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Adsorption capacity of methylene blue, an organic pollutant, by montmorillonite clay

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ABSTRACT

The isotherms and kinetics of the adsorption of a cationic dye in aqueous solution, methylene blue, on a local Algerian montmorillonite clay mineral (raw, sodium and thermally activated at 300 and 500°C) were determined experimentally. Various parameters influencing the adsorption were optimized, mainly solid–liquid contact time, mass of adsorbent, initial concentration of dye, pH of the solution and temperature. Results showed that the adsorption kinetics were fast: 30 min for the raw clay mineral, and 20 min for sodium clay mineral (SC) and thermally activated at 300°C, whereas with the clay mineral calcined at 500°C, the equilibrium was reached after 150 min only. The maximum adsorption capacity was reached at pH 6.6. Results deducted from the adsorption isotherms also showed that the retention follows the Langmuir model. In addition, it was found that the kinetics were in the order of 2 ($K = 2.457 \times 10^6$ g/mg.h) for sodium clay and were limited by an intra-particle diffusion. SC was found to be a better adsorbent to remove methylene blue from industrial wastewater.

Keywords: Adsorption; Methylene blue; Algerian montmorillonite; Dyes; Kinetics

1. Introduction

Wastewater from textile industry including dyes represents an important source of pollution and constitutes major environmental and health problems. For this purpose, it is essential to treat these wastes in order to limit the amount of pollutants discharged into the environment. There are several conventional techniques for eliminating the excess of colored organic pollutants (e.g. methylene blue) present in industrial wastes including biological treatments [1,2]. However, unsatisfactory results were achieved by these techniques. Other new processes such as electrocoagulation [3,4], advanced oxidation processes [5], coagulation-flocculation [6], and adsorption [7] were elaborated to meet the required standards. Among these techniques, adsorption is considered as the most

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efficient technology for the removal of dyes using local materials [8,9]. Several studies have demonstrated the effectiveness of activated carbon due to its high adsorption capacity of organic species, but in most cases, its use is costly [10,11]. Therefore, research has been directed towards natural and inexpensive materials with a large adsorption capacity such as clays mineral. Today, thanks to their abundance, clays mineral indeed appear to be a more economical alternative. Recent studies have shown that clays mineral have marked affinity for the adsorption of cationic heteroaromatic compounds [12,13]. The originality of this present work is to compare the performance and capacity of adsorption of methylene blue from different clays. Indeed, we propose to evaluate the removal efficiency of methylene blue in aqueous solution by adsorption using raw clay mineral (RC), sodium clay mineral (SC), and thermally activated clay mineral at 300 and 500˚C. Retention capacity is estimated by monitoring the kinetics of adsorption by adsorption isotherms. The essential parameters of the adsorption process, mainly contact time, mass of clay, temperature, initial concentration of dye, and pH of the aqueous solution were determined and optimized.

2. Materials and methods

2.1. Preparation of adsorbent

The type of clay used in this study is montmorillonite collected from Roussel, Hammam Boughrara, Maghnia, located in the West of Algeria. Its structural formula is $(Si_8)^{IV}(Al_{4-x}\ Mg_x)^{VI}O_{20}(OH)_4$. Before the activation process, we started by a raw clay sedimentation procedure to eliminate quartz and cristobalite. With this process, the fraction of montmorillonite (<2 μm) was recovered. The second step was the chemical activation which is based on the treatment of clay with HCl (1 N) to remove carbonates, and by hydrogen peroxide to remove organic components. The recovered solid phase was then saturated with sodium ions by stirring in sodium chloride solution (1 M). The obtained solid is named SC. Then, we have thermally activated the clay at temperatures of 300 and 500˚C, referred as CC 300˚C and CC 500˚C, respectively, [14] with a heating time of 12 h.

