Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2018, Volume 9, Issue 6, Page 1750-1761

https://doi.org/10.26872/jmes.2018.9.6.195

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Adsorption of Methylene Blue on raw and activated Clay: case study of Bengurir clay

K. Allam[1], K. Gourai[1], A. EL Bouari[1], B. Belhorma[2], L. Bih[3]

[1] *Laboratory of Physical Chemistry of Applied Materials, department of chemistry, Faculty of Sciences Ben M'sik, Hassan II University Casablanca B.P. 7955 20702, (Morocco)*
[2] *National Centre for Energy, Nuclear Science and Technology, CNESTEN, B.P. 1382 R.P. 10001 Rabat (Morocco)*
[3] *Group of physico-chemical of the Condensed Matter (PCMC), Faculty of sciences Meknes, University Moulay Ismail BP 11201 Zitoune, Meknès (Morocco).*

Received 12 Feb 2017,
Revised 05 Oct 2017,
Accepted 12 Oct 2017

Keywords
- ✓ Adsorption;
- ✓ Methylene blue;
- ✓ Water treatment ;
- ✓ Clay;
- ✓ Isotherm;
- ✓ Kinetic ;

khadijaallam@yahoo.fr ;
Phone:+212 06 77 92 39 25

Abstract

The experiments of adsorption of methylene blue (MB) on raw and activated Moroccan clay from Benguerir are reported. It is characterized by X-ray diffraction and Infrared spectroscopy (IR). This clay has been utilized as the adsorbent for the removal of a cationic dye, methylene blue (MB), from aqueous solution by the batch adsorption technique under different conditions such as initial dye concentration, solution pH, temperature, and adsorbent mass. The experimental results showed that adsorption of the dye on the raw and activated clay was pH and temperature dependent. The equilibrium data were well fitted by the Langmuir isotherm. Thermodynamic parameters suggested that the adsorption involved a physical process, spontaneous, and endothermic in nature. The kinetic study showed that the second-order model gives a better description of the kinetics of the adsorption reaction.

1. Introduction

The importance of water in human life is growing and the supply of fresh water becomes increasingly difficult, both because of population growth, urbanization, however, human activities: industrial, urban or agricultural, cause its pollution [1]. The permanent water pollution is linked to industrial discharges, waste water from urban origin, employment in agriculture of pesticides and fertilizers; this is added the exceptional pollution from transport accidents, all this constitute a source of environmental degradation in particular water. Currently, there is a particular international interest to the pollution of water [2]. Under the pressure of our needs, it is necessary to provide populates with water having good quality. Practically, more the quality of the water decreases, more the need for frequent and extensive controls becomes imperative. To deal with this major threat to the environment, much work has been made on pollution water in recent decades [3-6]. A wide variety of physical, chemical, and biological techniques has been developed; these methods include flocculation, precipitation, ion exchange, membrane filtration, irradiation and ozonation [7-12]. However, these methods are expensive and result in the generation of large amounts of sludge [13]. Among the decontamination processes adsorption technique remains relatively the most widely used and easy to implement. Researchers have shown that a wide variety of materials of natural origin had the ability to fix large quantities of organic pollutants present in the water [14-18]. Currently, the use of coal in the adsorption process is also highly sought. Activated carbon presents a strong capacity for adsorption due mainly to its large surface area but this process is very expensive, and many works highlight its effectiveness, but its use is limited because of the difficulty of regeneration and its high cost [19]. The search for another effective and less costly adsorbent is therefore interesting. In the present work our choice was focused on material clay that is found in abundance in Bengurir region in Morocco. The influence of different parameters on the adsorption such as: the contact time, the initial concentration of MB, the pH of the solvent is studied. The kinetics and isotherms of the adsorption process are also investigated.

2. Material and Methods

2.1. Adsorbate

Methylene blue (MB) was chosen for this study because of its known strong adsorption onto solids. (MB) is a cationic dye (chloride of 3,7-bis(dimethylamino-phenazathionium) index CI 52015; its formula is

C16H18N3SCl, its molecular weight is 319.85g.mol-1, and the maximum absorption occurs at wavelength of 664 nm [20]. The chemical structure of MB dye is shown in (Figure 1). A decentralized positive charge on the organic framework could play a major role in keeping the species on the surface of the clay [21].

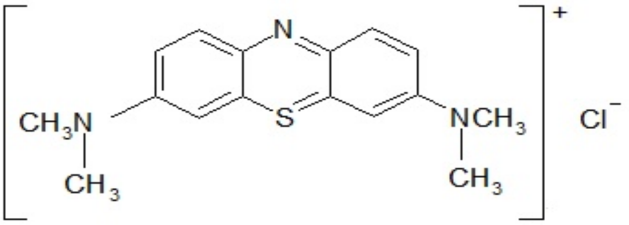

Figure 1 : The chemical structure of methylene blue

2.2. Adsorbent

The adsorbent material used in the present study is natural clay coming from bengurir zone in Morocco. Its chemical analysis was carried out by X-ray fluorescence spectrometry using a Bruker type S4 PIONEER, and gave the following composition: SiO_2 55 %, Al_2O_3 20 %, MgO 5 %, Na_2O 0.80 %, Fe_2O_3 0.60 % and CaO 0.50%. It is seen that this clay contains SiO_2 and Al_2O_3 as the major constituents and Mg^{2+}, Fe^{2+}or Na^+ as exchangeable cations [22]. This clay contains several mineral phases such as illite and smectite as will be seen in the x-ray diffraction section. These mineral phases are used as adsorbents in many cases. Moreover, it is reported [23]. That the smectite minerals had the highest capacity of adsorption. For these considerations, we have selected this natural clay as adsorbent material in the present work. To conduct the adsorption experiments, two forms of this clay are used. The raw clay (RC) without pre-treatment and the activated clay (AC)form by sulfuric acidic sieved to obtain a particle size of 80 µm are considered.

