JCHR (2022) 12(4), 563-574

Journal of Chemical Health Risks

**ORIGINAL ARTICLE**

# Study of the Adsorption Performance of a Cationic Dye onto a Moroccan Clay

Brahim Abbou[*1], Imane Lebkiri[1], Hanae Ouaddari[2], Lamya Kadiri[1], Abdelkarim Ouass[1], Abdlhay Elamri[1], Jaouad Bensalah[1], Amar Habsaoui[1], Ahmed Lebkiri[1], El Housseine Rifi[1]

[1] *Laboratory of Advanced Materials and Process Engineering, Faculty of Sciences, Ibn Tofail University, Kenitra, Morocco*

[2] *Laboratory of Materials, Membranes and Environment, Faculty of Sciences and Technologies of Mohammedia, Hassan II University, Casablanca, Morocco*

*(Received: 31 January 2021 Accepted: 27 November 2021)*

**KEYWORDS**
Cationic dye;
Methylene Blue;
Kinetic;
Isotherm;
Thermodynamic

**ABSTRACT:** The purpose of this study is to examine the adsorption process of a cationic dye, in this case Methylene Blue (MB), on Moroccan natural clay collected from Marrakech region. The influence of physicochemical parameters (contact time, pH, mass of the adsorbent, initial Methylene Blue concentration and temperature) on MB adsorption performance on clay was studied. Experimental results showed a remarkable and rapid elimination within the first twenty minutes of contact of the two phases. The adsorption kinetics of Methylene Blue was evaluated applying pseudo first and second order kinetic models. The kinetic study demonstrates that adsorption obeys the pseudo second order model. The adsorption process was determined by applying the Langmuir and Freundlich isotherms. The maximum adsorption capacity of the raw clay is about 32 mg $g^{-1}$. The temperature effect on dye adsorption was also examined and thermodynamic parameters were calculated.

## INTRODUCTION

The discharges from the textile industry are a huge nuisance to human health and the aquatic life [1, 2]. In particular, the various dyes used cause grave problems due to their low biodegradability and their high stability [3, 4]. As a result of this great threat to the environment, a lot of work has been done on water pollution control in recent years and several pollution control processes have been developed [5, 6]. These processes include ion exchange resin, electrodialysis, chemical precipitation, nanofiltration, adsorption, etc. [7, 8]. However, adsorption is still a relatively widely used method in wastewater treatment. Because of its high removal efficiency, and its easy-to-implement technique in liquid waste treatment processes [9]. Activated Carbon was the highly commonly used adsorbent due to its elevated adsorption capacity due to its highly developed porosity, large surface area, and high reactivity [10, 11]. However, this adsorbent is expensive and remains hard to regenerate [12]. The search for another efficient and cheaper adsorbent is interesting. In this regard, the usage of clay as an adsorbent is of great interest because of its efficiency, availability in nature and abundance [13].

The purpose of this work is to investigate the effect of physicochemical parameters (contact time, Clay mass,

*Corresponding author: abbou.brahim@gmail.com (B. Abbou)
DOI: 10.22034/jchr.2021.1922221.1252

solution pH, dye concentration and temperature) on the kinetics and thermodynamics of the adsorption of a cationic dye (MB), on a natural clay (taken from Marrakech region). The experimental results revealed that the retention of this dye onto clay depends on the initial concentration of the dye and the amount of raw clay and insignificantly influenced by the temperature of the medium and the solution pH. The kinetics of MB adsorption by the clay was evaluated applying the pseudo first and second order equations. The raw clay adsorption process was determined by Langmuir and Freundlich isotherms. Thermodynamic parameters such as the enthalpy ΔH, entropy ΔS, and free enthalpy ΔG were evaluated.

## MATERIALS AND METHODS

### *Adsorbent*

The adsorbent utilized in this study is a natural clay used in its raw state without prior physical or chemical pretreatment, collected from region of Marrakech in southern Morocco, crushed and the obtained material is sieved to obtain homogeneous fractions, lower than 112 µm and then dried, for 24 hours, at 100 °C to exclude any water molecules that may be present in the material.

### *Adsorbate*

Methylene Blue was purchased from Solvachim (Morocco). The structure of the molecule of MB, which is a cationic dye, of chemical formula $C_{16}H_{18}N_3SCl$ and molar mass of 319.85 mol $g^{-1}$, is given in Figure 1.

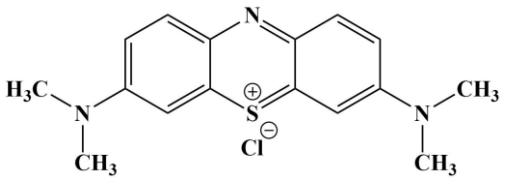


**Figure 1.** Methylene Blue Molecular Structure

The stock dye solution (1 g $L^{-1}$) was made by dissolving a precisely weighed amount of dye powder in 1000 mL of bidistilled water. All desirable working concentrations were obtained by diluting the stock solution.

### *Adsorption studies*

The adsorption experiments were carried out by introducing an accurately weighed amount of raw clay into a 0.1 L volume of colored solution at the desired concentration, pH, and temperature. Samples were taken in a regular time interval, and separated from the adsorbent by centrifugation. The filtrate absorbance was determined by a UV/Visible spectrophotometer (Selecta P, Model UV-2005) at the maximum absorption wavelength of MB ($\lambda_{max}$ = 665 nm).

The adsorption efficiency R% and capacity $q_t$ (mg $g^{-1}$) were determined using the following equations:

$$R\% = \frac{(C_0 - C_t)}{C_0} \times 100$$

$$q_t = \frac{(C_0 - C_t)}{m} V$$

With $C_o$ (ppm) is the dye initial concentration, $C_t$(ppm) is the concentration dye at moment t, V(L) is the solution volume and m(g) is the amount of the clay.

The pH effect on MB adsorption was studied over a pH interval (1.5-11). The pH was adjusted utilizing $10^{-1}$ M solutions from NaOH and HCl. The effect of the adsorbent mass (0.02-0.16 g) and the adsorbate initial concentration (10-300 ppm) were also studied.

