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Fast adsorption for removal of methylene blue from aqueuous solutions using of local clay

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Abstract:
In the present work we are interested in the study of the adsorption of a methylene blue cationic dye (BM) on natural material such as local clay (CM). For this reason, we carried out a parametric study of adsorption by studying the effect of several important parameters on the decolorizing power of the material used, in particular: contact time, adsorbent concentration, adsorbent dose, pH and temperature. A kinetic study was performed and kinetic models were applied to experimental results such as pseudo first order and pseudo second order. A modeling of the isotherms was carried out by applying known models such as Langmuir and Freundlich. The decolorization percentage was 92 %. Kinetic studies of dye on MB carried out the pseudo-second order at different dye concentration values. The Langmuir model describes satisfactory adsorption on the CM. Thermodynamic studies indicated that dye adsorption process by CM was spontaneous and endothermic in nature. On the other hand, different techniques of characterization of the CM adsorbent were used such as: scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

Keywords: *Cationic dye; Isotherm; Kinetic; Thermodynamic; Adsorption.*

1. Introduction

Several authors have signalize out that industries such as textiles, ceramics, paper and printing are known as industries that use significant amounts of dye and subsequently produce rejects loaded with dyes [1-2]. This Latter those are main contributors to mutagenic activity in wastewater [3]. The textile industry is one of the activities generating enormous risks; the quantity and the heavy load of the discharges resulting from this activity pose a real problem which influences the environment in a direct and not negligible way [4]. Several methods were developed in the literature for efficient removal of dyes from aqueous solution in the context of environmental protection, namely coagulation-flocculation, filtration, reverse osmosis, oxidation and adsorption [5-8]. The latter is one of the most effective methods that has been superior to other water treatment techniques by its simplicity of design, ease of operation and flexibility for the removal of wastewater color [9]. Scientists investigated the adsorption and removal of dyes by several materials, such as low cost adsorbent, activated carbon, zeolite, polymer resin adsorbents, pyrophyllite, aluminum oxide and other adsorbents [10-13]. The clay minerals for example, montmorillonite, sepiolite, and kaolin toward dye removal in aqueous phases, which has obtained good results [14]. However, in natural conditions, natural clays usually have a large capacity for cation exchange [15]. The objective of this work was to test the ability of the clay (CM) for the removal of methylene blue (MB) dye from aqueous solution by adsorption. Studies were carried out under various

parameters such as solution pH, adsorbents dose, contact time, initial concentration and temperature. The adsorption kinetic data were tested by pseudo-first-order and pseudo-second-order kinetic models. The equilibrium data were analyzed using Langmuir and Freundlich models. The effect of temperature on dye adsorption was also studied and the thermodynamic parameters were determined.

2. Materials and Methods

2.1. Preparation of adsorbent

The raw clay used in this work is taken from a natural basin of the region seghrouchen tahla, Taza, Morocco, it was crushed and sieved to obtain fractions <80 µm and dried at 105 °C for 24 hours.

2.2. Preparation of adsorbate

Methylene blue dye was 99% of purity provided by Ciba Specialty Chemicals Inc. The structure of this dye is illustrated in Fig 1 having a molecular weight of 319,852 g/mol. Besides, stock solution of MB was prepared by dissolving 1 g of accurately weighed dye in 1000 ml of distilled water. All chemicals used in synthesis and adsorption experiments, and were used without further purification.

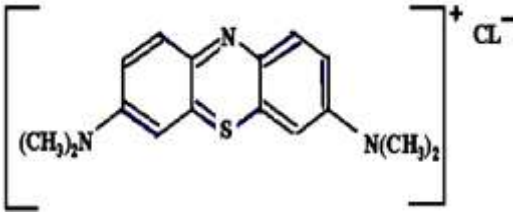

Fig.1. Structure of methylene blue.

