

Removal of Cationic Dye Methylene Blue from Aqueous Solution by Adsorption on Algerian Clay

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Abstract

The objective of this study was to demonstrate the potential of Tiout-Naama (TN) clay for removing a cationic Methylene blue (MB) dye from aqueous solutions which was used for the first time like an adsorbent. For this, the effect of several parameters such as contact time, adsorbent dose, pH and temperature have been reported. Nearly 30 min of contact time are found to be sufficient for the adsorption to reach equilibrium. The residual concentration of the dye is determined using UV/Vis Spectrophotometer at wavelength 664 nm. Langmuir and Freundlich isotherm models were used to describe adsorption data. The result revealed that the adsorptions of MB dye onto TN clay is the best-fit both Langmuir and Freundlich isotherms, further to understand the adsorption kinetics the adsorption data were analyzed by the second-order and the pseudo-second-order. The results show that the methylene blue adsorption follows pseudo-second-order kinetics.

Keywords: Dye; Adsorption; TN clay; Adsorption kinetics; Adsorption isotherms

Introduction

Water and soil pollution is a source of decay of the environment. Among these pollutants are the textile industry rejects which are heavily saturated by organic colorants. These colorants are usually used in excess to make the dye better, and consequently sewage is highly concentrated with colorants. In this objective, several methods are used to eliminate these colorants from industrial wastes Traditional process; such as chemical-physical treatments based on the addition of coagulant and flocculants (aluminium salts and polymers) [1] and biological process by the use of activation mud with a sufficient aeration [2], nevertheless these methods are not satisfying because of the weak colorant biodegradability [3]. The adsorption on active carbon is efficient but very expensive and has high operating costs due to the high price of the activated carbon and to the high water flow rate always involved [4]. In this way the majority of the processes are very selective according to the colorant categories to treat and some just move the pollution instead of removing it. It is necessary for the process to mineralize the colorant. Research is focussing on process using natural materials such as clay, agriculture waste residues [5] e.g wood, Waste. The different applications of the clay depend on their specific adsorption properties, the ion exchange and the surface nature. Due to these qualities, clay is used in different field, like in medical and pharmaceutical industries, organic molecule polymerization [6], and pollutant retention eg. Pesticides, organic colorants, heavy metals [7,8]. This paper presents the elimination of Methylene blue, an organic colorant used in textile industries, by adsorption on a natural material that is the clay of Tiout region in Algeria. This kind of clay fulfils all the environment protection conditions, and is very abundant and not expensive [9]. Kinetic and isotherm adsorption models are performed in order to better understand the organic colorant adsorption mechanisms [10].

Materials and Methods

Materials

The clay used in this work is montmorillonite type from Tiout region located south west Algeria . The clay undergoes a pretreatment by stirring it for two hours at room temperature. The obtained suspension is filtered, ground and heated until obtaining a constant weight, then stored in a securely closed flask against the moisture.

In order to show the clay capacity of decoloration, we chose an organic colorant that it has methylene blue taken as a reference for pollutants because of its middle-size molecule and its several uses in tests, has a high solubility in water and it is one of the Thiazine colorants having the chemical formula $C_{16}H_{18}N_3Cl$ and molecular weight of 319.89 g/mole. The chemical structure is presented in Figure 1.

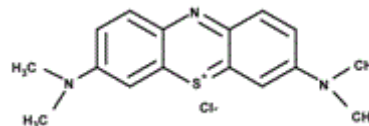


Figure 1: Chemical structure of methylene blue dye.

Chemical analysis showed the clay used is composed essentially of silica and alumina approximately 71.5% and of iron oxide 7.30% (Table 1), the presence of ions Na⁺, Ca⁺ and K⁺ in the clay gives it a swelling type. The ratio SiO₂/Al₂O₃=3.51 reveals its montmorillonite characteristics. The mineralogical composition of the natural clay was determined by X-ray diffraction (XRD) using DRX.D8 ADVANCE BRUKER generator with copper anticathode ($\lambda_{CuK\alpha}=1,5406 \text{ \AA}$). The Xray spectrum shows that the TN clay is a mixture of monmorillonite and impurities of calcite and quartz (Figure 2).

Elements	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	SO ₃ gyp	Cl	PF
% CCM	55.72	15.85	7.30	4.11	2.26	1.30	4.08	0.43	1.11	0.01	7.66

Table 1: Chemical composition of TN Clay.