The kinetic study was performed by shaking the previously determined optimum clay mass in 10 ppm methylene blue solution. Dye removal was monitored during 3 hours of contact with the adsorbent. Pseudo first and second order kinetic models were used to evaluate adsorption Kinetics. The adsorption equilibrium isotherms of Langmuir and Freundlich were studied and their parameters were determined. On the other hand, the temperature was varied from 25 to 55°C to inspect the effect of this parameter on the adsorption phenomenon and to deduce the thermodynamic parameters.

## RESULTS AND DISCUSSION

### *Characterization of the adsorbent*

### *X-ray fluorescence spectroscopy*

Table 1 represents the chemical composition of the raw clay. As can be seen from the table, silica and alumina are the predominant constituents, with a $SiO_2/Al_2O_3$ ratio equal to 3.64 which refers to the high presence of free quartz in our clay sample [14, 15]. Total composition of $Fe_2O_3$, $K_2O$, $Na_2O$ and MgO attains 8.16%, which indicates that the analyzed clay contains impurities [16]. In addition, the high content of these oxides compared to the level of other oxides probably shows that the clay contains exchangeable cations such as $Mg^{2+}$, $K^+$ or $Na^+$. The low percentage of CaO implies a low content of $CaCO_3$ [17].

**Table 1.** Clay chemical composition.

| Constituent | Concentration% | Constituent | Concentration % |
|---|---|---|---|
| **$SiO_2$** | 65.80 | $TiO_2$ | 0.76 |
| **$Al_2O_3$** | 18.10 | $P_2O_5$ | 0.17 |
| **$Fe_2O_3$** | 3.56 | $SO_3$ | 0.12 |
| **$K_2O$** | 2.12 | $MnO_2$ | 0.08 |
| **MgO** | 1.41 | BaO | 0.06 |
| **$Na_2O$** | 1.07 | $ZrO_2$ | 0.06 |
| **CaO** | 0.78 | Cl | 0.05 |
| **LoI** | 5.77 | ZnO | 0.01 |

***Infrared Fourier Transform Spectroscopy (FTIR)***

The analysis of the raw clay by Fourier Transform Infrared Spectroscopy was done by utilizing a Vertex 70 spectrometer with scanning range [4000-400 $cm^{-1}$]. The IR spectra shown in Figure 2, show a band located at 3420 $cm^{-1}$ refers to the elongation vibrations of OH [18, 19] and the wide band at 1628 $cm^{-1}$ is attributed to $H_2O$ deformation. The bands located at 1030, 787 and 693 $cm^{-1}$ refer to the Si–O stretching vibrations [20, 21]. Intense peaks observed at 533 $cm^{-1}$ and 472 $cm^{-1}$ assignable respectively to the deformation of Si–O–Al and Si–O–Mg [22]. The bands at 3622 and 923 $cm^{-1}$ are assigned to the deformation of Al-OH-Al [23].

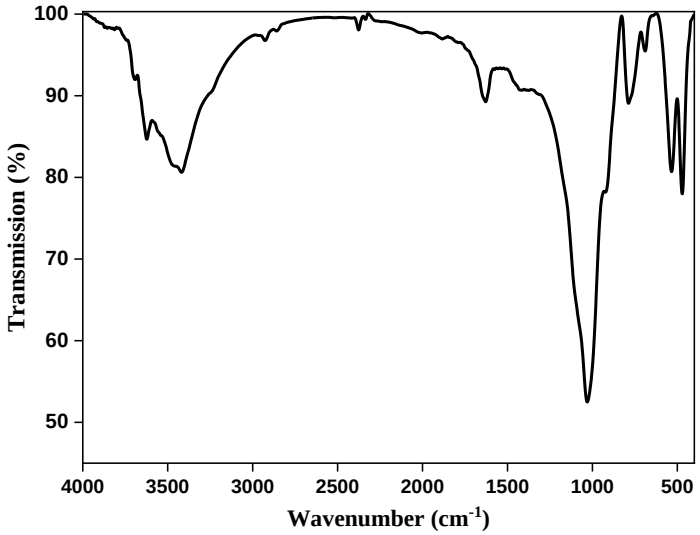


**Figure 2.** Infrared spectrum of raw clay.

***pH zero point charge (pHpzc)***

The pH zero point charge corresponds to the pH value for which, the net charge of the adsorbent surface is zero. When the pH<$pH_{pzc}$ the clay has a positive charge on the surface and has a negative charge on the surface when pH>$pH_{pzc}$ [24].

To determine the $pH_{pzc}$ value, in a series of 12 beakers, 20 mL of a $10^{-2}$ M NaCl solution is placed and the pH of each beaker is adjusted (values between 1 and 12) by adding a $10^{-1}$ M NaOH/HCl solution. 0.1 g of the clay is then introduced to each beaker. The suspension was stirred for 24 h and the final pH is then determined. The PZC of the sample was found by plotting $\Delta pH = f(pH_i)$ the intersection of the curve with x-axis gives the point $pH_{pzc}$ [24]. According to Figure 3, the $pH_{pzc}$ for our adsorbent was 8.4.