2.2. The adsorbate

Methylene blue is a cationic dye molecule belonging to the Xanthines family [15]. Its empirical formula is $C_{16}H_{18}ClN_3S$, corresponding to a molecular weight of 319.86 g/mol. It has a solubility of 50 g/L at 20˚C. This dye is also used to test the adsorption efficiency of the solids and to determine their specific surface area [15,16]. Its wavelength of maximum absorption is 664 nm.

2.3. Experimental protocol

Adsorption tests of methylene blue were carried out in a batch process by varying the mass of adsorbent. The concentration of adsorbate was measured at regular intervals of contact time ranging between 5 and 120 min and working at a constant stirring speed of 1,000 rpm. The adsorbent and adsorbate were then separated by centrifugation. Analyses were performed using a UV–vis spectrophotometer, type 2401 PC, controlled by a computer. The maximum wavelength was obtained by scanning the spectral range between 400 and 700 nm. The amount of dye adsorbed (mg/g) was calculated using the following equation:

$$q_e = \frac{X}{m} = \frac{(C_i - C_{eq})V}{m} \quad (1)$$

where q_e is the amount of dye adsorbed (mg/g), C_i is the initial concentration (mol/l), C_{eq} is the equilibrium concentration (mol/l), V is the volume of the solution (L), m is the mass of adsorbent used (g), and X number of grams of methylene blue adsorbed (mg).

2.4. Characterization method

The clays mineral used as adsorbent in this study were characterized by X-ray diffraction using a Philips Analytical X'Pert Pro diffractometer operating at the wave length of the copper Kα (λ = 1.5418 Å) and by spectroscopy using a FTIR spectrophotometer NICOLET 560. The specific surface area (BET) was measured by N_2 physisorption using a Micromeritics apparatus, Model 2100E. Samples were pretreated under vacuum (10^{-4} torr) at 150˚C for one hour. We also measured the cation exchange capacity (CEC) of the samples using conductometric titration.

3. Results and discussion

3.1. Characterization of the clay minerals

Results of characterization analyses are presented in Figs. 1 and 2.

The diffractograms of RCs, purified, and calcined are presented in Figs. 1 and 2. They confirm the purification of the clay mineral since peaks of impurities such as quartz 22.5˚, calcite 28.5˚, and cristobalite 26˚ completely disappeared after purification. It is further

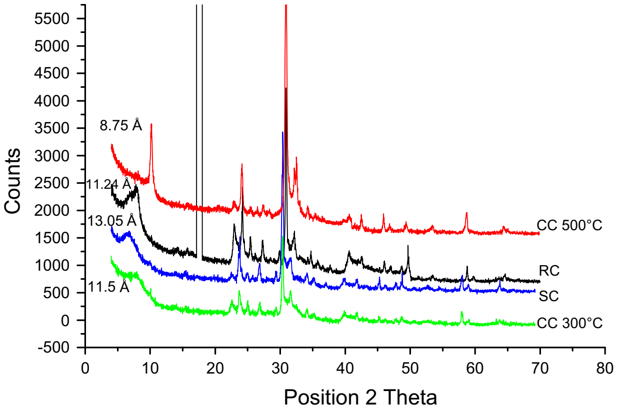

Fig. 1. Diffractograms of samples: RC, SC, CC 300℃, and CC 500℃.

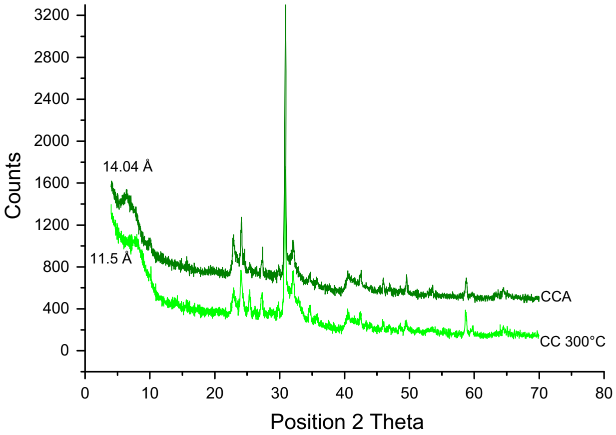

Fig. 2. Diffractograms of samples: CC 300℃ and CAA.

noted that there is a Bragg distance for the basal distance (d_{001}) for SC of about 13.05 Å. For CC 300℃ and CC 500℃, there was decrease in d_{001} reaching 11.5 and 8.75 Å, respectively. On the other hand, in the diffractogram of CAA, there is an increase of d_{001} up 14.04 Å. This variation is due to the presence of methylene blue molecules incorporated into the interlayer space during adsorption.