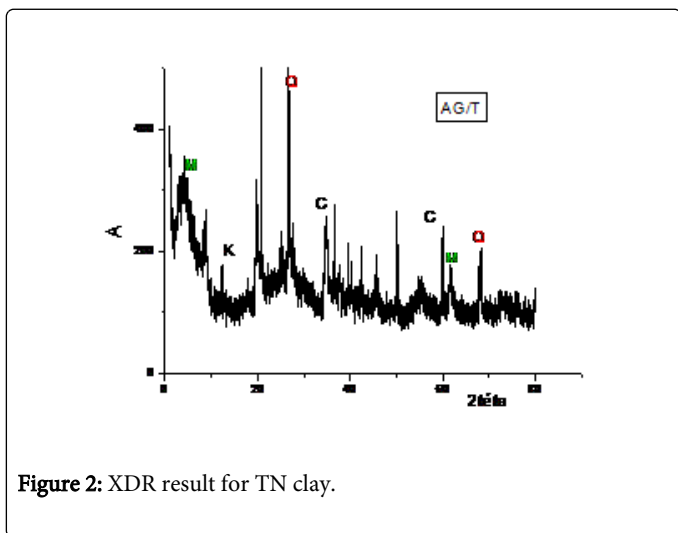


Figure 2: XDR result for TN clay.

Methods

In a series of 100 ml flasks, 80 mg of adsorbent (raw clay) is mixed with each 50 ml volume of Methylene blue aqueous solution having an initial concentration 25.59 mg/l. The adsorption tests are performed at natural pH, room temperature and magnetic stirring at 450 rpm at different time intervals. After equilibration, the aqueous phase was separated by centrifugation at 2500 rpm during 15 min. The concentration of the residual dye C_r was determined using SHIMADZU 1240, a spectrophotometer UV/Vis at 664nm of wavelength after 30 min. The equilibrium adsorption capacity q_e (mg/g) was calculated from the following equation:

$$q_t = (C_0 - C_r) \cdot \frac{V}{m} \quad (1)$$

q_e : is the amount of dye adsorbed at equilibrium (mg/g)

C_0 and C_r are the initial and equilibrium concentrations of the dye, respectively, computed from the calibration curve (mg/l).

V : is the volume of the solution (l).

m : is the mass of the adsorbent (g).

Results and Discussion

Effect of contact time

The influence of time is achieved at natural pH of the solution for an initial concentration of 25.59 mg/l, with a mass of clay of 80 mg/l and at room temperature. The amount of colorant adsorbed q_t at time t was determined by the following expression:

$$q_t = (C_0 - C_r) \cdot \frac{V}{m} \quad (2)$$

Figure 3 shows the time course of adsorption equilibrium of Methylene Blue onto raw clay. The amount of dye adsorbed by adsorption on raw clay was found to be rapid at the initial period of contact time and then become slow and stagnant with increase in contact time; the mechanism of adsorbent removal can be described in migration of the dye molecule from the solution to the adsorbent particle and diffusion through the surface [11,12]. A 30 min contact was recommended for carrying out adsorption experiments.

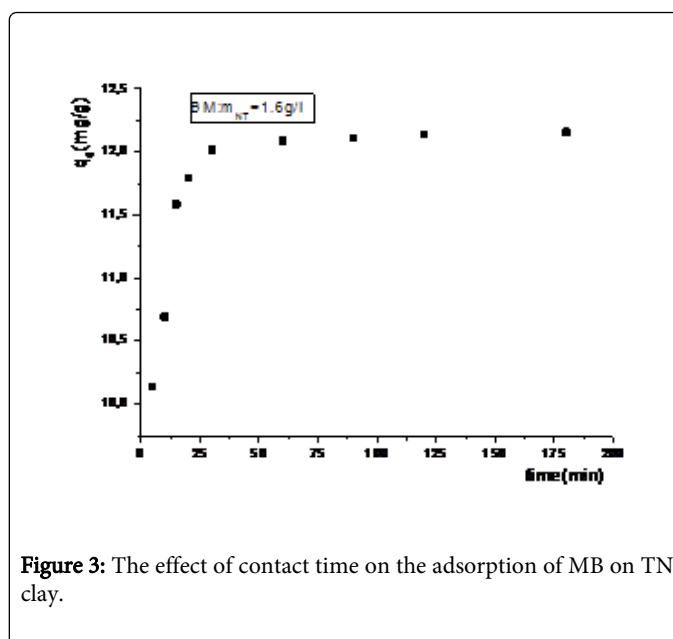


Figure 3: The effect of contact time on the adsorption of MB on TN clay.

