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STUDY OF METHYLENE BLUE ADSORPTION BY MODIFIED KAOLINITE BY DIMETHYL SULFOXIDE

Abstract: Tamazert kaolin was modified with dimethyl sulfoxide (DMSO). The starting material and resulting from the intercalation were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy (SEM). Intercalation caused considerable changes in our clay by increasing the basal spacing to 11.22 Å, an intercalation rate of 98 %. The adsorption of methylene blue was studied as a function of pH, contact time, temperature, dye concentrations and adsorbents. Kinetic data have been adequately described by the pseudo-second order and intraparticle scattering model. The adsorption isotherm is in good agreement with the Redlich-Peterson model. A change in thermodynamic values (ΔH° , ΔS° and ΔG°) was observed after intercalation. Adsorption became non-spontaneous exothermic and ordered.

Keywords: kaolin, DMSO, intercalation, adsorption, methylene blue

Introduction

Dyes are widely used in industries such as textiles, paper, leather, rubber, plastics, dyes synthesis, printing, food, pharmaceutical and cosmetic industries. The dyes generally have a synthetic origin and complex aromatic molecular structures that make them more stable and more difficult to biodegrade. Many organic dyes are harmful to humans and toxic to microorganisms, the elimination of dyes from sewage has received considerable attention in recent decades [1-3].

Currently, several techniques are used for the removal of pollutants. Among these, we can mention chemical precipitation, ion exchange, electrochemical treatment, reverse osmosis and adsorption. Chemical precipitation is inappropriate to remove low concentrations and produces a large amount of sludge. Despite its effectiveness, reverse osmosis is an expensive technique because it requires frequent replacement of membranes.

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Ion exchange is also a costly operation, while electrolytic processes are considered cost effective only for concentrated solutions [4-7]. Adsorption has proved to be an effective, economical and easy to implement technique. In addition, there is no formation of sludge. Its other advantages are applicability at very low concentrations and the possibility of regeneration, for continuous or discontinuous use.

A large number of studies have been reported on use of different materials for dye removal from aqueous solution: crystal violet with palm petiole-derived biochar [8], congo red with cetyltrimethylammonium bromide-graphene oxide composite [9], methylene blue with reduced-graphene oxide supported nanoadsorbents [10], basic blue 41 with organic-inorganic hybrid adsorbent material [11] etc.

The modification of clays by organic or inorganic agents has attracted the interest of several researchers for their applications in various scientific and industrial fields [12]. Intercalation is one of the most sought after changes. The intercalation is one of the most sought after modifications at the moment. Intercalation is one of the most popular modifications currently in progress. The intercalation of kaolinite was born in 1960 and since that time until now, the industrial uses of intercalated kaolinite continues to grow. This growth is directly linked to its reactivity and these surface properties, which are remarkably improved after modification [13]. Kaolinite has been intercalated by several polar compounds such as: N-methyl formamide [14], urea [15], potassium acetate [16-18], hydrazine hydrate [19] and dimethyl sulfoxide [20, 21]. These compounds are known to have the ability to break the interfoliar bond between the siloxane and hydroxy aluminium surfaces and to access the interfoliar space and thus forming a complex by hydrogen bonds at both surfaces [22].

This work investigated the feasibility of Algerian kaolin intercalated by DMSO, used as a low-cost adsorbent for the removal of methylene blue from an aqueous solution. The materials were characterised by X-ray diffraction (XRD), FTIR analysis and scanning electron microscope (SEM). To achieve the aim, the effects of adsorbent dosage, pH, contact time, methylene blue (BM) concentration, and solution temperature were studied. Kinetic data, equilibrium isotherms, and thermodynamic parameters were also determined and discussed.

Materials and methods

Materials

Kaolin of Tamazert from Djebel Debbagh, Guelma (eastern region of Algeria) is commercialized without additives by SOAKLA society. Before the experiments, kaolin was ground, ultrasonically dispersed in deionised water, centrifuged and dried at 373 K, 10 g of kaolin were dispersed in 100 cm³ of DMSO, and the whole is subjected to moderate stirring for 96 h at room temperature. The excess solution was removed, and the kaolin, separated by centrifugation, was oven dried at 333 K [23]. The starting materials and the resulting products were respectively abbreviated to K and KD and characterized.