2.3. Characterization techniques of clay (CM)

Different characterization techniques were used to identify the composition of the main constituents of the clay powder. Different characterization techniques were used to identify the composition of the main constituents of the clay powder.

2.3.1. Spectroscopie infrarouge à transformées de Fourier (FTIR)

La poudre d'argile a été analysée par la spectroscopie infrarouge à transformé de Fourier, de la société BRUKER (Vertex70). Les spectres IR ont été balayés sur une gamme de longueur d'onde 400-7500 cm^{-1}.

2.3.2. Morphological characterization (MEB-EDX)

The morphology of the dried clay surface was observed on a scanning electron microscope (Quanta 200 FEI equipped with EDAX probe for microanalysis of surfaces). Quantitative analysis of the elemental composition was studied by X-ray energy dispersive spectroscopy (EDX).

2.4. Adsorption experiments

The clay (CM) material tested for the adsorption of methylene blue dye reagent from aqueous solutions at room temperature using the batching technique.

The clay (CM) was tested for the adsorption of Methylene blue (MB) from aqueous solutions at room temperature conducted by mixing various amount of CM for MB dye removal in glass erlenmeyer flacks containing 250 ml of a dye solution at various pH using digital heating controlled magnetic stirrer (Stuart). Dye solutions were prepared using ultrapure water (MILLIPORE, direct-Q, UV3 with Pump). The effect of several variables of CM dose (0.5-2 g/l), pH (2-12), contact time (0-120 min) and initial dye concentration (30-50 mg/l) were studied.

At the end of the adsorption experiment the dye concentration was determined, 5ml of suspension was taken and then centrifuged for 10 min at a speed of 4000 rpm and the supernatant was filtered by filtration on 0.45µm diameter and then immediately dosed by UV spectrophotometer (Jasco V530).

The pH of the solution is adjusted by addition of a minor amount of HCl or NaOH (0, 1 M). At the end of the experiments of adsorption, the concentration of dye was given by measuring the absorbance of the solution with λ = 664 nm using a UV-visible spectrophotometer. All the experiments were carried out in double and the median values are presented.

The performance of adsorbent is usually depicted by adsorption capacity and removal percentage. The amount of MB adsorbed on the adsorbent per unit weight at any time t (q_t, $mg.g^{-1}$), at equilibrium (q_e, $mg.g^{-1}$) and removal percentage (%) are calculated as follows:

$$q_t = \frac{V(C_0 - C_e)}{W}$$

$$q_e = \frac{V(C_0 - C_e)}{W}$$

$$\text{Removal percentage (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

Where C_0 is the initial dye concentration (mg.L^{-1}) and C_t is the remaining dye (mg.L^{-1}) at time t, V is the volume of methylene blue solutions (L) and W is the mass of adsorbent (g).

3. Results and discussion

3.1. Characterization of adsorbents

3.1.1. Scanning Electron Microscopy Analysis of Clay (CM)

The application of these techniques made it possible to visualize the morphology of the surface of the adsorbent. Our sample was analyzed by SEM scanning electron microscopy. The images in Figure 2 show a lamellar structure of laminated form with a good distribution of leaves which explains our clay material has a porous appearance which facilitates the