Kinetics order

Adsorption kinetics is literary reviewed in different forms. In this paper kinetic laws of the second order and pseudo-second order are used. The second order kinetic model has the following formula.

$$\frac{dq}{dt} = k(q_e - q_t)^2 \quad (3)$$

Where k is the rate constant of second-order adsorption has the following formula.

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k \cdot t \quad (4)$$

For the pseudo-second-order model is given by the following equation.

$$\frac{dq_t}{dq_e} = k' \cdot (q_e - q_t)^2 \quad (5)$$

Where k' is the rate constant of pseudo-second-order adsorption has the following formula.

$$\frac{t}{q_t} = \frac{1}{k' \cdot q_e^2} + \frac{t}{q_e} \quad (6)$$

The kinetic data obtained using the second order and pseudo-second order is depicted in Figures 4 and 5.

R ²	0.99
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Table 2: The pseudo- second -order parameters of MB adsorption into TN clay.

Effect of adsorbent mass

The effect of adsorbent mass on the adsorption capacity was studied using 50 ml of Methylene blue (25.591 mg/l) onto 1-4 g/l of adsorbent with shaking at room temperature for 30 min, the solid particles were removed and the remaining concentration of colorant in the filtrate was measured by using the UV/Vis spectrophotometer at 664 nm.

The effect of sorbent quantity on dye removal is illustrated in Figure 6. From the figure it can be seen that an increase mass of crude clay 1 g/l down to a value of 4 g/l causes a decreases in residual dye concentration. The increase in Methylene blue adsorption with the increase in adsorbent mass is attributed to increase in surface area of micro pores and the increase in availability of vacant adsorption sites. The same results were obtained by other authors [17,18].

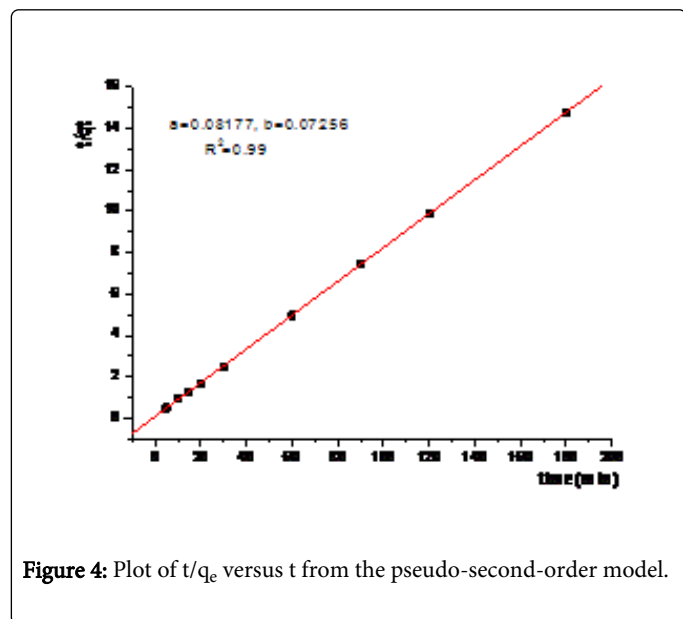


Figure 4: Plot of t/q_e versus t from the pseudo-second-order model.