The chemical treatment and the calcination of montmorillonite lead to an increase in the CEC and porous volume of this clay mineral. Note that the specific surface area and CEC of the burned samples both depend on the calcination temperature, namely calcination at higher temperature leads to a lower CEC and a lower d_{001}.

The results showed that the specific surface area of the RC is 42 m^2/g, purified clay mineral is 96 m^2/g, and the calcined clay mineral at 300 and 500℃ are 60.66 and 6.65 m^2/g, respectively; to a higher temperature of 500℃, there is a gradual decline and collapse in the specific surface area of the montmorillonite. Furthermore, the CEC of the RC is 45.86 meq/100 g, SC is 74.6 meq/100 g, and calcined clay mineral at 300 and 500℃ is 56.16 meq/100 g and 48.96 meq/100 g, respectively.

3.2. Influence of pH on λ_{max} of methylene blue

To study the influence of pH on the maximum wavelength of adsorption of the methylene blue (λ_{max}), we fixed its initial concentration to 5 mol/L and the pH of the solution was varying between 3 and 10. It appears that this parameter has practically no effect on the values of λ_{max}.

3.3. Effect of contact time

To examine the influence of contact time on the retention of methylene blue, a series of experiments was conducted using the following protocol: 0.05 g of adsorbent in 50 mL solution with two different initial concentrations of methylene blue: 50 and 100 mg/L. Fig. 3 shows the evolution of the percentage of discoloration of methylene blue solution as a function of contact time. The results indicate that the adsorption kinetics is rather fast for SC, with 99% of adsorption being quickly reached after 20 min of contact only. With RC and CC 300℃, the equilibrium was reached after 30 min with 60 and 96%, respectively. On the other hand, with CC 500℃, the time required to complete the adsorption was higher, reaching 120 min with 89%.

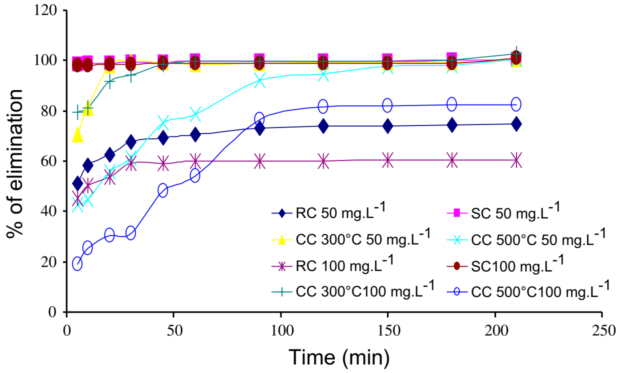

Fig. 3. Effect of contact time for adsorption of methylene blue on different types of clay minerals.

3.4. Effect of pH on the adsorption

The pH is one of the most important factors in controlling the adsorption of the dye on the particles in suspension. The influence of methylene blue solution on pH, presented in Fig. 4, is therefore studied. The initial pH of the solution ranges between 2 and 10 by adding HCl or NaOH to adjust the desired starting value.