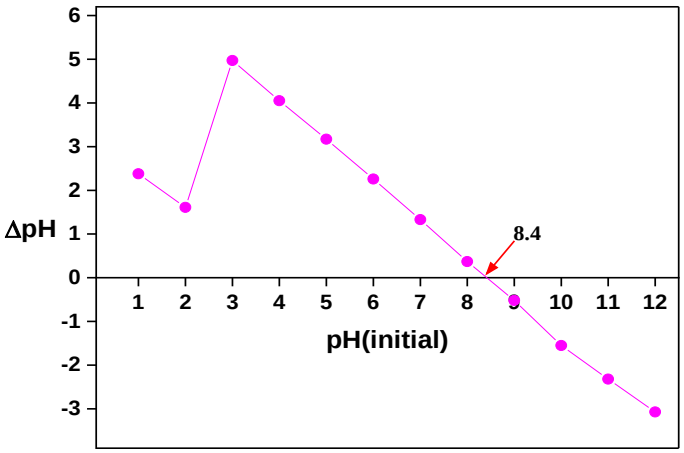


**Figure 3.** $pH_{pzc}$ of clay material

***Effect of clay dose***

To investigate the effect of the clay dose on dye removal, volumes of 100 mL of 10 ppm MB solution were contacted with adsorbent masses between 0.02 and 0.16 g. under constant agitation for 180 min, at 25°C and initial solution pH of 5.5. Figure 4 indicates that the removal percentage of dye increases significantly from 0.02 g to 0.1 g. The increase in clay dose implies an increase in the specific surface area and the active sites of adsorption [25, 26]. Above 0.1 g, there is no significant change since the elimination percentage remains unchanged and close to 100%. Thus, the optimal mass of adsorbent will be set at 0.1 g for subsequent experiments.

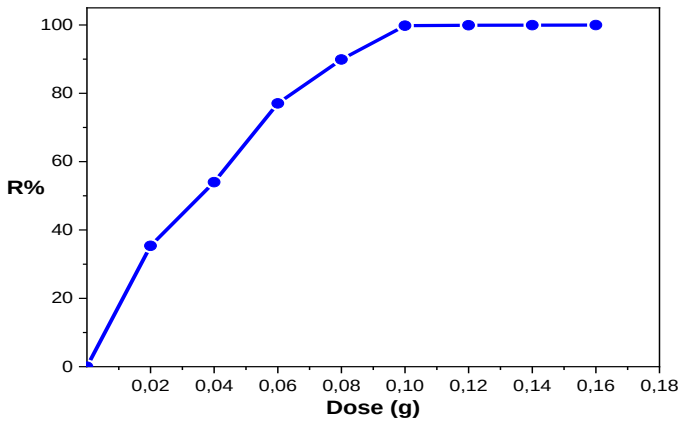


**Figure 4.** Variation of the MB elimination efficiency in function of the clay mass.

***Adsorption kinetics***

The kinetic study of MB adsorption by raw clay was conducted, at room temperature and pH 5.5, by introducing a clay mass equivalent to 0.1 g in 0.1 L of the MB colored solution of a concentration equal to 10 ppm.

Figure 5 represents the time effect on MB adsorption. A rapid elimination of MB was recorded for the first 20 min and equilibrium is observed at approximately 60 min of contact. This rapid adsorption can be attributed to the significant availability of abundant active sites located on the clay surface. Subsequently, with the progressive occupation of the active sites, the adsorption became less important. The decrease in MB concentration from 9.50 to 0.02 ppm is accompanied by an increase in pH values from 5.5 to 6.8, which shows that the clay substrate balances with the colored solution by capturing $H^+$ proton and $MB^+$ cations.

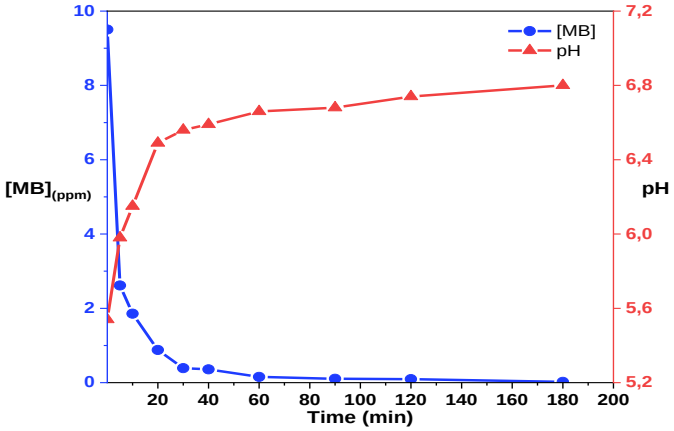


**Figure 5.** Simultaneous variation of pH and [MB] as a function of time.

***Effect of pH***

The pH is a significant parameter that should be considered during an adsorption study. The effect of this parameter on the adsorption capacity was examined over a pH interval from 1.5 to 11. The results shown in Figure 6 show that the rate of elimination of the dye is generally very little influenced by the pH variations [27, 28]. This indicates the high affinity of the dye for clay and that the $H^+$ and $OH^-$ ions have a small effect on the adsorption capacity of dye. This also indicates that the ionic exchange between the solution and the clay is not the only mechanism in this system, other types of interactions can also probably occur (hydrogen bonding, van der Waals interactions) [29]. Other studies for different dyes were also found to be independent of pH [11, 29-31].

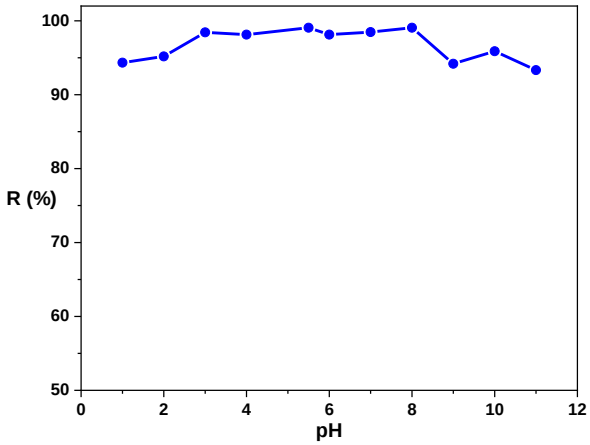


**Figure 6**. Initial pH effect on dye uptake by clay ($m_{clay}$ = 0.1 g, [MB] = 10 ppm, V = 0.1 L, T=25°C).

***Effect of MB initial concentration***

The initial concentration effect on MB adsorption was studied. The initial dye concentration effect on clay adsorption rates is explored in the concentration range of 10 to 300 ppm (Figure 7). It's clear from the graph that

the amount of MB adsorbed increases from 9.48 to 31.55 mg $g^{-1}$. It is obvious that the elimination of the MB by the clay adsorbent depends on the concentration of Methylene Blue solution since increasing the initial concentration promotes the adsorption process. In fact, increasing concentration causes concentration gradient elevation, thus increasing the diffusion of MB molecules across the adsorbent surface [32].