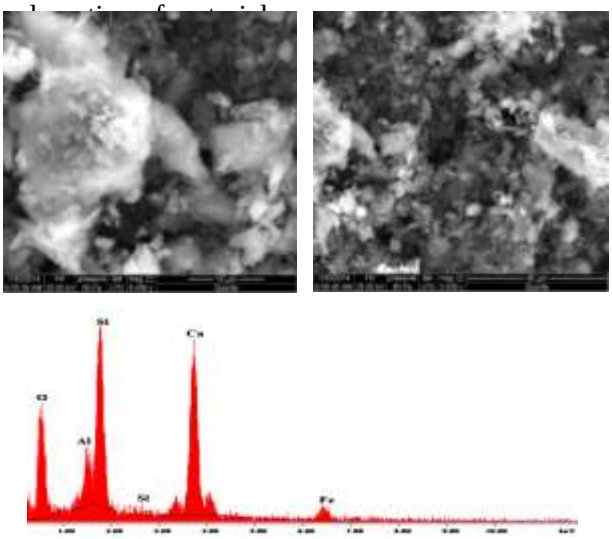

Figure 2: SEM microscopy coupled with EDX

3.1.2. Analysis of Fourier Transform Infrared

Figure 3 shows the spectrum of clay (CM) obtained by Fourier transform infrared spectroscopy. The FTIR spectrum was scanned over a wavelength range between 400-7500 cm^{-1}. The characteristic bands of the clay are shown in Figure 3.

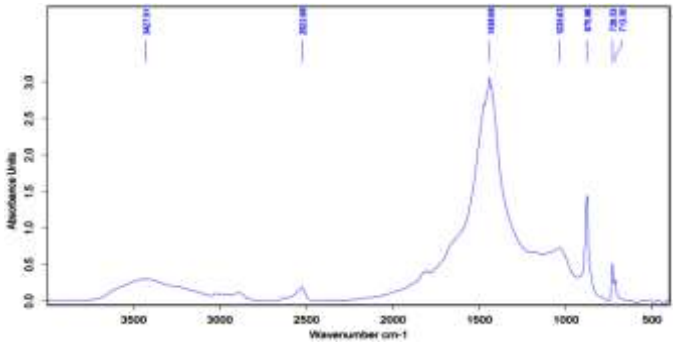

Figure 3: FTIR spectroscopy of clay (CM).

The adsorption bands observed confirms the presence of the bonds characterizing the clay (CM). Among these bands, we cite mainly: the bands located at 3427 cm^{-1} and 2522 cm^{-1} correspond to the elongation vibration group of the OH constitution water, the band 1438 cm^{-1} corresponding to the elongation vibrations of CO_3, the band 1035 cm^{-1} corresponds to the valence vibrations bond of the Si-O, the bands at 875 cm^{-1}, 728 cm^{-1} and 713 cm^{-1} relating to deformation vibrations of O-Si-O [16-19].

3.2. *Effect of various parameters on the adsorption of the methylene blue*

3.2.1. The effect of contact time on the adsorption of MB

Achieving the time after which the adsorption equilibrium is reached is necessary in order to determine the time required for the adsorbent-solute equilibrium which undoubtedly depends on the nature of the adsorbed molecules. Since adsorption is a process of transferring the pollutant from the liquid phase to the solid phase, the time between the two phases acts as a limiting factor. The effect of the initial concentration of dye on the adsorption phenomenon, which has been studied while keeping the other parameters constant (adsorbent dose= 1 g/L, T=20 °C, stirring speed = 300 rpm)

When the adsorption process was started, a rapid initial rate of adsorption happened and then slower adsorption was carried out and no significant uptake was finally observed.

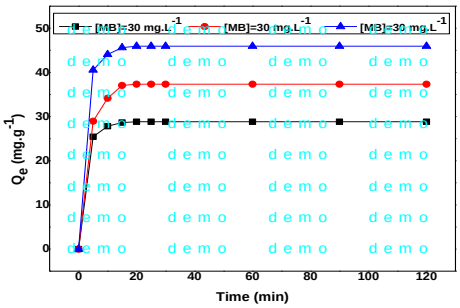

Fig.4. The effect of contact time and MB dye concentration.