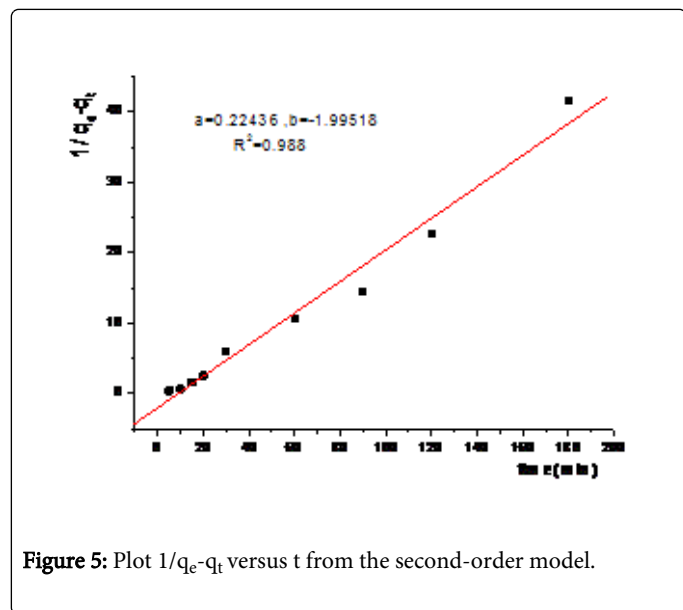


Figure 5: Plot $1/q_e - q_t$ versus t from the second-order model.

The q_e value calculated from the pseudo-second-order model is in accordance with the experimental q_e value. The correlation coefficient R^2 of the linear plot is very high. The result is shown in Table 2. The value of kinetic constant and q_e indicates that the adsorption follow the pseudo-second order model. Several studies found that the kinetics of adsorption of dyes on clay supports obey to the pseudo-second-order [13-16].

Parameters	Pseudo-second-order
K' (g/mg min)	0.092
Q_{ecal} (mg/g)	12,229
$q_e \text{ épx}$ (mg./g)	12,183

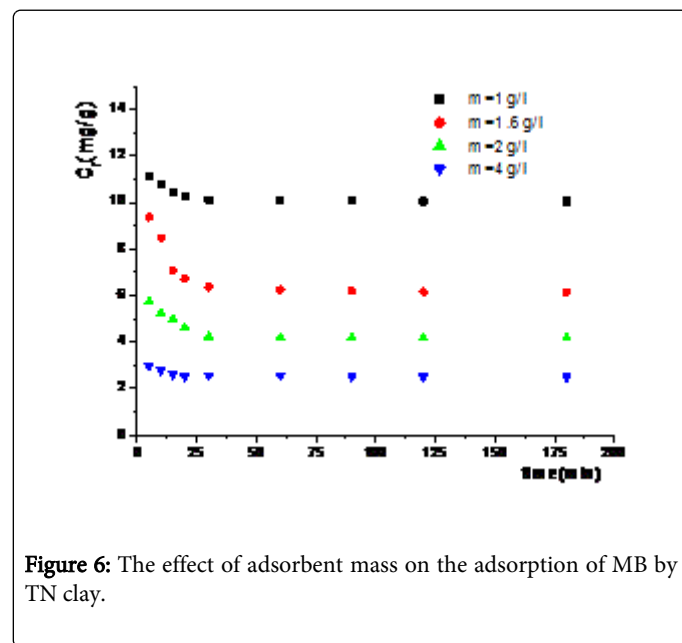


Figure 6: The effect of adsorbent mass on the adsorption of MB by TN clay.

Effect of pH

The influence of pH on dye removal was determined by performing the adsorption experiments at different initial pH of the solution (2-11) at room temperature. The pH of the solution was adjusted with HCl (0.1 N) or NaOH (0.1 N) solution by using a HANNA 210 pH-meter equipped with a combined pH electrode. The adsorption of Methylene blue onto clay is highly dependent on pH of the solution. The Figure 7 shows that the adsorption increased with increasing pH. The removal dye is low in the acid pH region because the hydrogen ions neutralize the negatively charged clay surface thereby decreasing the adsorption of the positively charged cation because of reduction in the force of attraction between adsorbate and adsorbent. The removal of dye is more at higher pH, because the surface of used clay is negatively charged. Therefore, the electrostatic attractive force between the colorant dye, which has a positive charge, and the adsorbent surface increases, and consequently, the rate of dye adsorption increases, the highest dye removal was detected in pH 9.

Similar results have been reported for the adsorption of Methylene blue on Morocco clay [19,20].