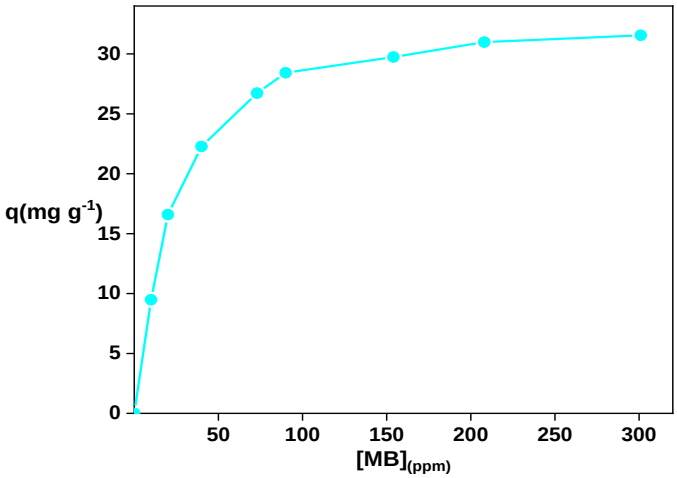


**Figure 7** . Variations of q(mg $g^{-1}$) as a function of MB initial concentration.

A similar trend was found for the removal of different dyes such as Methylene Blue on Coriandrum Sativum seeds [33], Reactive Blue 221 on Kaolinite [34], and Activated Carbon for the removal of Methyl Violet and Methyl Orange [35].

***Effect of temperature***

The temperature effect on adsorption phenomenon were studied by changing this parameter from 25 to 55°C. The tests were performed by adding 0.1 g of raw clay to 100 mL of the 10 ppm Methylene Blue solution.

Figure 8 illustrates the variation in the efficiency of MB adsorption versus temperature. We noticed that the efficiency of adsorption increases moderately with increasing temperature, which indicate that temperature has no significant effect on MB adsorption onto clay [36].

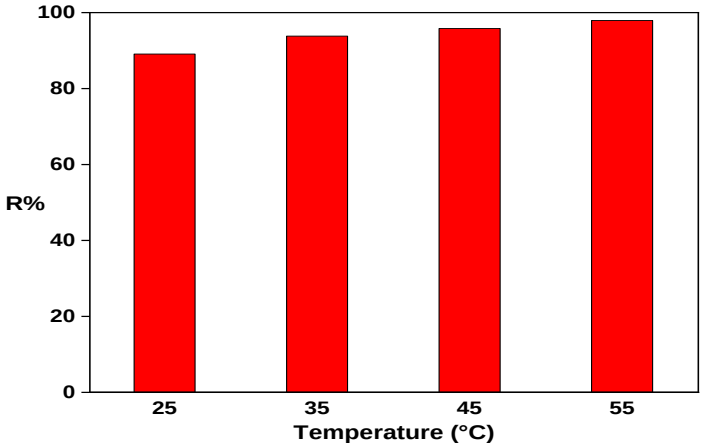


**Figure 8**. Variations in MB adsorption efficiency at different temperature values as a function of time.

***Kinetic study***

***Pseudo first order***

This model was suggested by Lagergren [37] and assumes that the rate of adsorption at a time t is proportional to the difference between the adsorbed amount at equilibrium and at time t. The model is given by the following relation:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$

where $q_e$ and $q_t$ are respectively the quantities of the dye adsorbed on the clay at equilibrium and at time t expressed in (mg $g^{-1}$). $k_1$($min^{-1}$): speed constant. $k_1$ and $q_e$ are obtained by representing log($q_e$ - $q_t$) versus t.

***Pseudo second order***

The adsorption data were examined according to pseudo second order kinetic model equation [38] :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$$

With $q_e$(mg $g^{-1}$) is the adsorbed dye amount onto clay at equilibrium, $k_2$(g $mg^{-1}.min^{-1}$) is the pseudo second order rate constant. $q_e$ and $k_2$ are obtained by representing $t/q_t$ = f(t).

Figure 9 shows the two kinetic models, according to this representation the pseudo second order is the best suited kinetic model to translate the dye adsorption by clay.

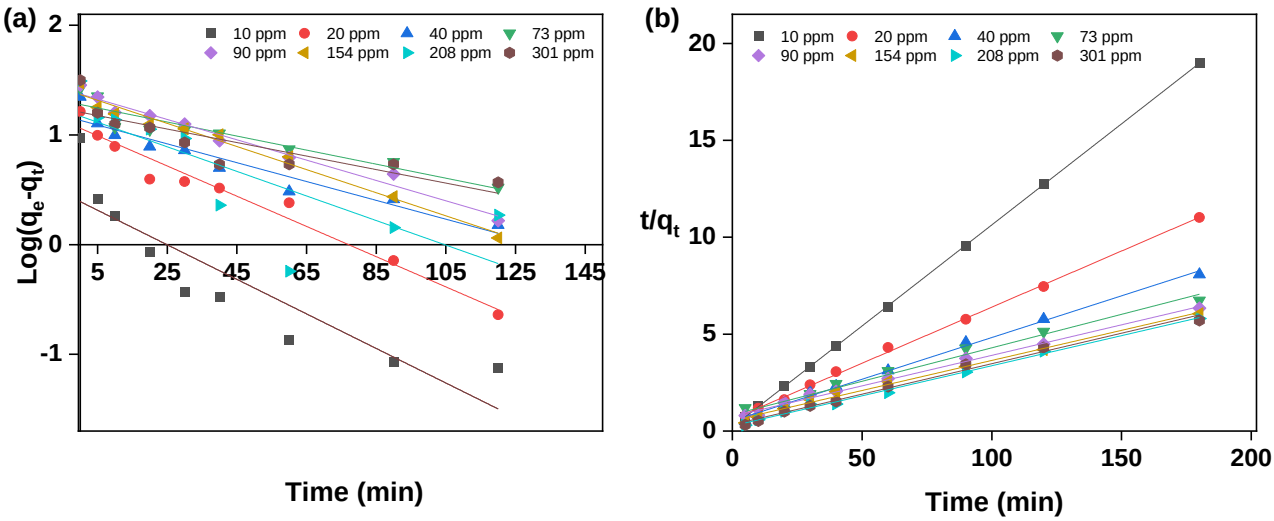


**Figure 9**. Representation of pseudo first order model (a) and pseudo second order model (b).

The kinetic parameters determined by these two models verify the conformity of the pseudo second order model to best describe MB adsorption onto raw clay. As shown in Table 2, $R^2$ is close to unity and the values of the adsorption capacity ($q_e$) determined by the pseudo second order model are close to those found experimentally.