The uptakes versus contact time data for Methylene blue-clay (MB-CM) adsorption system at various MB initial concentrations (30–50 mg/L) are shown in Fig. 4. Enhanced performance for CM toward MB is noticed with time until equilibrium at about 15 min. Fig. 4 shows sharp increase in MB uptakes for all concentrations at the first 10 min and become slight afterward. Then, insignificant adsorption of MB molecules on CM clay is occurred. This behavior is attributed to presence of more active sites for rapid adsorption followed by slow adsorption due to saturation of some sites and competitive attraction of dyes molecules towards porous structure of clay and, finally the obtaining of the plateau is probably due to the almost total occupation of the available adsorption sites. Thus, the equilibrium state for the MB-CM system at studied concentrations range is reported at 15 min. At this time, an increase in initial concentration of MB from 30 to 50 mg/L enhances its uptakes from 28.83 mg/g to the highest value of 45.94 mg/g.

3.2.2. The effect of adsorbent dose

The dose of adsorbent is an important parameter that affects adsorption capacity. In this reason, to observe the minimum possible dose of adsorbent which gives maximum adsorption, the effect of CM dose on MB removal was studied by keeping all other experimental conditions constant (Fig.5). The effect of dose is examined by varying the amount of the adsorbent from 0.5 to 2 g/L of dye solution (50 mg/L).The results revealed that removal efficiency and adsorption capacity showed inverse relationship with adsorbent dose.

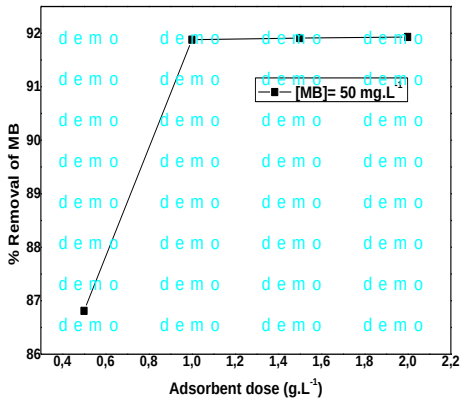

Fig.5. Effect of adsorbent dose on the adsorption of MB on CM.

3.2.3. The effect of pH

The study of the acid-base behavior of the surface of the adsorbent (CM) in the presence of the dye (MB) or the effect of the pH of the dye solutions on the adsorptive efficiency of the supports allows us to predict a probable mechanism of adsorption of species on solids. In this case, a mass of 1 g/L of the adsorbent is introduced into a solution of the concentration dye of 50 mg/L. Similarly, we varied the pH (2-12) solution in the volume of the solution. In addition, the pH value was adjusted by adding a few drops of NaOH and HCl. Fig. 6 display that the adsorption quantity of MB on the clay increases with increasing pH value.

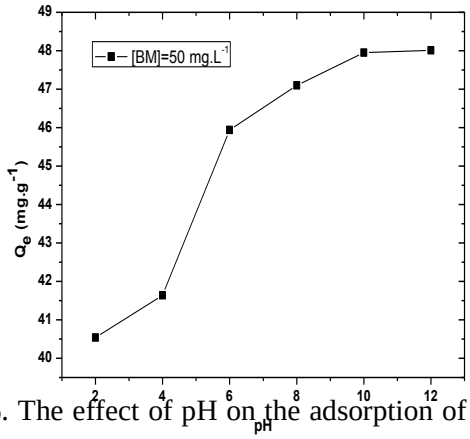

Fig.6. The effect of pH on the adsorption of MB on to CM.

3.2.4. The effect of temperature

The temperature is a strongly major parameter in the adsorption process. It is important to include the influence of this parameter during the Methylene blue (MB) adsorption on clay (CM). Fig.7 shows the adsorption capacity of MB adsorbed on CM in the

range of 20–50°C at various temperatures. The adsorption capacity increases with the increase of temperatures, indicating that the adsorption of MB on CM is endothermic and high temperatures contribute to the adsorption process.