2.3. Activation of clay

It is well known that useful modifications of the adsorption properties of clay minerals can be achieved by acid activation [24-26]. This operation induces an increase of both surface area and adsorption capacity. In this study we have activated the clay using H_2SO_4 in a similar way that used elsewhere [27-29]. The clay is activated by a sulfuric acid solution (0.25 M) in the proportions 10 g of clay to 100 ml solution for 4 hours. The clay / acid mixture is then separated by centrifugation. The solid phase is washed with distilled water to remove excess of sulfuric acid permeating its outer surface, dried in an oven at 150 °C for 24 hours, crushed and stored away from moisture before undergo different adsorption experiment.

The identification of the raw and activated clay is performed by X-ray diffraction (XRD) technique, using a Bruker D8 Advance apparatus. Infrared spectroscopy (IR) was used to identify the vibrational groups of the samples by using Perkin Elmer Spectrometer. Infrared spectra were recorded in the 4000–400 cm^{-1} region.

2.4. Adsorption Procedure

The experiments of adsorption were performed in batch method. The adsorption tests were carried out by introducing a precise n amount of adsorbent precisely weighed into a 100 ml solution of pure methylene blue dye 10 $mg.l^{-1}$. At the end of the adsorption period, the solution was centrifuged for 5 min at 2600 rpm. After centrifugation, the dye concentration in the supernatant solution was analyzed using a UV spectrophotometer (VWR, V 3100). The samples were pipetted from the solution colored by the aid of a very thin point micropipette, which prevented the transition to the solution of the clays samples. The amount of dye adsorbed was calculated using the equation:

$$\boldsymbol{q_e = \frac{(C_0 - C_e) \cdot V}{m}} \qquad (1)$$

Where, q_e (mg/g) is the quantity of the dye adsorbed per unit of adsorbent mass, C_0 (mg/l) is the initial dye concentration, C_e (mg/l) is the equilibrium concentration of dye (mg/l), m the adsorbent mass (g) and V the volume (l) of the adsorption solution.

2.5. Effect of initial concentration

A 0.6g of clay was added to 100 ml of (MB) solutions of initial concentrations 10, 20, 50 and 80 mg/l and the experiments were carried out at constant temperature 25°C.

2.6. Effect of temperature

A 0.6 g of clay was added to 100 ml of (MB) aqueous solutions with initial concentration 10 mg/l. The experiments were carried out at various tempertures 25, 40, 60 and 80 °C.

2.7. Effect of initial pH

Effect of initial pH was investigated at pH values 2, 4, 6, 8, 10, and 12 by addition of NaOH and HCl. In the experiments, a 0.6 g of clay was added to 100ml of (MB) aqueous solutions having an initial concentration 10 mg/l.

2.8. Effect of the adsorbent mass

A 0.6 g of clay was added to 100 ml volume of (MB) aqueous solutions having an initial concentration of 10 mg/l. Different amounts of clay (10, 20, 40, 60, 80 mg) ware added to the above mentioned solution. The experiments were carried out at a fixed temperature of 25 °C.

3. Results and discussion

3.1. X-ray diffraction and IR analysis of the adsorbent samples

The XRD patterns of the raw and activated samples are shown in figure 2. For the RC, the diffraction pattern shows the presence of peaks associated to quartz (2θ= 26.99, 50.1 degrees), calcite (2θ= 29.50, 39.57, 47.32 degrees), kaolinite (2θ= 12.09, 19.44, 24.85 degrees), Dolomite (2θ= 30.53 degrees), Illite (2θ= 36.69) and two Smectites phases: (i) montmorillonite (2θ= 19.06, 19.85, 35.36, 54.29, 59.02, 65.9 degrees), (ii) Beidellite (2θ= 28.40, 34.44, 41.80, 44.17, 61.91 degrees) . After activation of the RC, peaks of kaolinite and Dolomite have become insignificant, while those of quartz, calcite and Smectites became more intense.

IR spectra of raw and activated clay samples are given in figure. 3. The RC sample showed a bond at 3622 cm^{-1} corresponding to the deformation of Al-OH band and a band at 3455 cm^{-1} ascribed to the deformation of H-OH.