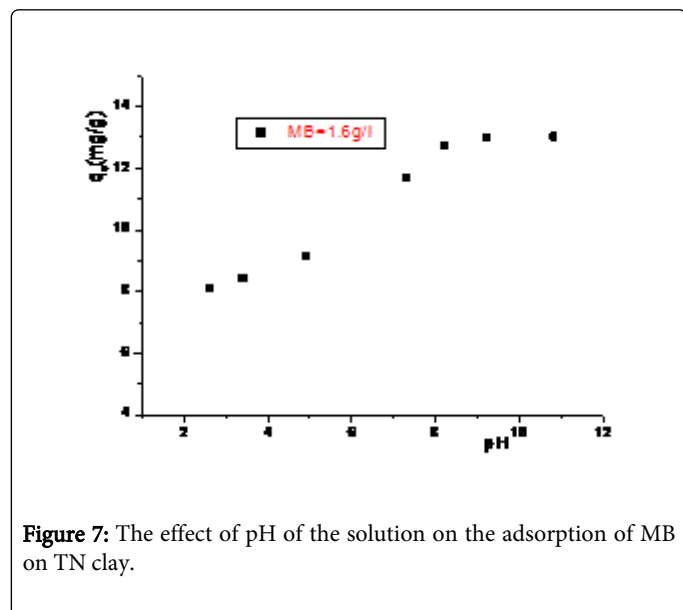


Figure 7: The effect of pH of the solution on the adsorption of MB on TN clay.

Effect of temperature

The amount of dye adsorbed on Tiout-Naama clay was determined at 20, 30, 40 and 60°C to investigate the effect of temperature. 80 mg of adsorbent was added to 50 ml dye solution with initial concentration of 25.59 mg/l. The contents in the flasks were agitated for 30 min.

The Figure 8 shows that as temperature increases from 20°C to 60°C, the adsorbed amount of dye at the same equilibrium concentration increased. Similar observations have been reported in the literature [21]. When temperature increased, the physical bonding between the organic compounds (including dyes) and the active sites of the adsorbent weakened. Besides, the solubility of Methylene blue also increased with increase in temperature.

Thermodynamic parameters

The Gibbs energy is calculated from the given equation:

$$\Delta G = -RT \ln K_c \quad (7)$$

K_c represented the ability of the retain the adsorbate and extent of movement of it within the solution. The value of K_c can be deduced from the following formula:

$$K_c = \frac{q_e}{C_e} \quad (8)$$

Where:

q_e : is the amount of dye adsorbed at equilibrium (mg/g)

C_e : is the equilibrium concentrations of the dye in the solution.

The thermodynamic equation:

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

And the Vant'Hoff formula:

$$\Delta G = -RT \ln K_c \quad (10)$$

Can be deduced the following formula:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{R} \cdot \frac{1}{T} \quad (11)$$

The values and can be obtained by plotting the versus $1/T$ (Figure 9).

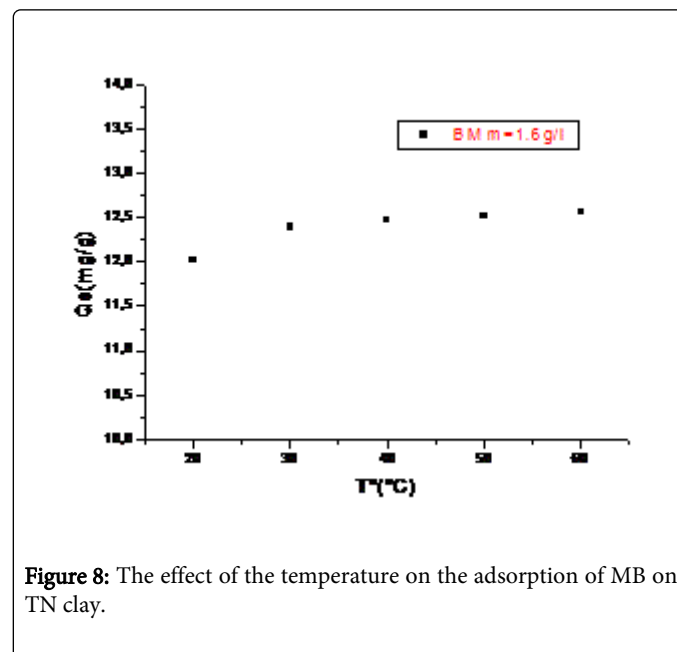


Figure 8: The effect of the temperature on the adsorption of MB on TN clay.