The influence of pH is more significant for SC. The adsorption increases with pH up to pH 6.6 and then decreases significantly for more basic pH [17,18]. These developments could be explained as follows [19]:

- At low pH, the clay mineral is characterized by a capacity of anionic exchange; the addition of H^+ cations creates a positive charge. Anions in solution will thus be more attracted towards this surface, which disadvantage the adsorption of cationic methylene blue.
- At high pH, the CEC grows: the OH groups on the clay mineral deprotonate to react with OH^- in solution which brings a negative charge, so the methylene blue cations in solution will be attracted to the surface according to the following reactions:

$$MOH + H^+ \leftrightarrow MOH_2^+ \tag{2}$$

$$M - OH + OH^- \leftrightarrow MO^- + H_2O \tag{3}$$

where M is the cation of Si, Al or Fe.

Similar results were reported for the adsorption of methylene blue on kaolinite [20].

3.5. Effect of adsorbent mass

The changes in discoloration percentage as a function of the mass of adsorbents (RC, SC, CC 300°C, and CC 500°C) with constant stirring and pH 6.6 are presented in Fig. 5. The initial concentrations were 50 and 100 mg/L. We noticed that the percentage of bleaching increased as the mass of adsorbent increased, reaching an optimal value at 0.1 g/50 mL.

3.6. Adsorption isotherm

The adsorption isotherms were performed with different initial concentrations of methylene blue at pH 6.6. They are assessed by plotting the relation of q_e as a function of C_e as illustrated (Fig. 6) after adsorption tests, we obtained: q_e (RC) = 33 mg/g; q_e (SC) = 330 mg/g; q_e (CC 300°C) = 224 mg/g and q_e (CC 500°C) = 124 mg/g.

Analysis of the isotherms results shows that the adsorption capacity increases with the initial concentration. A remarkable difference was observed in the amount adsorbed with the nature of the adsorbent. The recorded highest rate of adsorption was observed for SC. The isotherm shows a steady state value (plateau) indicating the saturation of the surface and therefore formation of a monolayer. A similar behavior was obtained in the case of methylene blue adsorption on a copper montmorillonite [21,22]. The isotherm has a horizontal plateau indicating the description of the adsorption isotherms by applying the Langmuir and Freundlich models. The linearization of the Langmuir equation, shown in Fig. 7, enables to calculate the maximum adsorption capacity q_m and the affinity coefficient K_L of the Eq. (4).

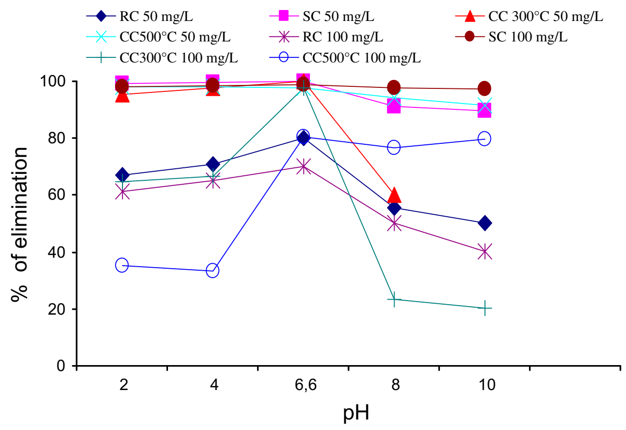

Fig. 4. Effect of pH on the adsorption of methylene blue.

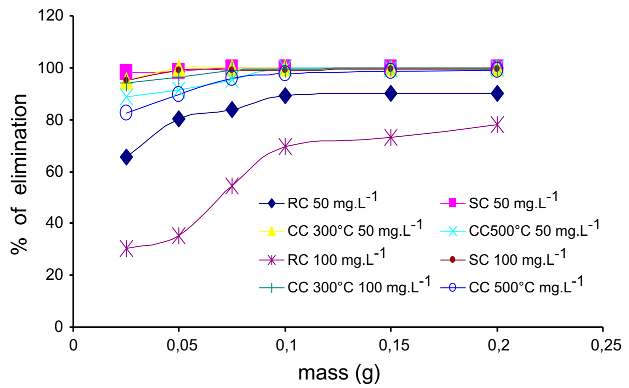

Fig. 5. Effect of adsorbent mass on adsorption of methylene blue.