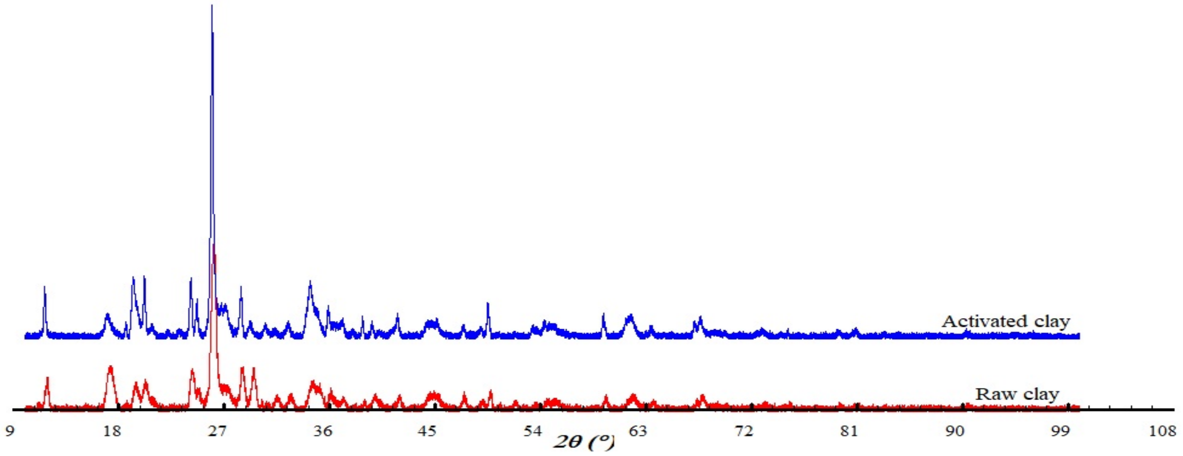

Figure 2: X-ray diffractometer analysis of the raw and activated clay

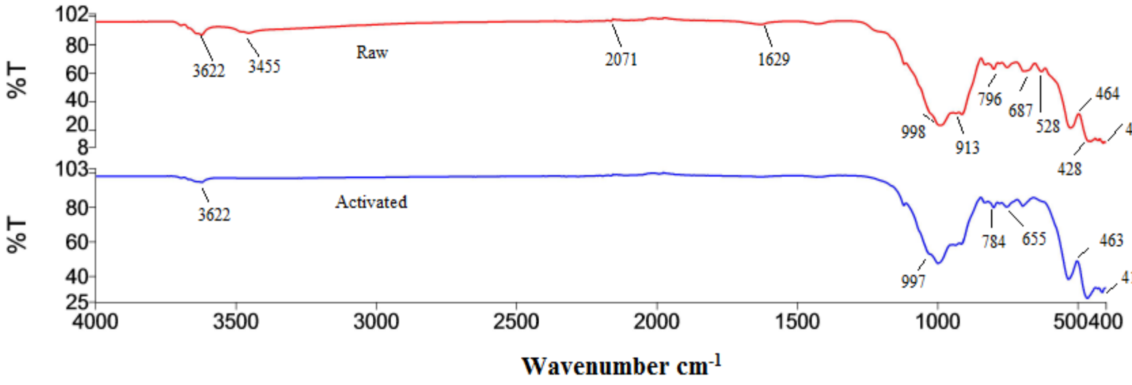

Figure 3: IR Spectra of the raw and activated clay

Low band at 1629 cm^{-1} is attributed to deformation vibrations of the H_2O molecules absorbed between the layers. A low-intensity band at 796cm^{-1} is assigned to the tetravalent silicon due to the presence of amorphous silica. This latter became low intense in the spectrum of the AC. The bands appearing at 528 cm^{-1}, 464 cm^{-1}, 428cm^{-1} and 407 cm^{-1} are ascribed to the deformation of Si-O-Al, Si-O-Mg, Si-O-Si and Si-O-Fe respectively [30]. The presence of kaolinite is justified by the presence of low band at 687cm^{-1}. This latter become very weak in the AC. The band at 913 cm^{-1} is assigned to stretching vibrations of the Si-O band in quartz. The band at 998 cm^{-1} is attributed to the deformation of (CO_3) and/or Al_2OH. The band located at 2071 cm^{-1} could be explained by the presence of Fe_2O_3. One can note that this band disappeared for activated clay, due to the cationic exchange of Fe^{3+} by proton H^+ [31].

3.2. Influence of different parameters on MB adsorption

3.2.1. Effect of initial dye concentration and contact time on adsorption process

Figure 4 represents the curves of the evolution of the quantity of dye adsorbed versus contact time and the dye removal ratio using different initial dye concentrations (10, 20 and 50, 80 mg/l) for the raw and activated clay. The contact time necessary to reach equilibrium depends on the initial dye concentration and the content of the adsorbate MB. Obtained result is in agreement with the reported data [32, 33]. Which showed that the adsorption capacity increases with this concentration and the initial MB concentration provided the necessary driving force to overcome the mass transfer resistance of MB between the aqueous and solid phases. By analyzing these kinetic curves is found that equilibrium is reached, suddenly after exceeding the transient state for the first 30 minutes. Therefore each time that is superior to it will be considered as equilibrium time.

From figure 4, we noticed that the amount adsorbed at equilibrium increases with the concentration. It is also observed that the adsorption of MB onto RC and AC is happened quickly for all the initial MB concentration 10, 20, 50, and 80 mg/l. This indicates that the initial dye concentration plays an important role in the adsorption capacity of dye. It could be concluded that the initial concentration of adsorbate (MB) in solution provided the necessary driving force in overcoming mass transfer resistance of MB between the aqueous and the solid phases. The equilibrium time of different initial MB concentrations was determined and the results showed that the initial MB concentrations had little effect on the adsorption equilibrium time. Indeed, this latter is nearly equal for all the initial concentrations. Additionally, in terms of the percentage removal, as illustrated by figure 4, the removal ratio of MB onto raw and activated clay was higher at low concentration. The reason was the limited number of adsorption sites available for the uptake of MB at a fixed adsorbent dosage [34, 35].