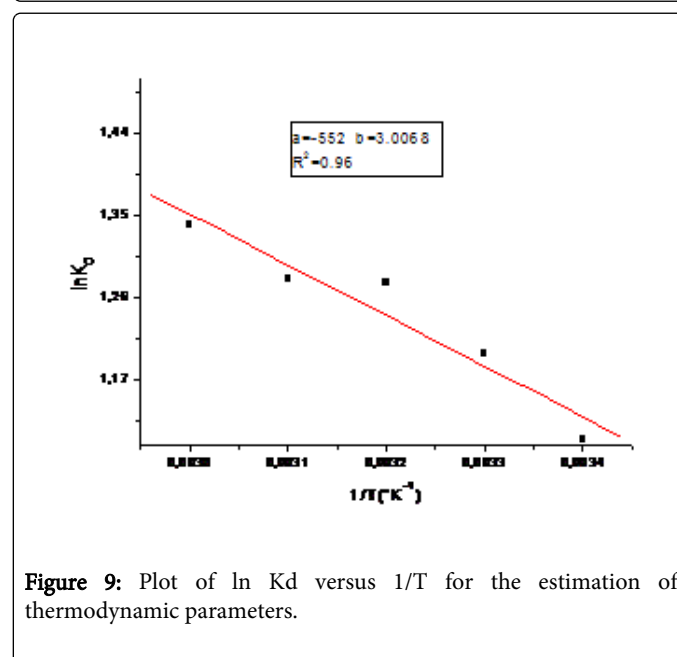


Figure 9: Plot of $\ln K_d$ versus $1/T$ for the estimation of thermodynamic parameters.

According to the thermodynamic parameters represented in Table 3, we realized that the ΔH enthalpy of the system is positive so the adsorption process on Tiout-Naana clay is endothermic, the low value of this energy (<40 KJ/mole) shows that it is a physical adsorption, the positive value of ΔS shows the attraction of the adsorption according to the dye, the negative value of ΔG indicates that the adsorption is done through a spontaneous and favourable process [22].

Adsorbant	Colorant	T (°K)	ΔG KJ/mol	ΔH KJ/mol	ΔS mol.K	R ²
TN clay	MB	20	-2.90	4.58	24.96	0.92
		30	-2.98	-	-	
		40	-3.23	-	-	
		50	-3.48	-	-	
		60	-3.72	-	-	

Table 3: Thermodynamic parameters of MB adsorption into TN clay.

Adsorption isotherm

Several laws have been proposed for the study of adsorption. They express the relation between the amount adsorbed and the concentration of aqueous solution at a specific temperature; the most commonly models used for adsorption are Langmuir and Freundlich isotherms those have been selected in this study.

The Langmuir isotherm is valid for monolayer adsorption onto a surface with a finite number of identical sites. The homogeneous Langmuir adsorption isotherm is represented by the following equation:

$$q_e = q_{max} \cdot \frac{bC_e}{(1 + bC_e)} \quad (12)$$

Where q_e is the amount adsorbed at equilibrium (mg/g), C_e equilibrium concentration (mg/l), b constant related to the adsorption energy (l/mg), and q_{max} the maximum adsorption capacity (mg/g).

The linear form of Langmuir equation may be written as

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b} \cdot \frac{1}{C_e} \quad (13)$$

By plotting $(1/q_e)$ versus C_e , q_{max} and b can be determined if a straight line is obtained.

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on heterogeneous surfaces, and adsorption capacity is related to the concentration of colorant at equilibrium. The heterogeneous Freundlich adsorption isotherm is represented by the following equation:

$$q_e = C_e^{1/n} \cdot K_F \quad (14)$$

Where the K_F is Freundlich constant related to the adsorption capacity (mg/g) and $1/n$ shows the adsorption intensity (l/mg).

The linear form of Freundlich equation may be written as

$$\log q_e = \frac{1}{n} \cdot \log C_e + \log K_F \quad (15)$$

The values of n and K_F can be determined by plotting the $\log q_e$ versus $\log C_e$ if a straight line is obtained.

In the experiments of equilibrium adsorption isotherm, a fixed amount of 80 mg adsorbent is contacted with 50 ml of aqueous solutions Methylene bleu have different concentrations (10–250 mg/l). The adsorption was carried at room temperature while keeping all other parameters constant and the result is shown in Figures 10 and 11. Values for q_{max} , b , n and K_F , are summarised in Table 4. It can be seen, the result revealed that the adsorption of Methylene bleu dye onto raw clay was the best-fit both Langmuir and Freundlich isotherms. The n value is greater than 1 which indicates that the adsorption process is favourable [23].