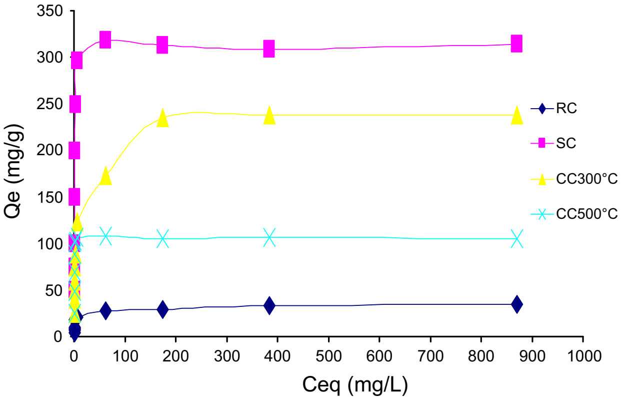

Fig. 6. Adsorption isotherm of the methylene blue by different types of clay minerals.

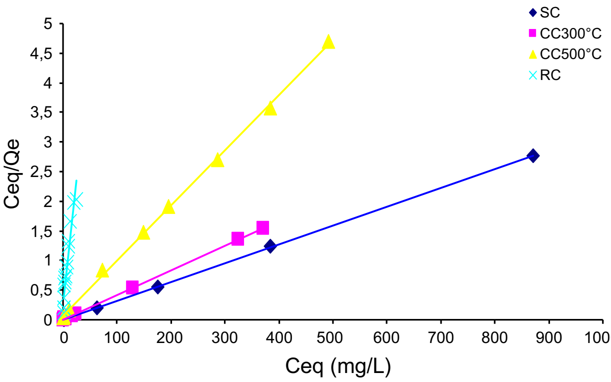

Fig. 7. Transformed linear Langmuir isotherms for adsorption of methylene blue on different types of clay minerals.

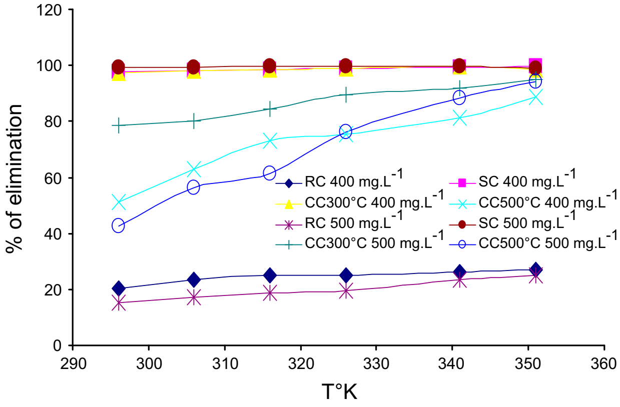

Fig. 8. Effect of temperature (between 25 and 80˚C) on the adsorption of methylene blue.

$$\frac{C_{\mathrm{eq}}}{q_{\mathrm{e}}} = \frac{1}{K_{\mathrm{L}} q_{\mathrm{m}}} + \frac{C_{\mathrm{eq}}}{q_{\mathrm{m}}} \tag{4}$$

The constants K_L and q_m of Langmuir model for the different samples were calculated from the equations. A good linear regression was obtained for the Langmuir model since the correlation coefficients R^2 exceed 0.99 except for RC. This indicates the probable formation of a monolayer of dye without mutual interactions of localized sites whose energy is identical.

3.7. Effect of temperature

To study the influence of temperature on the adsorption process of methylene blue, a series of experiments was conducted at different temperatures ranging between 25 and 80˚C (Fig. 8). The adsorption capacity has been more or less affected by temperature: the percentage of methylene blue discoloration for SC increases from 98 to 99.80% with an increase in temperature from 25 to 80˚C. This indicates that methylene blue adsorption on the surface of the clay mineral is an endothermic process [23].