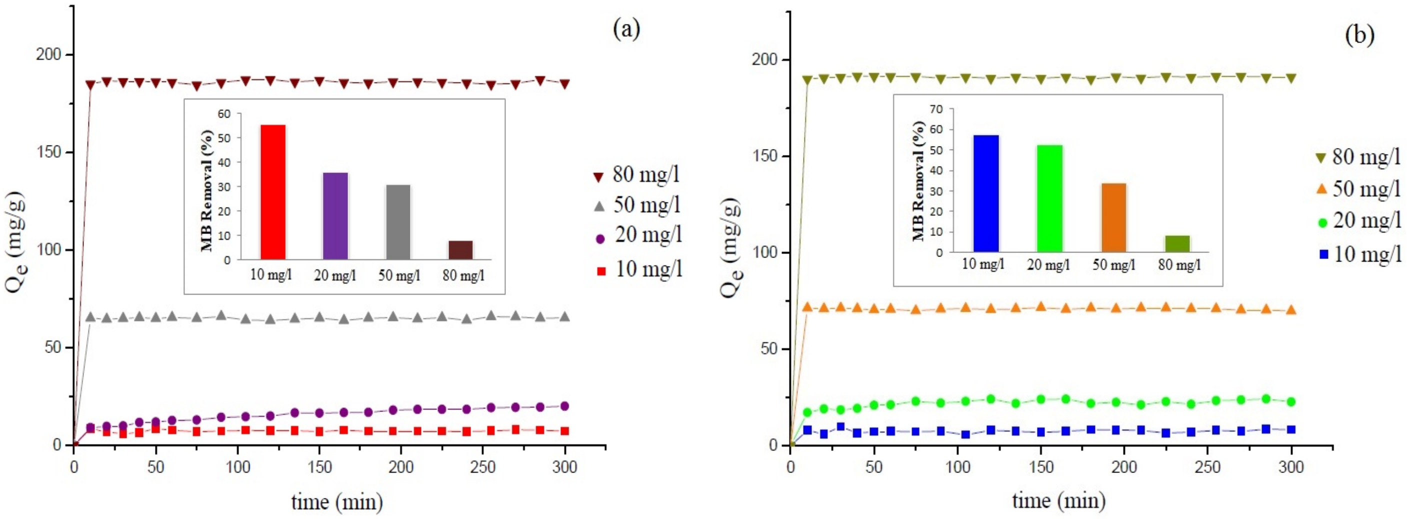

Figure 4: Effect of initial concentration and contact time on MB adsorption onto (a) the raw and (b) activated clay

3.2.2. Effect of initial pH

Many studies suggest that pH is an important factor in the adsorption process [36-38]. This test is followed at pH values between 2 and 12; the pH of the solution is adjusted by adding solutions of NaOH (1N) and HCl (1N). The experiments were performed at ambient temperature by keeping constant the contents of methylene blue and raw and activated clay (60 mg). The percentage of dye removal was calculated by the following equation (2):

$$\textbf{Removal}\,\% = \mathbf{100} \times \frac{(C_0 - C_e)}{C_0} \qquad (2)$$

Where C_0 the initial dye concentration (mg/l), C_e the equilibrium concentration (mg/l). The obtained results for raw and activated clay samples are presented in Figure 5.

The analysis of these results showed that the quantity of MB adsorbed on the RC and AC increases with increasing pH. Generally, the removal ratio is higher than 86% for both raw and activated clay. The low value of removal ratio for pH<4 is due to the competition between the methylene blue ions and protons H^+ from the acid. When the pH value exceeds 6, the quantity of methylene blue removed from the solution is growing rapidly, and reaches a removal of approximately 99.96% for AC and 98.36% for RC. Hence, it is clear that the adsorption process is dependent on the pH of the solution; the percentage of MB adsorbed increases with pH and being at a maximum at pH 12. The pH appears to be a key factor affecting the adsorption characteristics of MB onto clay. The methylene blue produces molecular cations in aqueous solution and the adsorption of methylene blue (MB) on the clay surface is primarily influenced by the surface charge on the adsorbent [21, 39].

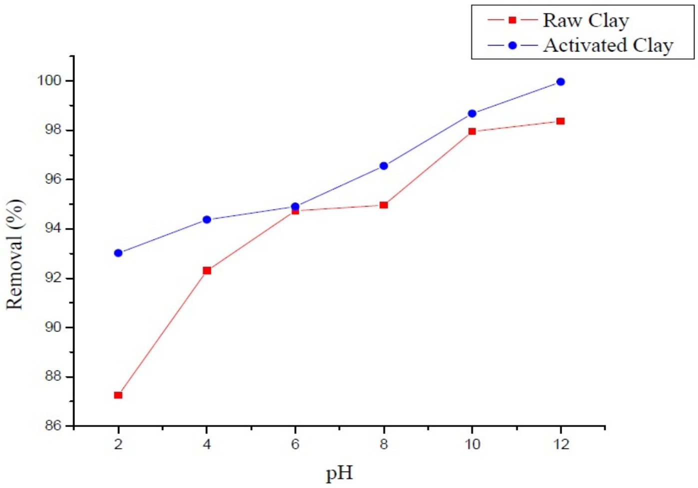

Figure 5: Influence of pH on the adsorption of methylene blue on the raw and activated clay

Therefore, the point of zero charge (pHpzc) of the adsorbent is the main parameter influencing the adsorption phenomenon. The pHpzc value of the clay is found to be in the range between 8 and 9.5 [40]. When the solution has pH > pHpzc the surface of the clay is negatively charged which promotes the adsorption of methylene blue cationic dye. For pH < pHpzc the surface of the clay is charged positively, and thus likely to be repulsive to the dye cations. Therefore, as pH of the system decreases, the number of negatively charged adsorbent sites decreases and the number of positively charged surface sites increases, and on the other hand when the pH of the system increases, the number of negatively charged adsorbent sites increases and the number of positively charged surface sites decreases [21]. This behavior is in agreement with the electrostatic repulsion between the positively charged surface and the positively charged dye molecule. There might be another mode of adsorption (ion exchange) [41, 42] and the results are in harmony with the literature reports [43, 44].

- At low pH, electrostatic repulsion occurred between the dye ions and the edge groups with positive charge (M-OH_2^+) on the surface as follows:

$$MOH + H^+ \rightarrow MOH_2^+$$

- At high pH, the surface of clay becomes negatively charged and electrostatic repulsion decreases, the methylene blue cations in solution will be attracted to the surface according to the following reactions

$$\boldsymbol{MOH + OH^- \rightarrow MO^- + H_2O}$$

Where M is the cation of Si^{2+}, Al^{3+} or Fe^{2+}

3.2.3. Effect of the adsorbent mass

The effect of the initial mass of the adsorbent has been studied at ambient temperature using 100 ml MB solutions at a concentration of 10 mg/l. The pH of the solution is equal to 6.5. The experiments were conducted by adding 20, 40, 60, 80 and 100 mg of clay. Figure 6 shows the obtained results.