Methylene blue (BM), a cationic dye, was used as an adsorbate. The characteristics of the dye are listed in Table 1.

Table 1

Properties and characteristics of MB

Generic name	Methylene blue
Chemical name (IUPAC)	3,7-bis(Dimethylamino)-phenazathionium chloride tetramethylthionine chloride
Chemical formula	$C_{16}H_{18}ClN_3S \cdot 3H_2O$
Molecular weight [g/mol]	373.90
Molecular volume [cm ³ /mol]	241.9
Molecular diameter [nm]	0.80
λ specific [nm]	660
Chemical structure	

Characterisation

The X-ray powder diffraction patterns were obtained using a RIGAKU diffractometer (Netherlands) with CuK α radiation operating at 40 kV and 25 mA. The XRD data were collected over a 2 h range of 5-30° with a step width of 0.01°. The IR spectra were acquired through a Fourier transform spectrometer. The device used is SHIMADZU (FTIR-8400S). The structure band region (400-4000 cm⁻¹) was investigated using KBr wafers containing 0.5 % of sample. The morphological analysis is performed by a JSM-7200F scanning electron microscope with a field effect gun (Schottky).

Adsorption procedure

The adsorption experiments of methylene blue were performed via the batch method at 298 K. 0.02 g of the clay were mixed with 20 dm³ of methylene blue in a concentration range of 10-400 mg/dm³. The effects of dye and adsorbent concentrations, pH, contact time, and temperature were studied. The experimental conditions are outlined in Table 2. pH of the dispersions was adjusted by adding negligible volumes of 0.1 M HCl or 0.1 M NaOH. After each experiment, the solution was separated by filtration. The filtrate was analysed by visible spectrophotometry at $\lambda = 660$ nm using a Shimadzu 1240 UV-VIS spectrophotometer.

Table 2

Experimental conditions during the adsorption of methylene blue

Adsorbent concentration	Clay: 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/dm ³ Temperature 298 K, contact time 2 h
pH	pH (BM): 2, 3, 4, 5, 6, 7, 8, 9 and 10 Clay 1 g/dm ³ , temperature 298 K, contact time 2 h
Kinetics	Contact time: 1, 3, 5, 10, 20, 30, 60, 90 and 120 min Clay 1 g/dm ³ , temperature 298 K, pH = 5
Isotherms	BM concentration: 10, 20, 40, 60, 100, 150, 200, 300 and 400 mg/dm ³ . Clay 1 g/dm ³ , temperature 298 K, contact time 1 h, pH = 5
Temperature	Temperature: 298, 313, and 328 K. Clay 1 g/dm ³ , BM: 10, 20, 40, 60, 100, 150, 200, 300 and 400 mg/dm ³ , contact time 1 h, pH = 5

The amounts of adsorbed BM [mg/g] were determined using the following equation:

$$Q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

where C_i and C_e are the initial and the equilibrium dye concentrations [mg/dm³], V is the volume of dye solution used [dm³], and m is the mass of material used [g].

Theoretical considerations

Adsorption kinetics

In order to investigate the controlling mechanism of adsorption processes, various kinetic equations are applied to model the kinetics of methylene blue adsorption onto the unmodified and modified kaolinites.

The first model that we used in our kinetic study is the pseudo-first order model which is given by the following relation [24]:

$$\log(Q_e - Qt) = \log Q_e - (K_1 \cdot t / 2.303) \quad (2)$$

where Qt is the amount adsorbed at time t [mg/g], Q_e the adsorption capacity at equilibrium [mg/g], K_1 the pseudo-first order rate constant [min⁻¹], and t is the contact time [min].

The adsorption kinetics may also be described by a pseudo-second order reaction. The linearized-integral form of the model is [25]:

$$t / Qt = (1 / K_2 \cdot Q_e^2) + t / Q_e \quad (3)$$

where K_2 is the pseudo-second order rate constant of adsorption [g · (mg · min)⁻¹]. The initial adsorption rate h , as $t \rightarrow 0$, can be defined as:

$$h = K_2 \cdot Q_e^2 \quad (4)$$

The plot of t/Qt versus t should give a linear relationship, from which K_2 and h can be determined from the slope and intercept of the plot.