**Table 2.** Kinetic parameters of MB adsorption dyes at various concentration.

| $[MB]_{(ppm)}$ | $q_{e(exp)}$ | Pseudo first order | | | Pseudo second order | | |
|---|---|---|---|---|---|---|---|
| | | $q_{e(cal)}$ | $K_1$ | $R_1^2$ | $q_{e(cal)}$ | $K_2$ | $R_2^2$ |
| 10 | 9.48 | 2.47 | 0.0364 | 0.8078 | 9.59 | 0.0532 | 0.9999 |
| 20 | 16.59 | 11.52 | 0.0318 | 0.9661 | 17.27 | 0.0060 | 0.9987 |
| 40 | 22.28 | 13.60 | 0.0198 | 0.9185 | 23.26 | 0.0039 | 0.9964 |
| 70 | 26.73 | 18.97 | 0.0147 | 0.8886 | 28.99 | 0.0017 | 0.9798 |
| 90 | 28.42 | 23.60 | 0.0214 | 0.9757 | 31.75 | 0.0016 | 0.9938 |
| 150 | 29.74 | 23.37 | 0.0242 | 0.9781 | 32.26 | 0.0021 | 0.9916 |
| 200 | 30.98 | 14.86 | 0.0258 | 0.6248 | 32.26 | 0.0039 | 0.9954 |
| 300 | 31.55 | 16.14 | 0.0143 | 0.7440 | 31.85 | 0.0030 | 0.9906 |

***Isotherms of adsorption***

***Langmuir Model***

To interpret the phenomenon of MB adsorption onto the clay studied, we applied Langmuir [39] and Freundlich [40] models.

The Langmuir isotherm is founded on the assumption of a limited number of active sites uniformly dispersed over the adsorbent surface. It is then assumed that once an MB

dye molecule occupies a site, no additional adsorption can take place in that site. The Langmuir isotherm equation is expressed by the following linear form:

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

With: $K_L$ (L mg$^{-1}$) adsorption Langmuir constant, $q_m$ (mg g$^{-1}$): maximum adsorbed amount of solute on the solid phase, $q_e$ (mg g$^{-1}$): adsorbed amount of solute at equilibrium per one gram of adsorbent and $C_e$: the adsorbate concentration at equilibrium in (ppm).

The straight line is obtained by plotting $C_e/q_e$ versus $C_e$ in the dye concentration range from 10 to 300 ppm for the raw clay (Figure 10(a)). It can be seen (Table 3) that the correlation coefficient ($R^2$= 0.999) is near to 1. This evidences the homogeneous nature of the raw clay surface [41]. $q_m$ and $K_L$ were obtained, respectively, from the intercept and the slope of the plot $C_e/q_e$= f($C_e$). The maximum adsorption capacity is 31.55 mg g$^{-1}$.

To verify if the adsorption is favorable, we calculated $R_L$ the separation factor defined by:

$$R_L = \frac{1}{(1 + K_L C_0)}$$

With $C_0$ : initial concentration (ppm) and $K_L$ : Langmuir constant (L mg$^{-1}$).

- $R_L$ > 1 signifies that the adsorption is unfavorable.
- $R_L$ = 1 indicates that the adsorption is linear.
- 0 < $R_L$ < 1 indicates that the adsorption is favorable.
- $R_L$ = 0 implies that the adsorption is irreversible.

The variation of $R_L$ values is shown in Figure 10(b), the $R_L$ values are between 0 and 1 implying that adsorption is favorable.

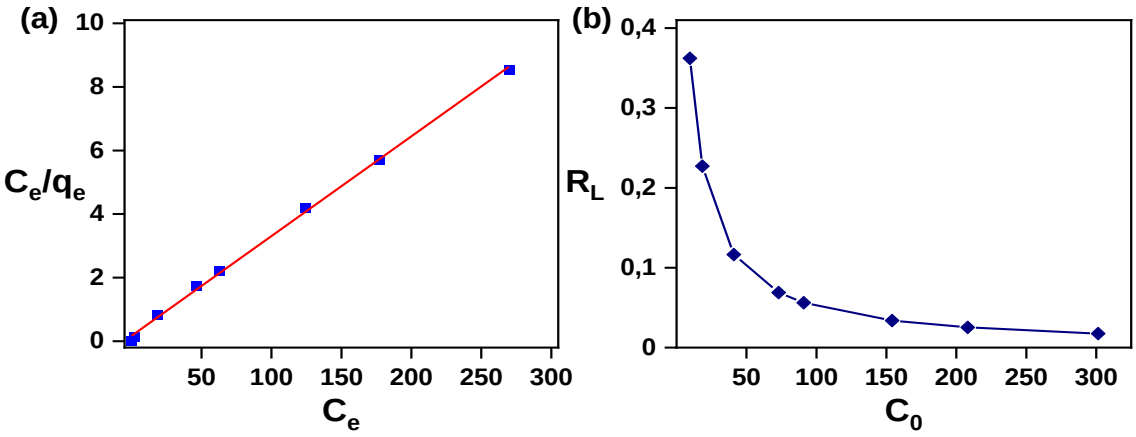


**Figure 10**. (a) Langmuir isotherm for MB adsorption onto clay, (b) Evolution of separation factors versus MB concentration.