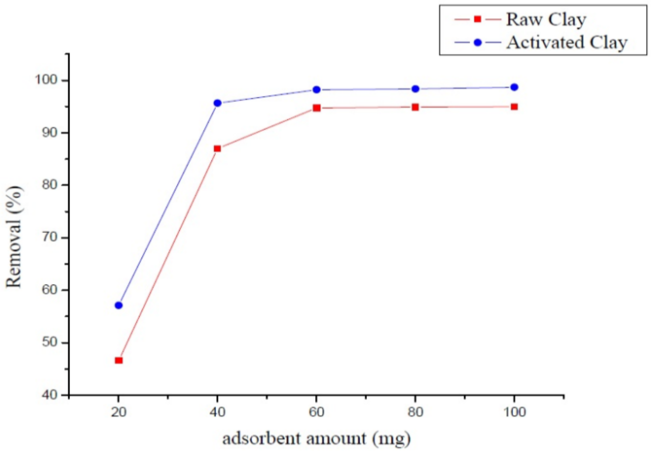

Figure 6: Influence of the amount of adsorbent (raw and activated clay) on the adsorption of methylene blue

As predicted, the uptake of the dye increases with the amount of clay and the maximum dye removal is achieved when the adsorbent mass exceeds 60 mg. It is explained by the availability of active sites on the surface of adsorbent material which can fix the colorant ions and as well this trend by the fact that the free superficial area of adsorbent grains is more exposed and consequently MB removal by adsorption is more favoured [45]. These sites increase with the increase in dose raw and activated clay.

We can also notice that the chemical activation of clay improves removal of MB, because acid attack causes the reorganization of the crystal lattice of clay, then a vacuum is formed and the valences of the ions therein become unsaturated and consequently tend to fix other particles in solution.

3.2.4. Effect of temperature

The influence of temperature on the adsorption of methylene blue dye by the raw and activated clay was studied (figure 7). It is worth to note that the experiments are conducted at different temperatures from ambient up to 80 °C since during the experiments we have not observed any evaporation of the solutions. The results show when the temperature increases from 25°C to 80°C the adsorption capacity increases from 13.49 to 16.35 for the raw clay and from 14.54 to 17.52 for the activated clay. The mobility of molecules increases generally with a rise in temperature, thereby facilitating the formation of surface monolayers. Since the retention capacity of the clay is enhanced with increasing temperature it is assumed that the adsorption process is endothermic, in agreement with the literature reports [46, 47].

A study of the temperature dependence of the adsorption process gives valuable information about thermodynamic aspect of the adsorption [48]. The thermodynamic parameters for the present study including Gibbs free energy of adsorption ΔG°, changes in enthalpy of adsorption (ΔH°) and changes in entropy of adsorption (ΔS°), were determined using the following equations :

$$\boldsymbol{\Delta G° = -RTLn(K_D)} \qquad (3)$$

$$\boldsymbol{LnK_D = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}} \qquad (4)$$

Where R is the universal gas constant (8.314J/mol.K) and T is the solution temperature in K.

The equilibrium constant (K_D) can be calculated using the equation below:

$$\boldsymbol{K_D = \frac{q_e}{C_e}} \qquad (5)$$

Equilibrium constant (K_D) for the adsorption process was determined by plotting ln q_e/C_e vs q_e and extrapolating to zero q_e. The values of ΔH° and ΔS° were obtained from the slope and the intersection with the intercept at the origin of ln (K_D) versus 1/T (Figure 8).

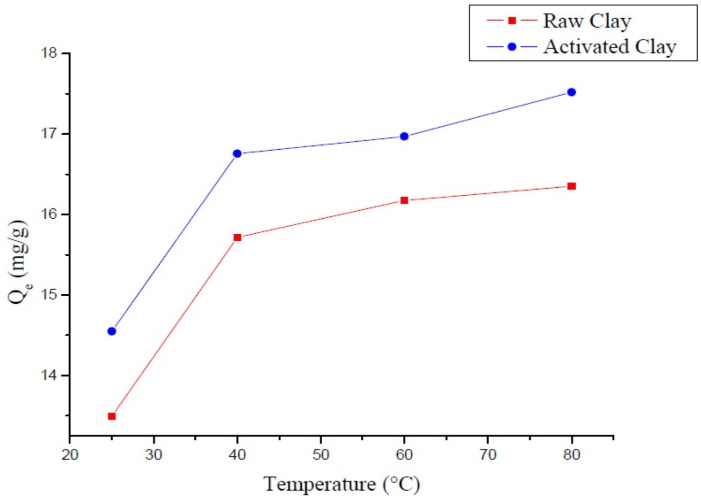

Figure 7: Influence of temperature on the adsorption of methylene blue onto the raw and activated clay

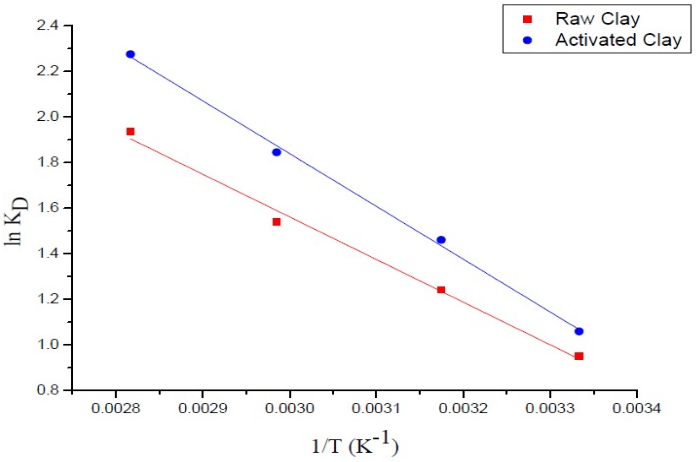

Figure 8: Plot of ln (K_D) versus temperature (1/T) for the adsorption of MB on the raw and activated clay