3.8. Thermodynamic parameters

The influence of temperature on the adsorption of methylene blue was investigated to determine the thermodynamic parameters of the system (adsorbate/adsorbent) [24–26]. Ln K as a function of $1/T$, presented in Fig. 9, gives a straight line allowing the calculation of the entropy and the enthalpy of adsorption, ΔS_{ads} and ΔH_{ads}, respectively. Similarly, one can assume the free energy ΔG.

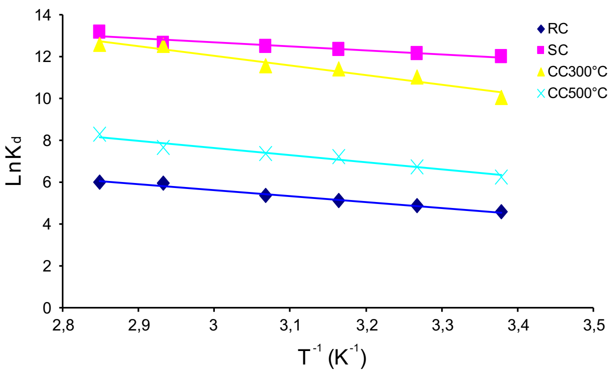

Fig. 9. Ln k_d vs. T^{-1} for the adsorption of methylene blue on different types of clay minerals.

$$\mathrm{Ln}\,K_d = \frac{\Delta S_{ads}}{R} - \frac{\Delta H_{ads}}{RT} \quad (5)$$

$$\Delta G = \Delta H_{ads} - T\Delta S_{ads} \quad (6)$$

From the results, the positive values of ΔH_{ads} (15.36–31.32 kJ/mol) confirm that the character of the adsorption process is endothermic, whereas the small values found suggest that the adsorption is a physical phenomenon, as it was observed in most cases [27]. Negative values of free energy ΔG (−20 to 0 kJ/mol) confirm the spontaneous nature of the adsorption [28,29]. Also, we noticed that for different adsorbents, ΔG decreases with the increase of the solution temperature. This can be explained by the fact that the adsorption becomes increasingly faster during adsorption; the change in the entropy of the adsorbate ΔS_{ads}, is necessarily negative, indicating that the solid state is more stable than the liquid state. Indeed, the methylene blue loses at least one degree of freedom with adsorption. Positive values of ΔS_{ads} (0.12–0.19 kJ/mol) show that the reactions are irreversible. Overall, from the previous observation the binding of methylene blue on different adsorbents is an irreversible physical adsorption which is characterized mainly by the speed and spontaneity of the system at higher temperatures [30].

3.9. Adsorption kinetics

The kinetics of the adsorption on the different types of adsorbents was studied by following the variation of methylene blue concentrations with time. In order to gain a better understanding of the adsorption process of methylene blue, the data was analyzed by applying the pseudo-first order, pseudo-second-order, and the model of intra-particle diffusion (Eqs. (7)–(9)) [31,32]. The application of the pseudo-second-order equation for the adsorption of different adsorbents on methylene blue is shown in Figs. 10 and 11.

$$\mathrm{Log}(q_e - q_t) = \mathrm{Log}(q_e) - \left(\frac{K_1}{2.303}\right)t \quad (7)$$

$$\frac{t}{q_t} = \left(\frac{1}{K_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \quad (8)$$

$$q_t = \frac{X}{m} = K_{diff}\, t^{1/2} \quad (9)$$

where q_t and q_e are the amount of adsorption at time t and at equilibrium (mg/g), respectively; k_1 is the constant rate of pseudo-first order (1/min); k_2 is the constant rate of pseudo-second order (g/(mg min)); and k_{diff} is the intra-particle diffusion coefficient (mg/(g min)).