***Freundlich model***

The Freundlich isotherm supposes that the adsorbent surface is heterogeneous and the active sites located on the surface have a non-uniform distribution of energy.

The linear form of this model is represented by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

With: 1/n : the adsorption intensity, $K_F$ the adsorption capacity, $q_e$(mg g$^{-1}$): the adsorbed quantities at equilibrium per one gram of adsorbent and $C_e$(ppm): the adsorbate concentration at equilibrium.

The value of 1/n is an indicator on the adsorption validity, a value of 1/n between 0 and 1 implies a favorable adsorption. A high $K_F$ value means that the adsorption power of the solid phase is important.

The graphical representation of log ($q_e$) = f(log($C_e$)) is a straight line of the steering coefficient 1/n and intercept

log ($K_F$) (Figure 11). The value of 1/n is between 0 and 1, which indicates that the adsorption is favorable (Table 3).

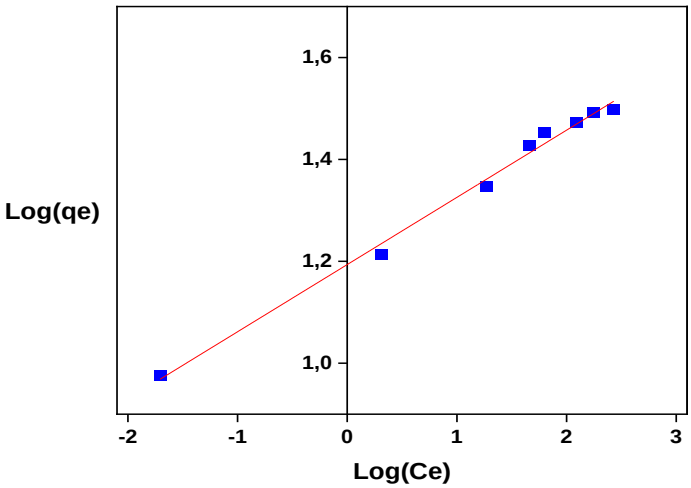


**Figure 11**. Freundlich isotherm for adsorption of MB onto clay.

**Table 3.** Parameters of the Langmuir and Freundlich adsorption model.

| | | | | | |
|---|---|---|---|---|---|
| **Freundlich** | **$K_F$** | | **1/n** | **n** | **$R^2$** |
| | 15.621 | | 0.132 | 7.587 | 0.993 |
| **Langmuir** | **$q_{m,exp}$** | **$q_{m,calc}$** | **$K_L$** | **DR%** | **$R^2$** |
| | 31.552 | 31.847 | 0.185 | 0.936 | 0.999 |

The adsorption isotherms models of MB onto clay are satisfactorily described by the two isotherms models of Langmuir and Freundlich. On the basis of the correlation coefficients presented in Table 3, we conclude that Langmuir isotherm ($R^2$ = 0.999) is better adapted to adsorption than Freundlich isotherm ($R^2$ = 0.993).

***Thermodynamic parameters***

The thermodynamic parameters are important in the comprehension of adsorption process, the parameters ΔG, ΔH and ΔS can be determined applying the following relations:

$$\Delta G = -RT \ln K_d$$

$$lnK_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

Where T (K): temperature, R (J $mol^{-1}$ $K^{-1}$): universal gas constant, and $K_d$: equilibrium constant.

The plot of Ln ($K_d$) versus $\frac{1}{T}$ (Figure 12) is a straight line with a slope $\frac{\Delta H}{R}$ and an intercept $\frac{\Delta S}{R}$.

The adsorption thermodynamic parameters were calculated from the experimental data obtained at various temperatures (Table 4).

**Table 4.** Thermodynamic parameters of adsorption.

| T(k) | $K_d$(g $L^{-1}$) | ΔG (KJ $mol^{-1}$) | ΔH(KJ $mol^{-1}$) | ΔS(KJ $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|
| 298 | 14.19 | -6.571 | 30.731 | 0.126 |
| 308 | 28.20 | -8.551 | | |
| 318 | 32.73 | -9.223 | | |
| 328 | 47.32 | -10.518 | | |

The negative values of ΔG signify that the adsorption of the Methylene Blue onto raw clay is spontaneous. The endothermic nature of the process is verified by the positive value of the enthalpy ΔH, the low value of ΔH (< 40 KJ $mol^{-1}$) shows that it is a physisorption [42], while the positive value of ΔS reveals an increase in randomness at the clay/solution interface during the process of adsorption [43, 44].

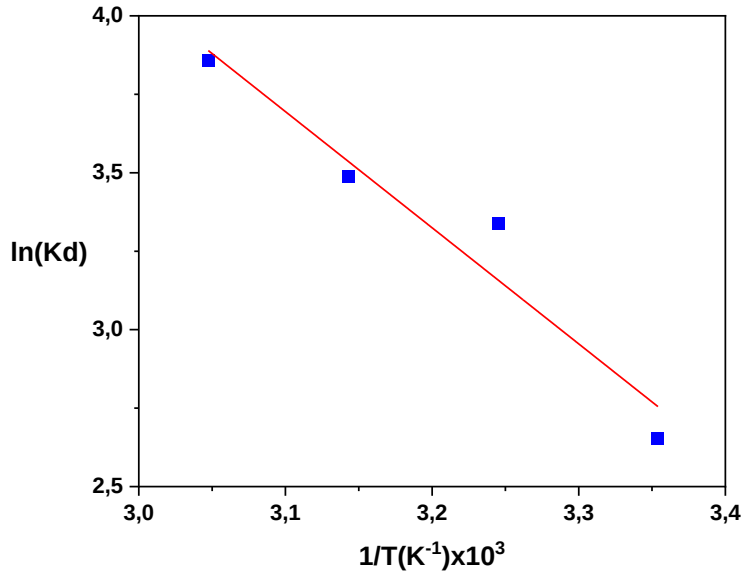


**Figure 12**. Representation of ln($K_d$) as a function of temperature (1/T).

## CONCLUSIONS

The study of the Methylene Blue adsorption process onto clay was the subject of this work. The results showed that the removal percentage R% is related to the clay dose: an increase of R% from 35.4% to 99.7% was observed when the clay dose was increased from 0.02 to 0.16 g. The percentage of discoloration is little influenced by the variation of the pH and temperature.