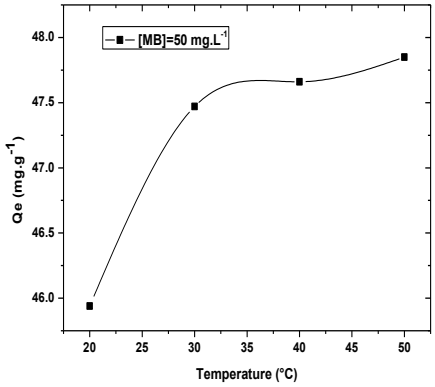

Fig.7. The Effect of temperature on adsorbed quantity

3.3. Adsorption kinetics

In order to examine the mechanism of the adsorption process (mass transfer, chemical reaction), we examined kinetic models to analyze our experimental results. Several models are applied in batch system in order to describe the phenomenon of transport of pollutants in the pores of the solid. Two mathematical models were chosen on the one hand for their simplicity and on the other hand for their application in the field of the adsorption of organic compounds on different natural and synthetic solids. Lagergren [20] proposed a kinetic model of pseudo first order expressed by the following relation:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (4)$$

The integration of equation (4) gives:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t \qquad (5)$$

The kinetic model of pseudo second order expressed by the following relation [21]:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (6)$$

The linear form of equation 6 is as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_2} \qquad (7)$$

Where q_e and q_t (mg/g) are uptakes at saturation and time t, respectively, K_1 (1/min), K_2 (g/mg.min) the constants of speed.

The linear representation of $\log(q_e-q_t)$ versus time gives a straight line whose slope and intercept help us to determine the values of the K_1 rate constant and the maximum adsorption capacity. This indicates that the adsorption kinetics of MB on CM does not correspond to the pseudo-first order kinetics.

The constants K_2 and qe are determined from the intercept and slope of the right $t/q_t = f(t)$.

The modeling of the adsorption kinetics of MB on the adsorbent CM by the pseudo-second order model is presented in Fig.8.

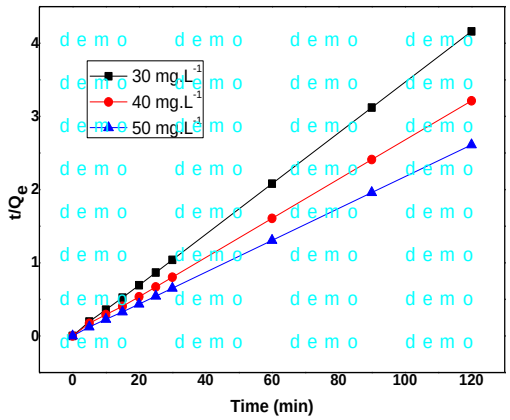

Fig.8. Pseudo-second order model for the adsorption of Methylene blue on clay adsorbent.

The corresponding parameters have been grouped together in Table 2 which also displays the correlation coefficients.

Table 1: Parameters characterizing the adsorption kinetics of MB on the adsorbent CM.

C_o (BM) (mg.L^{-1})	**Q_{exp} (mg. g^{-1})**	**Kinetic of 2st ordre**		
		K_2 (g.mg^{1}.min^{-1})	Q_{cal} (mg.g^{-1})	R^2
[CM]= 30 mg/L	28.83	0.165	29.41	0.999
[CM]= 40 mg/L	37.33	0.06	37.03	0.999
[CM]= 50 mg/L	47.85	0.112	47.201	0.999

Based on the linearity of the experimental points and consequently on the correlation coefficient (R^2), the

second order model is the closest to characterize the kinetics of this adsorption (Table 1). From the values of the maximum adsorption capacities qe calculated from the second order, we find that the values q_e are close to those determined experimentally, which also shows that the model of the pseudo second order describes well the kinetics of the reaction adsorption of methylene blue on clay adsorbents.