The thermodynamic parameters are summarized in Table 1. It can be seen from this table that all the (ΔG°) values are negative, which indicates that the adsorption is spontaneous and thermodynamically favorable [49]. Furthermore, researchers have reported that the change in free energy ΔG˚ in the case of physical adsorption ranges from −20 to 0 kJ/mol and in the case of chemical adsorption it ranges from −80 to −400 kJ/mol [50]. In the present study, the thermodynamic values obtained are inside the range of physical adsorption indicated that the physisorption might dominate the adsorption of MB onto raw and activated clay. The positive sign of ΔH° confirmed the endothermic nature of adsorption process [51]. As indicated from Table1, the value of ΔH° is lower than 40 kJ/mol indicating that the adsorption is physical [52]. Besides, the positive values of the ΔS° show the increased randomness at the solid/liquid interface, with some structural changes in the adsorbate and adsorbent [53]. Moreover, it could be deduced from the given data of table 1 that the adsorption of MB is more favorable in the AC than in the RC**.**

Table1: Thermodynamic parameters for the adsorption of methylene blue dye on the raw and Activated clay

	Raw clay			**Activated clay**		
T (K)	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol.K)**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol.K)**
300	- 2.48	16.91	64.44	- 2.72	20.79	78.39
315	- 3.38			- 3.90		
335	- 4.67			- 5.47		
355	-5.96			- 7.04		

3.3. Methylene Blue Adsorption Isotherms

The adsorption equilibrium isotherm is an important factor for describing the way in which the adsorbate molecules can distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state. Several isotherm equations are available, and two important isotherms were selected for this study: the Langmuir and Freundlich isotherms [54, 55]. The equations relative to these isotherms are described in the following.

3.3.1. Langmuir isotherm

The Langmuir model is suited to describe the adsorption of monolayer onto homogeneous surfaces. The adsorption can be represented by the following equation:

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{K_L . q_m} \times \frac{1}{C_e} \qquad (6)$$

Where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e (mg/l) is the equilibrium concentration, K_L (l/g) is the Langmuir constant and q_m is the monolayer adsorption capacity.

In addition, one can use the Langmuir isotherm to extract a dimensionless term R_L called the separation factor. The value of R_L indicates the type of the isotherm (i) unfavorable ($R_L > 1$), (ii) linear ($R_L = 1$), (iii) favorable ($0 < R_L < 1$), or (iv) irreversible ($R_L = 0$) [56]. It is defined as:

$$R_L = \frac{1}{1 + K_L . C_0} \qquad (7)$$

Where K_L is the Langmuir constant and C_0 is the initial concentration of adsorbate in solution.

3.3.2. Freundlich isotherm

The Freundlich model is based on the fact that the adsorption takes place on heterogeneous surfaces and assumes that the absorption occurs on sites with different adsorption energies. The model gives a representation of the equilibrium between the amount of adsorbate in solution and that on the surface of the adsorbent. This equation is also applicable to multilayer adsorption [57] and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (8)$$

Where q_e is the amount of solute adsorbed per unit mass of adsorbent ($mg.g^{-1}$), C_e is the equilibrium concentration, K_F is the Freundlich constant and n is the heterogeneity factor. The value K_F is related to the adsorption capacity, while the value of (1/n) is related to the adsorption intensity. When n=1, the adsorption is linear, meaning that sites are homogeneous and there is no interaction between the adsorbed species; when $1/n < 1$, adsorption is favorable and the adsorption capacity increases while new adsorption sites appear. When $1/n > 1$ adsorption is not favorable, adsorption bonds become weak and the adsorption capacity decreases [58].

The amount of adsorbed quantities of MB at the equilibrium (q_e) versus equilibrium dye concentration (C_e) was drawn in Figure 9. One can suggest that it is an isotherm of the type H in Giles classification [59, 60].

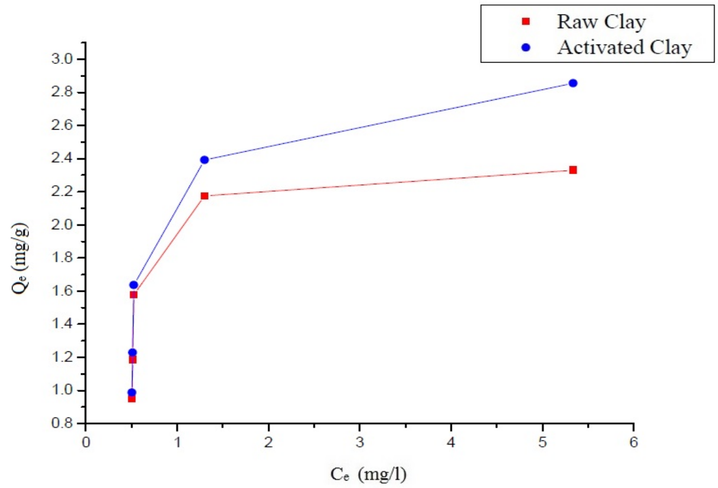

Figure 9 : Plot of (q_e) versus (C_e) for the adsorption of MB on the raw and activated clay

Generally, isotherm type H results from the dominance of strong ionic adsorbate–adsorbent interactions [61]. By using the above equation, we have determined the parameters characterizing the two models. The Langmuir plot (figure 10) of the data shows a good linear fit and the derived parameters are presented in Table 2. As can be observed from this table, the correlation coefficient R^2 for the raw clay (R^2 =0.9865) and the activated clay (R^2 =0.9992) are very close to 1 and the maximum adsorption capacity are 30 mg/g and 50.22 mg/g respectively. Tthe values of q_m and R^2 are higher for the adsorption of AC than for the RC. The separation factor (R_L) is between 0 and 1 for both raw and activated clay indicating that the adsorption processes are favorable.