Modelling of the adsorption results showed that the pseudo second order model provides a better correlation of kinetic data and that the Langmuir model better describes the adsorption isotherm, so the dye molecules adsorb in monolayers and without any interactions between them. The maximum adsorption capacity of methylene blue dye is 31.85 mg $g^{-1}$. The thermodynamic parameters obtained revealed that the adsorption of the MB cationic dye onto the raw clay is a spontaneous and endothermic process. All these results indicate that Clay as a low-cost and efficient adsorbent material can potentially contribute to the elimination of dyes from textile effluents.

## REFERENCES

1. Achour Y., Khouili M., Abderrafia H., Melliani S., Laamari M.R., El Haddad M., 2018. DFT Investigations and Experimental Studies for Competitive and Adsorptive Removal of Two Cationic Dyes onto an Eco-friendly Material from Aqueous Media. International Journal of Environmental Research. 12(6), 789-802.

2. Achour Y., Bahsis L., Ablouh E.-H., Yazid H., Laamari M.R., Haddad M. E., 2021. Insight into adsorption mechanism of Congo red dye onto Bombax Buonopozense bark Activated-carbon using Central composite design and DFT studies. Surfaces and Interfaces. 23, 100977.

3. P. Panneer S., Preethi S., Basakaralingam P., N.Thinakaran, Sivasamy A., Sivanesan S., 2008. Removal of rhodamine B from aqueous solution by adsorption onto sodium montmorillonite. Journal of Hazardous Materials. 155(1-2), 39-44.

4. Regti A., Laamari M.R., Stiriba S.E., El Haddad M., 2017. Use of response factorial design for process optimization of basic dye adsorption onto activated carbon derived from Persea species. Microchemical Journal. 130, 129-136.

5. Lebkiri I., Abbou B., Kadiri L., Ouass A., Essaadaoui Y., Rifi E. H., Lebkiri A., 2019. Removal of methylene blue dye from aqueous solution using a superabsorbant hydrogel the polyacrylamide: isotherms and kinetic studies. Mediterranean Journal of Chemistry. 9(5), 337-345.

6. Weng C.H., Pan Y.F., 2007. Adsorption of a cationic dye (methylene blue) onto spent activated clay. Journal of

Hazardous Materials. 144 (1-2), 355-362.

7. Robinson T., Marchant R., Nigam P., 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresource Technology. 77(3), 277-255.

8. LebkİRİ İ., Abbou B., Kadiri L., Ouass A., Elamrİ A., Ouaddari H., Elkhattabİ O., LebkİRİ A., RİFİ E. H., 2021. Equilibrium, Kinetic Data, and Adsorptıon Mechanism for Lead Adsorptıon onto Polyacrylamıde Hydrogel. Journal of the Turkish Chemical Society Section A: Chemistry. 731-748.

9. El Kassimi A., Boutouil A., El Himri M., Rachid Laamari M., El Haddad M., 2020. Selective and competitive removal of three basic dyes from single, binary and ternary systems in aqueous solutions: A combined experimental and theoretical study. Journal of Saudi Chemical Society. 24(7), 527-544.

10. Juang R.S., Wu F.C., Tseng R.L., 1997. The Ability of Activated Clay for the Adsorption of Dyes from Aqueous Solutions. Environmental Technology. 18(5), 525-531.

11. Regti A., Laamari M.R., Stiriba S.E., Haddad M.E., 2016. Removal of Basic Blue 41 dyes using Persea americana-activated carbon prepared by phosphoric acid action. International Journal of Industrial Chemistry. 8(2), 187-195.

12. Karagozoglu B., Tasdemir M., Demirbas E., Kobya M., 2007. The adsorption of basic dye (Astrazon Blue FGRL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon: Kinetic and equilibrium studies. Journal of Hazardous Materials. 147(1-2), 297-306.

13. Roulia M., Vassiliadis A.A., 2005. Interactions between C.I. Basic Blue 41 and aluminosilicate sorbents. Journal of Colloid and Interface Science. 291(1), 37-44.

14. Besq A., Malfoy C., Pantet A., Monnet P., Righi D., 2003. Physicochemical characterisation and flow properties of some bentonite muds. Applied Clay Science. 23(5-6), 275-286.

15. Abbou B., LebkİRİ İ., Ouaddari H., Elkhattabİ O., Habsaoui A., Lebkiri A., Rifi E. H., 2021. Kinetic and thermodynamic study on adsorption of cadmium from aqueous solutions using natural clay. Journal of the Turkish Chemical Society Section A: Chemistry. 677-692.

16. Abbou B., Lebkiri I., Ouaddari H., Kadiri L., Ouass A., Habsaoui A., Lebkiri A., Rifi E. H., 2021. Removal of Cd(II), Cu(II) and Pb(II) by adsorption onto natural clay: kinetic and thermodynamic study. Turkish Journal of Chemistry. 45 (2), 362-376.

17. Sadki H., Ziat K., Saidi M., 2014. adsorption of dyes on activated local clay in aqueous solution. Journal of Materials and Environmental Science. 5(1), 2060-2065.

18. Essaadaoui Y., Lebkiri A., Rifi E., Kadiri L., Ouass A., 2018. Adsorption of cobalt from aqueous solutions onto Bark of Eucalyptus. Mediterranean Journal of Chemistry. 7(2), 145-155.

19. Ouaddari H., Beqqour D., Bennazha J., El Amrani I.E., Albizane A., Solhy A., Varma R.S., 2018. Natural Moroccan clays: Comparative study of their application as recyclable catalysts in Knoevenagel condensation. Sustainable Chemistry and Pharmacy. 10, 1-8.