3.4. Adsorption isotherm

Various equations described in the literature have been proposed to describe the adsorption isotherms, the most classic of which are the Langmuir and Freundlich models [22]. The Langmuir model describes most of the adsorption reactions. This model makes it possible to calculate the maximum adsorbed quantity and the adsorption constant. In addition, the ease of application of this model has helped to make it a common tool in the approach of adsorption phenomena. It is theoretically applicable only in the case of localized adsorption sites, homogeneous and without lateral interactions between the adsorbed particles with a reversibility of the adsorption-desorption reaction. The linear form of the equation characterizing the Langmuir model is given by the following relation [23]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \qquad (8)$$

The separation factor R_L (dimensionless) is calculated by the following equation (5).

$$R_L = \frac{1}{1 + K_L C_e} \qquad (9)$$

The Freundlich model is often applied when Langmuir's model is not applicable [24]. Its empirical equation is widely used for the practical representation of the adsorption equilibrium. The linear form of Freundlich equation is as follows:

$$LnQ_e = LnK_f + \frac{1}{n_f} lnC_e \qquad (10)$$

With K_L: constant of Langmuir; C_e: Residual concentration in solution at adsorption equilibrium (mg/L); Q_e: amount of adsorbed in equilibrium (mg/g); Q_{max}: maximum of amount adsorbed (mg/g); K_f and n_f: empirical constants of Freundlich.If based on the correlation factor our results do not describe the Freundlich model. The results obtained are presented in Table 2, the correlation coefficient for Langmuir is good (≥ 0.99) and showing good linearity for the adsorbent studied; this indicates that this model is verified and the adsorption of the MB on the surface of the material PB is monolayer. The calculated Hall parameter value is summarized in Table 2. The results obtained show that the adsorption isotherms of the MB on CM are all favorable. A similar result was obtained in recent studies such as Miyah et al. [13].

Table 2: Parameters of the Langmuir and Freundlich model

	Langmuir				Freundlich		
	Q_{max} (mg/g)	K_L (L/mg^{-1})	R_L(L.mg^{-1})	R^2	K_f (mg/g)	n_f	R^2
CM	47,612	1.312	0.015	0,999	32.49	2.044	0,993

3.5. Thermodynamic studies

The thermodynamic parameters represented by changes in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for MB –CM system are determined as follows [25-26]:

$$K_d = \frac{Q_e}{C_e} = e^{\left(\frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}\right)} \quad ===> \quad lnK_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (11)$$

The values of ΔH° and ΔS° were calculated from both the slope and the interception of the $\ln K_d$ while plot as a function of 1/T. ΔG ° can be calculated using the relationship below:

$$\Delta G^0 = -RT \ln K_d \quad ===> \quad \Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (12)$$

Where, R (J/mol.K) represents the constant of perfect gas (8.314) and T (K) is adsorption temperature. The values of ΔG°, ΔH°, and ΔS° are obtained by correlation of In (K_d) versus 1/T data with Equations of (11) and (12) using a regression analysis (Table 3). The positive value of ΔH° (8.563 kJ/mol) reflects the endothermic nature and preferred adsorption at high solution temperatures [27]. The negative ΔG °values and their increase with heating, confirm the spontaneous and favorable methylene blue adsorption at high temperatures [28]. The positive values of ΔS° (Table 4) shows the increased disorder and randomness at the solid solution interface of MB with CM adsorbent that brings about some structural changes in the MB.

Table 3: Thermodynamic parameters of the MB adsorption process on CM at various temperatures.

	ΔH° (kJ.mol^{-1})	ΔS° (J.mol^{-1}.K^{-1})	ΔG° (kJ.mol^{-1})			
			20° C	30° C	40° C	60° C
CM	8.563	52.39	-6.788	-7.312	-7.836	-8.360

Conclusion

The present work shows that Methylene blue could be eliminated from aqueous solutions in eco-friendly conditions using clay adsorbent. We concluded that the Langmuir model is most likely to characterize blue methylene adsorption on CM clay support. The study of dye retention kinetics (MB) on CM shows that this process is generally consistent with kinetics of pseudo second order. The adsorption is greatly pH dependent, with a low uptake of dye at low pH and high uptake at high pH. Thermodynamic studies indicated that the dye adsorption onto CM was a spontaneous, endothermic and physical reaction in nature.

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