Parameters	Langmuir	Freundlich
q_{max} (mg/g)	56.850	-
R ²	0.99	0.99
b	2.94	-
$1/n$	-	0.759
LogKF	-	0.479

Table 4: Isotherm constants for adsorption of MB on TN clay.

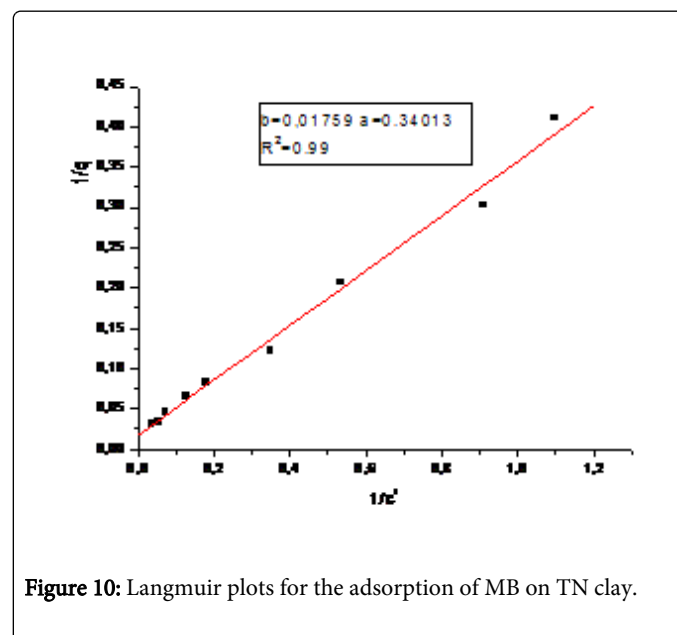


Figure 10: Langmuir plots for the adsorption of MB on TN clay.

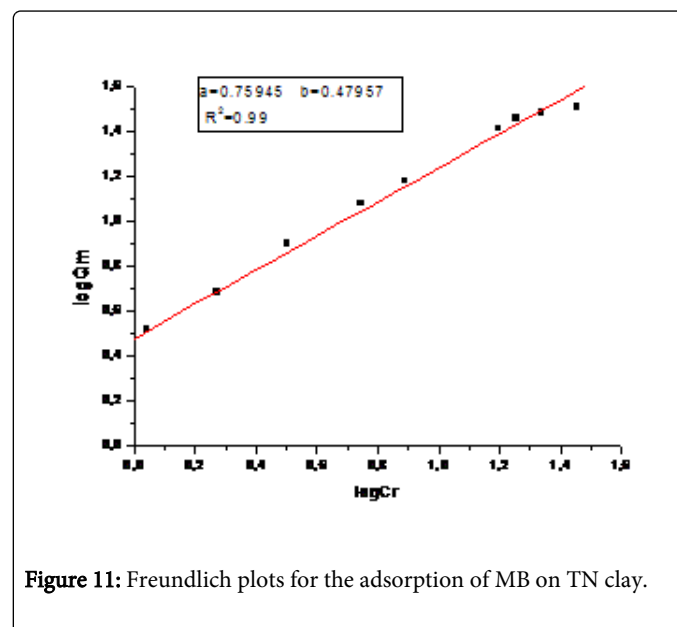


Figure 11: Freundlich plots for the adsorption of MB on TN clay.

Conclusions

The present study shows that the natural Algerian clay, abundant low-cost clay, can be used as sorbent for the removal of Methylene

blue dye from aqueous solution. The value of kinetic constant and q_e indicates that the adsorption follows the pseudo-second order model.

Nearly 30 min of contact time are found to be sufficient for the adsorption to reach equilibrium. When the amount of crude clay increases from 1 g/l to a value of 4 g/l causes decreases in residual dye concentration. The results suggested that the adsorption capacity of organic compound colorant on raw clay adsorbent increased with increasing pH, rising the temperature induces a slight growth in the adsorption capacity, the negative value of ΔG indicates that the adsorption is done through a spontaneous and favourable process, the result revealed that the adsorption of Methylene blue dye onto Tiout-Naama clay was the best-fit both Langmuir and Freundlich isotherms and the maximum adsorption capacity is in the order of 56.85 mg /g.

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