20. Bentahar Y., Hurel C., Draoui K., Khairoun S., Marmier N., 2016. Adsorptive properties of Moroccan clays for the removal of arsenic(V) from aqueous solution. Applied Clay Science. 119, 385-392.

21. Latifi N., Meehan C.L., Majid M.Z.A., Horpibulsuk S., 2016. Strengthening montmorillonitic and kaolinitic clays using a calcium-based non-traditional additive: A micro-level study. Applied Clay Science. 132-133, 182-193.

22. Eloussaief M., Kallel N., Yaacoubi A., Benzina M., 2011. Mineralogical identification, spectroscopic characterization, and potential environmental use of natural clay materials on chromate removal from aqueous solutions. Chemical Engineering Journal. 168(3), 1024-1031.

23. Madejová J., Pálková H., 2017. NIR Contribution to The Study of Modified Clay Minerals Developments in Clay Science, pp. 447-481: Elsevier.

24. Fayoud N., Tahiri S., Alami Younssi S., Albizane A., Gallart-Mateu D., Cervera M.L., de la Guardia M., 2016. Kinetic, isotherm and thermodynamic studies of the adsorption of methylene blue dye onto agro-based cellulosic materials. Desalination and Water Treatment. 57(35), 16611-16625.

25. Bensalah J., Habsaoui A., Abbou B., Kadiri L., Lebkiri I., Lebkiri A., Rifi E.H., 2019. Adsorption of the anionic dye methyl orange on used artificial zeolites: kinetic study and modeling of experimental data. Mediterranean Journal of Chemistry. 9(4), 311-316.

26. Liu R., Zhang B., Mei D., Zhang H., Liu J., 2011. Adsorption of methyl violet from aqueous solution by halloysite nanotubes. Desalination. 268(1-3), 111-116.

27. Bouaziz F., Koubaa M., Kallel F., Chaari F., Driss D., Ghorbel R.E., Chaabouni S.E., 2015. Efficiency of almond gum as a low-cost adsorbent for methylene blue dye removal from aqueous solutions. Industrial Crops and Products. 74, 903-911.

28. Yang R., Li D., Li A., Yang H., 2018. Adsorption properties and mechanisms of palygorskite for removal of various ionic dyes from water. Applied Clay Science. 151, 20-28.

29. Regti A., Laamari M. R., Stiriba S.E., El Haddad M., 2017. Potential use of activated carbon derived from Persea species under alkaline conditions for removing cationic dye from wastewaters. Journal of the Association of Arab Universities for Basic and Applied Sciences. 24(1), 10-18.

30. Shabudeen P.S.S., Venckatesh R., Pattabhi S., 2006. Preparation and Utilization of Kapok Hull Carbon for the Removal of Rhodamine-B from Aqueous Solution. E-Journal of Chemistry. 3(2), 83-96.

31. Regti A., Ayouchia H.B.E., Laamari M.R., Stiriba S.E., Anane H., Haddad M.E., 2016. Experimental and theoretical study using DFT method for the competitive adsorption of two cationic dyes from wastewaters. Applied Surface Science. 390, 311-319.

32. Deniz F., Saygideger S.D., 2010. Investigation of adsorption characteristics of Basic Red 46 onto gypsum: Equilibrium, kinetic and thermodynamic studies. Desalination. 262(1-3), 161-165.

33. Kadiri L., Ouass A., Essaadaoui Y., Rifi E.H., Lebkiri A., 2018. Coriandrum Sativum seeds as a green low-cost biosorbent for methylene blue dye removal from aqueous solution: spectroscopic kinetic and thermodynamic studies. Mediterranean Journal of Chemistry. 7(3), 204-216.

34. Karaoğlu M.H., Doğan M., Alkan M., 2010. Kinetic analysis of reactive blue 221 adsorption on kaolinite. Desalination. 256(1-3), 154-165.

35. Chen S., Zhang J., Zhang C., Yue Q., Li Y., Li C., 2010. Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from Phragmites australis. Desalination. 252(1-3), 149-156.

36. Bagane M., 2000. Elimination d'un colorant des effluents de l'industrie textile par adsorption. Annales de Chimie Science des MatÃ©riaux. 25(8), 615-625.

37. Lagergren S., 1898. Zur Theorie der Sogenannten Adsorption gel Osterstoffe Kungliga Svenska vetenskapsakademiens. Handlingar. 24, 1-39.

38. Gurses A., Dogar C., Yalcin M., Acikyildiz M., Bayrak R., Karaca S., 2006. The adsorption kinetics of the cationic dye, methylene blue, onto clay. Journal of Hazardous Materials. 131(1-3), 217-228.

39. Langmuir I., 1918. THE ADSORPTION OF GASES ON PLANE SURFACES OF GLASS, MICA AND PLATINUM. Journal of the American Chemical Society, 40 (9), 1361-1403.

40. Freundlich H., 1907. Über die Adsorption in Lösungen. Zeitschrift für Physikalische Chemie. 57(1), 385-471.

41. Karim A. B., Mounir B., Hachkar M., Bakasse M., Yaacoubi A., 2010. Élimination du colorant basique « Bleu de Méthylène » en solution aqueuse par l'argile de Safi. Revue des sciences de l'eau. 23(4), 375.

42. Benguella B., Yacouta-Nour A., 2009. Elimination des colorants acides en solution aqueuse par la bentonite et le kaolin. Comptes Rendus Chimie, 12 (6-7), 762-771.

43. Ouass A., Kadiri L., Essaadaoui Y., Belakhmima R. A., Lebkiri A., Rifi E. H., 2018. Removal of trivalent chromium ions from aqueous solutions by Sodium polyacrylate beads. Mediterranean Journal of Chemistry, 7(2), 125-134.

44. Lebkiri I., Abbou B., Kadiri L., Ouass A., Elamri A., Ouaddari H., Elkhattabi O., Lebkiri A., Rifi E. H., 2021. Swelling properties and basic dye adsorption studies of polyacrylamide hydrogel. Desalination and Water Treatment. 233, 361-376.