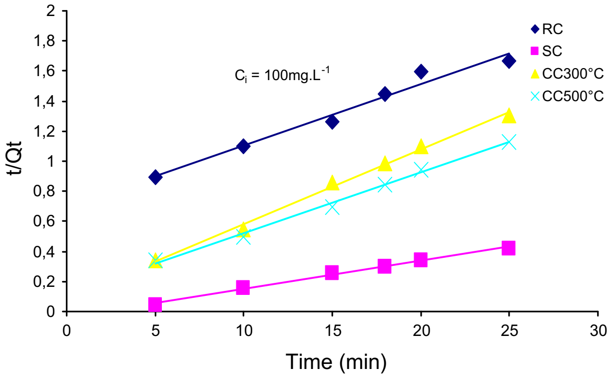

Fig. 10. Pseudo-second order for the adsorption of methylene blue on different types of clay minerals.

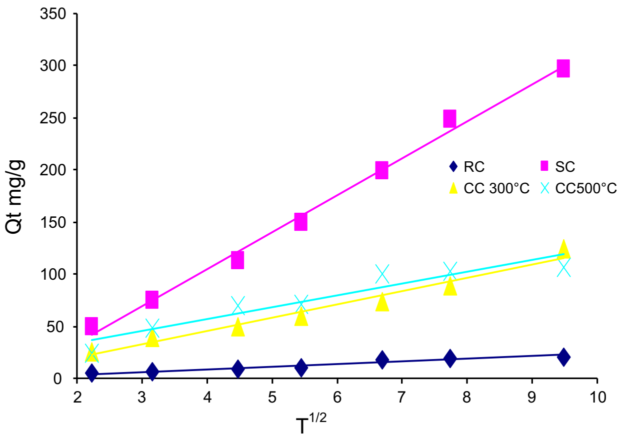

Fig. 11. Intra-particle diffusion for the adsorption of methylene blue on different types of clay minerals.

The constant rates k_1, k_2 and k_{diff}, and the amount of adsorption at equilibrium q_e were calculated from the slope and intercept of the corresponding linear lines, respectively. The results obtained by calculation using the equations (Eqs. (7)–(9)) show that the adsorption of methylene blue follows well the model of the pseudo-second order with an intra-particle diffusion since the obtained correlation coefficients were high (0.99–1.00) for all adsorbents.

4. Conclusions

This work aims to study the retention of methylene blue on clays mineral having undergone different treatments. The experimental results showed that:

- The adsorption kinetics was fast enough: 30 min for the RC, 20 min for SC and thermally activated clay mineral at 300°C (CC 300°C), whereas with the clay calcined at 500°C (CC 500°C), the equilibrium was reached after 150 min.
- The maximum adsorption was reached at pH 6.6.
- The adsorption isotherms showed that the retention follows Langmuir model.
- The adsorption of methylene blue is endothermic and spontaneous, and of a physical type.
- The adsorption of methylene blue on clay mineral followed a second-order kinetics with intra-particle diffusion.
- SC proved to be the best adsorbent, among those studied in this work, in removing methylene blue from industrial effluents.

Nomenclature

CAA	—	clay mineral after adsorption
CC 300°C	—	clay mineral calcined at 300°C
CC 500°C	—	clay mineral calcined at 500°C
k_d	—	partition coefficient of adsorption
C_{eq}	—	equilibrium concentration (mol/L)
C_i	—	initial concentration (mol/L)
K_L	—	affinity coefficient
k_1	—	constant rate of pseudo-first-order adsorption (g/mg.min)
k_2	—	constant rate of pseudo-second-order adsorption (g/mg.min)
m	—	mass of the adsorbent (g)
MB	—	methylene blue
q_e	—	amount of dye adsorbed at equilibrium (mg/g)
q_m	—	maximum adsorption capacity (mg/g)
q_t	—	amount of dye adsorbed at time t (mg/g)
RC	—	raw clay mineral
SC	—	sodium clay mineral
V	—	volume of the solution (L)
X	—	number of grams of methylene blue adsorbed (mg)
λ_{max}	—	maximum wavelength of absorption of methylene blue
ΔH_{ads}	—	enthalpy of adsorption
ΔS_{ads}	—	entropy of adsorption
ΔG	—	free energy of adsorption

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