During adsorption under batch mode, there is a possibility of transport of adsorbate species into the pores of adsorbent, which is often the rate-controlling step. The intraparticle diffusion rate equation can be written as follows [26]:

$$Qt = K_{id} \cdot t^{1/2} + C \quad (5)$$

where K_{id} is the intraparticle diffusion rate constant [mg · g⁻¹ · min^{-1/2}] and C is a constant. The values K_{id} and C are calculated from the slope and the intercept, respectively, of the plot of Qt versus $t^{1/2}$.

Adsorption isotherms modelling

The equilibrium models of Langmuir, Freundlich, and Redlich-Peterson (RP) were used to fit the experimental data. The Langmuir equation can be written in the following form [27]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (6)$$

where Q_e is the equilibrium amount removed from solution [mg/g], C_e is the equilibrium concentration [mg/dm³], K_L is a constant related to the affinity of binding sites [dm³/mg],

and Q_m is the maximum amount per unit weight of adsorbent for complete monolayer coverage [mg/g].

The Freundlich model has been widely adopted and may be written in the form [28]:

$$\log Qe = \log K_F + \frac{1}{n} \log Ce \quad (7)$$

where K_F is a constant taken as an indicator of adsorption capacity [dm^3/g] and $1/n$ is a constant indicative of the adsorption intensity. The Redlich-Peterson model including three adjustable parameters was also used and is given by [29]:

$$Qe = \frac{K_{RP} Ce M}{1 + (K_{RP} Ce)^\beta} \quad (8)$$

where K_{RP} is the equilibrium constant [dm^3/mg], β is the heterogeneity factor that depends on surface properties of the adsorbent, and M is the maximum amount adsorbed [mg/g].

Thermodynamic study

The thermodynamic parameters for the adsorption process, ΔG° , ΔH° and ΔS° , were evaluated using the equation:

$$\ln K_d = \left(\frac{-\Delta H^\circ}{R \cdot T} \right) + \left(\frac{\Delta S^\circ}{R} \right) \quad (9)$$

where ΔH° and ΔS° are the change in enthalpy [J/mol] and entropy [J/(mol · K)], respectively. T the absolute temperature [K], R gas constant [$\text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$], and K_d is the distribution coefficient [dm^3/g]. This coefficient is given by:

$$K_d = Qe / Ce \quad (10)$$

The enthalpy and entropy changes are determined graphically by plotting $\ln K_d$ versus $1/T$, which gives a straight line. According to thermodynamics, the Gibbs free energy change, ΔG° , is related to ΔH° and ΔS° at constant temperature by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (11)$$

Results and discussion

XRD analysis

The diffractograms of the different samples are shown in Figure 1. The DRX spectrum of the starting material, K, shows intense basal reflections characteristic of kaolinite: a first at 7.15 \AA ($2\theta = 12.41^\circ$) corresponding to the (0 0 1) plane, a second at 04.47 \AA ($2\theta = 19.97^\circ$), another at 03.59 \AA ($2\theta = 25.01^\circ$) and one last at 03.59 \AA ($2\theta = 25.01^\circ$). This shows that Tamazert kaolin is essentially kaolinite. Quartz (q) at low intensity was detected.

Chemical treatment with DMSO has caused a considerable change in our clay. Effectively, the X-ray diffraction shows an increase in the basal spacing of the reflection of the 001 lattice plane, from 7.16 to 11.22 \AA . This increase in the basal distance is due to the intercalation of DMSO in the interfoliar space of our clay. To calculate the intercalation rate (IR), we used the relation of Wiewiora and Brindley [30] which is given by the following equation:

$$IR = \frac{I_{i001}}{(I_{i001} + I_{r001})} \quad (12)$$

I_{i001} refers to the first reflection of the intercalated phase and I_{r001} is the residuary (0 0 1) reflection in the intercalate.