On the other hand, the experimental results were analyzed by the Freundlish model (figure 11).

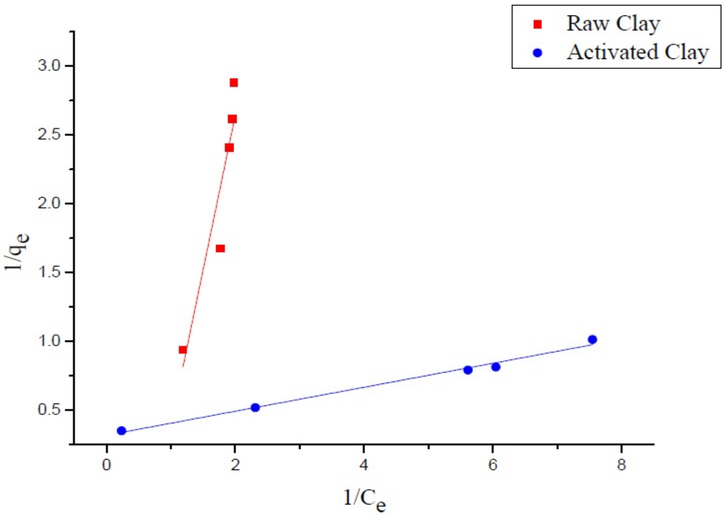

Figure 10: Langmuir isotherm for adsorption of methylene blue on raw and activated clay

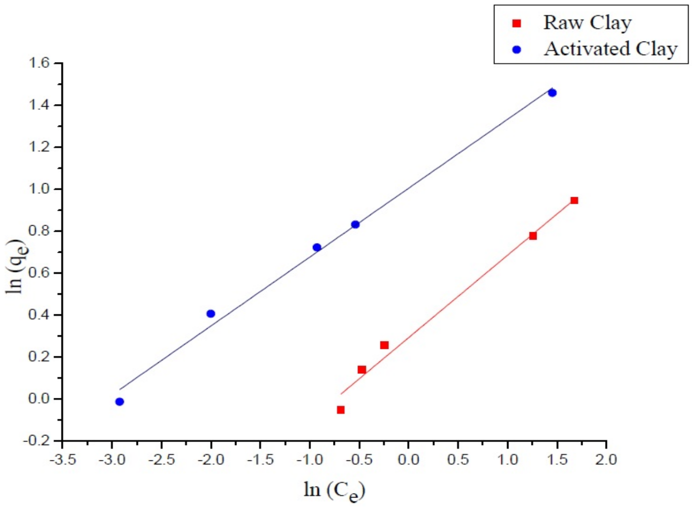

Figure 11: Freundlich isotherm for the adsorption of methylene blue on raw and activated clay

The obtained parameters of this model such as homogeneity factor n, correlation coefficient R^2 and Freundlich constant (K_F) are given in table 2. Here the values of n are between 0 and 1 which prove that the adsorption process is favorable onto both raw and activated clay.

Based on the correlation coefficient R^2 shown in table 2, the raw and activated clay can be better described by the Langmuir model. The Langmuir equation also yields a better fit of the experimental data than the Freundlich equation for raw and activated clay.

In order to situate the clay capacity with other adsorbents, table 3 compares maximum adsorption capacity of MB onto various adsorbents. It is deserved that the activated clay by the sulfuric acid presents the adsorption capacity in the same order of that reported in the literature [62, 40]. Moreover, one can assume that the activation of the clay is one of the strategies allowing the increase of the adsorption process and elimination of organic pollutant from water.

Table 2: Langmuir and Freundlich parameters for the adsorption of methylene blue dye on raw and activated clay

	Isotherme of Langmuir				**Isotherme of Freundlich**		
Parametres	**q_m (mg/g)**	**KL (l/mg)**	**R_L**	**R^2**	**K_f (l/Kg)**	**n**	**R^2**
Raw clay	30	3.13	0,03	0.9865	24.29	0.32	0.6511
Activated clay	50.22	5.88	0,02	0.9992	47.08	0.4	0.8469

Table 3: Adsorption capacity (q_e) of methylene blue on various adsorbents

Adsorbent	**q_e (mg/g)**	**References**
Kaolinite	17	35
Zeolite	25	62
Turkey Clay	58.2	63
Afyon/Turkey Clay	24.87	64
Safi/MoroccanActivated clay	68.49	40
Malatya/Turkey pyrophyllite	70.42	65
Bengurir raw clay	30	This study
Activated clay	50.22	This study

3.4. Kinetic Studies of Methylene Blue Adsorption

The rate at which contamination is removed from aqueous solutions is a parameter allowing comprehending the adsorption process. In order to investigate the mechanism of adsorption the pseudo-first-order and the pseudo-second-order kinetic models were used to test dynamical experimental data [66]. The applicability of the pseudo-first-order and pseudo-second-order model was tested for the adsorption of methylene blue onto raw and activated clay.

The kinetic model of the pseudo-first-order is expressed as follows:

$$\frac{d_{q_t}}{d_t} = k_1(q_e - q_t) \qquad (9)$$

Where q_e and q_t are adsorption capacity (mg/g) at equilibrium and at time t, respectively. k_1 is the adsorption rate constant (min^{-1}).

