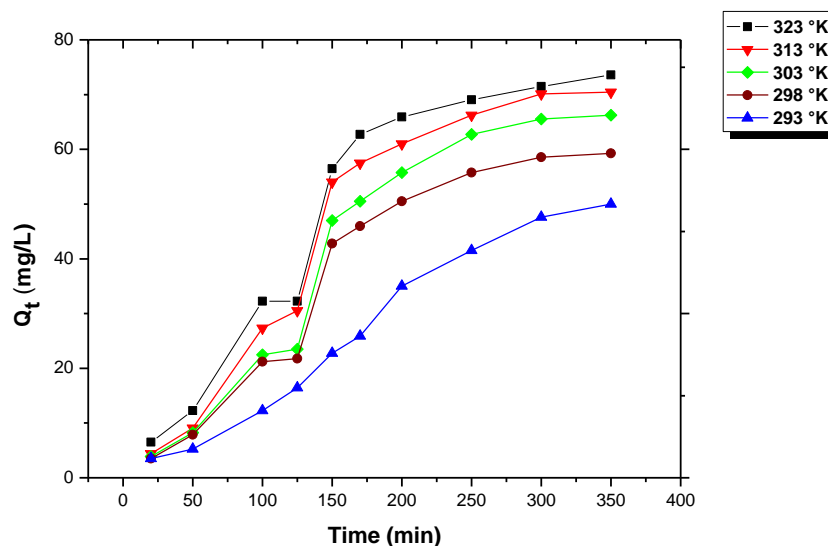


Figure.11 Effect of temperature on (BM) adsorption by ([MB] = 30 mgL⁻¹, pH 7,5, [Activated clay] = 0.5 g L⁻¹).

Data for MB adsorption by natural clay are both fitting well to Langmuir model and Freundlich model and that the Freundlich model gives a little better fit to the experimental data than the Langmuir model based on the correlation coefficient R^2 . The calculated Langmuir and Freundlich isotherm constants are given in table 2. The observed MB uptakes by natural and activated clay in different temperatures for fitting Langmuir parameters are close to the stoichiometric uptakes by natural clay; the increase in the value of b ($b = K_L Q_m$) with increasing temperature is attributed to the increase in adsorption capacity of the adsorbent for MB and endothermic nature of the process. Decreasing values of K_L with temperature are accompanied by low energy requirement for MB adsorption [16]. For fitting Freundlich parameters, the values of n between 0 and 0.7 represent good adsorption of MB on Natural and activated Clay.

The temperature dependence of adsorption process is associated with changes in several thermodynamic parameters such as standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of adsorption. The calculations were done by using the following Eq. (5) [17]:

$$\Delta G^\circ = -R \times T \times \ln b \quad (5)$$

Where R is the universal gas constant, T the temperature (K) and b the Langmuir constant ($b = K_L Q_m$). According to Van't Hoff model (Eq. (6))

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R \times T} \quad (6)$$

Table 2. Langmuir and Freundlich isotherm constants for adsorption of MB by natural and activated clay

Temperature (°K)	Langmuir			Freundlich		
	Q_m (mg.g ⁻¹)	K_L (L .mg ⁻¹)	R^2	n	KF (L .g ⁻¹)	R^2
293	45	0.2	0.96	0.6	67	0.94
298	68.02	0.2	0.96	0.9	157.98	0.98
303	222.22	0.010	0.97	0.67	29.14	0.98
313	270.27	0.008	0.99	0.79	16.18	0.91
323	277.77	0.0067	0.98	0.73	6.209	0.94

Temperature (°K)	Langmuir			Freundlich		
	Activated Clay	Q_m (mg.g ⁻¹)	K_L (L .mg ⁻¹)	R^2	n	K_F (L .g ⁻¹)
293	55	0.1	0.97	0.5	30	0.97
298	106.38	0.045	0.95	0.7	24.46	0.97
303	250	0.012	0.95	0.57	107.37	0.98
313	303.03	0.0088	0.93	0.64	300.67	0.999
323	325	0.0032	0.8	0.67	304.38	0.92

The values of ΔH° and ΔS° were evaluated from the slope and intercept of the Van't Hoff plot respectively by regression method and presented in table 3. The positive value of ΔH° confirms the endothermic nature of adsorption. The negative values of ΔG° at different temperatures (293–323 K) indicate the spontaneous nature of MB adsorption. The positive value of ΔS° suggests the increased randomness at the solid/solution interface during the adsorption of MB on Natural and Activated Clay.