After integration and application of boundary conditions this model can be expressed in a linear form as Equation (10):

$$\log(q_e - q_t) = \log(q_e) - k_1.\frac{t}{2.303} \qquad (10)$$

k_1 and q_e were obtained from slope of the linear plots of log (q_e −q_t) vs. t (figure 12). The obtained results are given in table 4.

According to the pseudo-second-order model, the adsorption is expressed by the equation (11).

$$\frac{t}{q_t} = \frac{1}{K_2.q_e^2} + \frac{t}{q_e} \qquad (11)$$

Where q_e and q_t are the absorption capacity (mg/g) at equilibrium and time t, respectively. A constant k_2 represents the constant rate of adsorption (g / mg.min).

The parameters q_e and K_2 are obtained by representing $\frac{t}{q_t}$ versus t (figure 13). The obtained values for these parameters are gathered in table 4. The best-fit model was selected based on the linear regression correlation coefficient, R^2, values

From figure 12 which shows non-linear plots, we deduce that the kinetic of MB adsorption on raw and activated clay are not described by the pseudo-first-order kinetics model. On the other hand, the linear representation of t/qt vs time (figure 13) indicates that the mechanism of the MB adsorption onto the studied clays could be described by the pseudo-second-order model. Indeed, we note that R^2 correlation coefficient are close to 1 (table 4) and the calculated adsorption capacities ($q_e$cal) from this latter model are similar to the experimental data ($q_e$exp) as can be seen in table 4.

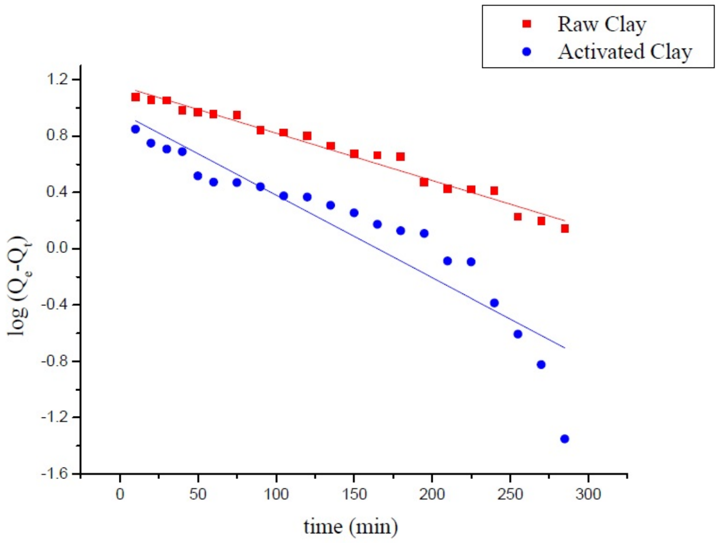

Figure 12 : Pseudo-first-order kinetic model for adsorption of methylene blue dye on raw and avticated clay

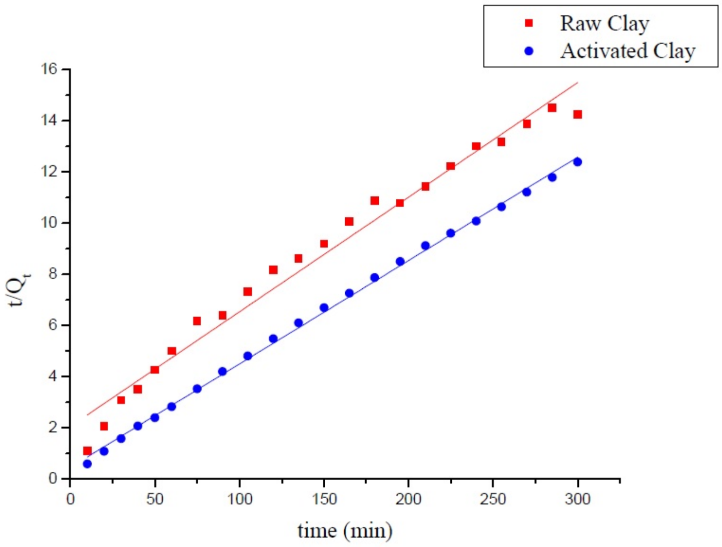

Figure 13: Pseudo-second-order kinetic model for adsorption of methylene blue dye on raw and activated clay

Table 4 : Kinetic parameters for methylene blue adsorption onto raw and activated clay.

	$q_{e,exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		$q_{e,calc}$ (mg/g)	K_1(min)	R^2	$q_{e,calc}$ (mg/g)	K_2(g/min mg)	R^2
Raw clay	21.03	2.63	0.020	0.8618	22.32	0.016	0.9789
Activated clay	44.30	3.18	0.014	0.9765	45.30	0.011	0.9984

Conclusions

Raw and activated clay are tested to eliminate the BM from water. The investigation has allowed the comparison of their adsorption capacity. The adsorption tests have shown that the amount of methylene blue adsorbed increased with pH and the initial dye concentration. Adsorptions of MB onto the clays are more described by the Langmuir model with a maximum adsorption capacity of 30 and 50, 22 mg.g^{-1} for the raw and activated clays respectively. These values showed that activated clay presented a better adsorption capacity. The adsorption mechanism can be described by a pseudo-second-order kinetic model. The obtained thermodynamic parameters indicate that the adsorption of MB on raw and activated clay was a spontaneous and endothermic process. According to the actual results one can consider that the activated clay of Bengurir in Morocco could be used to remove organic pollutants from water.

Acknowledgments - The authors acknowledge the Institute for Research in Solar Energy and New Energies (IRESEN) for the financial support.

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(2018) ; http://www.jmaterenvironsci.com