Table 3 Gibbs free energy, enthalpy, entropy changes associated with MB adsorption by Natural and Activated Clay

Temperature (°K)	ΔG° (kJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
Natural Clay	-5.35	63.82	219.57312
293	-5.204	63.82	219.57312
298	-2.013	63.82	219.57312
303	-2.00	63.82	219.57312
313	-0.47	63.82	219.57312
323	-5.35	63.82	219.57312
Temperature (°K)	ΔG° (kJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
Activated Clay	- 4.15	51.82	179.04
293	-3.88	51.82	179.04
298	-2.77	51.82	179.04
303	-2.55	51.82	179.04
313	-0.105	51.82	179.04
323	- 4.15	51.82	179.04

Kinetic models and adsorption mechanism: Kinetic modeling not only allows estimation of sorption rates but also leads to suitable rate expressions characteristic of possible reaction mechanisms. In this respect, several kinetic models including the first-order kinetics model (Eq. (7)) [18], pseudo-second-order kinetics models (Eq. (8)) [18] and the Elovich equation (Eq. (7)) were tested [19].

$$\ln(Q_e - Q_t) = \ln Q_e - (K_1 \times t) \quad (7)$$

$$\frac{t}{Q_t} = \frac{1}{(K_2 \times Q_e^2)} + \frac{1}{(Q_e \times t)} \quad (8)$$

where Q_e (mg g⁻¹) and Q_t (mg g⁻¹) are the adsorption loading of MB at equilibrium and at time t (min), respectively, k_1 (min⁻¹) and k_2 (mg (g min)⁻¹) the rate constant of first order and pseudo-second-order adsorption.

Data for MB adsorption by natural and activated clay was fitted best by the pseudo-second-order model based on the correlation coefficient (R^2), which indicates that the pseudo-second-order model is more

suitable in describing the adsorption kinetics of MB on natural and activated clay, the results of fitting experimental data to pseudo-second-order diffusion are given in Table 4. The experimental $Q_{e,exp}$ values consist well with the calculated ones obtained from the pseudo-second-order kinetics model. The pseudo-second-order model is based on the adsorption loading of the solid phase and is in agreement with a chemisorption mechanism being the rate-determining step. Another advantage of the pseudo-second-order model is that it predicts the behavior over the whole range of the adsorption process.

Table 4 Initial MB concentrations, kinetic parameters and correction coefficient (R^2) for the pseudo-second-order kinetic model.

[MO] ₀ (mg. L ⁻¹)	T (°K)	Natural Clay				Activated Clay			
		$Q_{e,exp}$ (mg. g ⁻¹)	$Q_{e,cal}$	$k_2 \times 10^{-4}$ (mg (g.min) ⁻¹)	R^2	$Q_{e,exp}$ (mg. g ⁻¹)	$Q_{e,cal}$	$k_2 \times 10^{-4}$ (mg (g.min) ⁻¹)	R^2
10	293	55.6	60	1.92	0.97	57.3	61.2	3.7	0.96
30	293	75.7	78.7	1.34	0.96	78	80.3	1.8	0.96
50	293	88.1	89.3	0.98	0.99	88.5	90.3	1.2	0.99
70	293	95.25	98	0.36	0.96	98.7	100.4	0.72	0.96
30	298	39.25	40	3.16	0.90	59.25	72.46	4.8	0.93
30	303	56.25	57.14	3.93	0.94	66.25	72.99	5.81	0.90
30	313	58.95	59.82	7.91	0.96	70.45	78.74	7.34	0.96
30	323	60.45	66.66	26.23	0.99	73.6	86.95	7.39	0.89

An Arrhenius plot (not shown here) of the adsorption rate against the different temperatures was performed using the kinetic data, giving a reasonably straight line ($R^2 = 0.96$). The gradient of this plot is $-(E_a/R)$, according to the well-known Arrhenius expression given in Eq. (9), and the activation energy can thus be calculated.

$$K_e = \left(A \times e^{-\left(\frac{E_a}{R \times T}\right)} \right) \quad (9)$$

For diffusion-controlled processes, the activation energy of adsorption is less than 20 kJ mol⁻¹ [20]. The calculated E_a value in our case, 66.5 kJ mol⁻¹, indicates that the process of Methylene Blue removal is controlled by the rate of reaction of Methylene Blue with the natural and activated clay rather than diffusion.

APPLICATIONS

The Activated Clay can be used as the effective adsorbent for the removal of methyl orange (MB) from aqueous solution.

CONCLUSIONS

Adsorption isotherms were both well described by the Freundlich and Langmuir models. A maximum capacity of MB adsorbed on Natural and Activated Clay at equilibrium (Q_e) (78 mg g⁻¹ and 75.7 mg g⁻¹) with a fixed adsorbent dose of 0.5 g L⁻¹ was observed at MB concentration of 30 mg L⁻¹, 293° K, pH 7.5 and 270 min equilibrium time. The positive value of ΔH° indicated that the adsorption process was endothermic in natural and Activated Clay, the negative values of ΔG° at different temperatures (293–323° K) indicated the spontaneous nature of MB adsorption. The adsorption kinetics can be successfully fitted to pseudo-second-order kinetic model. An E_a value of 66.5 kJmol⁻¹ indicates that the MB uptake process by Activated Clay is controlled by the rate of reaction of MB with the Activated Clay rather than diffusion. The results reported here demonstrate that Activated Clay can be used as the effective adsorbent for the removal of methyl orange (MB) from aqueous solution.

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