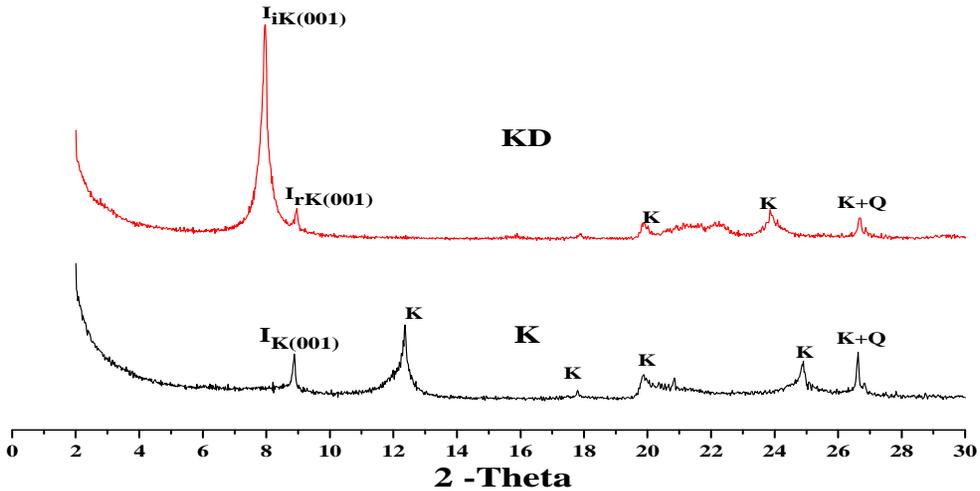


Fig. 1. XRD patterns of unmodified kaolin (K) and modified by DMSO (KD)

With an intercalation rate of 98 %, we can say that our clay is easily intercalated compared to other kaolinites. Indeed, Mbey et al. [31] found a ratio of 62.4 % for the intercalation of DMSO in a Cameroonian kaolinite. Zhang and Xu [32] achieved an 80 % intercalation rate when preparing kaolinite/DMSO composite under activated microwave radiation.

FTIR analysis

The IR spectra were acquired through a Fourier transform spectrometer. The device used is SHIMADZU (FTIR-8400S). The FTIR spectra of all our samples are shown in Figure 2.

The intercalation of DMSO caused considerable changes in vibrational spectra. The intercalation reaction destroys the inherent hydrogen bonding of the starting material and emphasizes new bonds, which changes the intensity and location of the characteristic bands of the hydroxyl groups of the inner surface. The disappearance of the band at 3703 cm^{-1} proves that $(\text{CH}_3)_{\text{SO}}$ interacts with the hydroxyls of the inner surface of the clay, through new hydrogen bonds with the S = O groups.

The presence of intermediate DMSO is also evidenced by the asymmetric stretching ($\nu_{\text{as}} \text{CH}_3$) and symmetric stretching ($\nu_{\text{s}} \text{CH}_3$) of the methyl C-H at 3023 and 2929 cm^{-1} , respectively. The 1405 and 1427 cm^{-1} bands are assigned to $\delta_{\text{as}} \text{CH}_3$ and $\delta_{\text{s}} \text{CH}_3$.

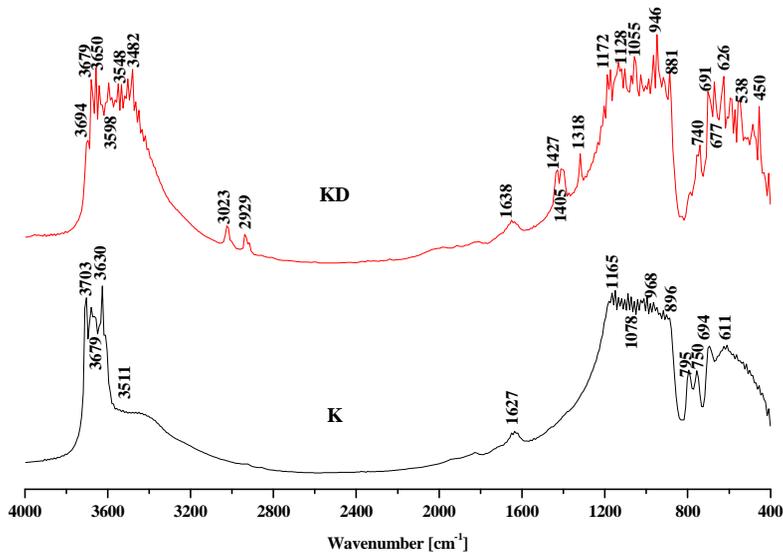


Fig. 2. FTIR spectra of the unmodified kaolin (K) and DMSO-intercalated kaolin (KD)

Scanning electron microscopy

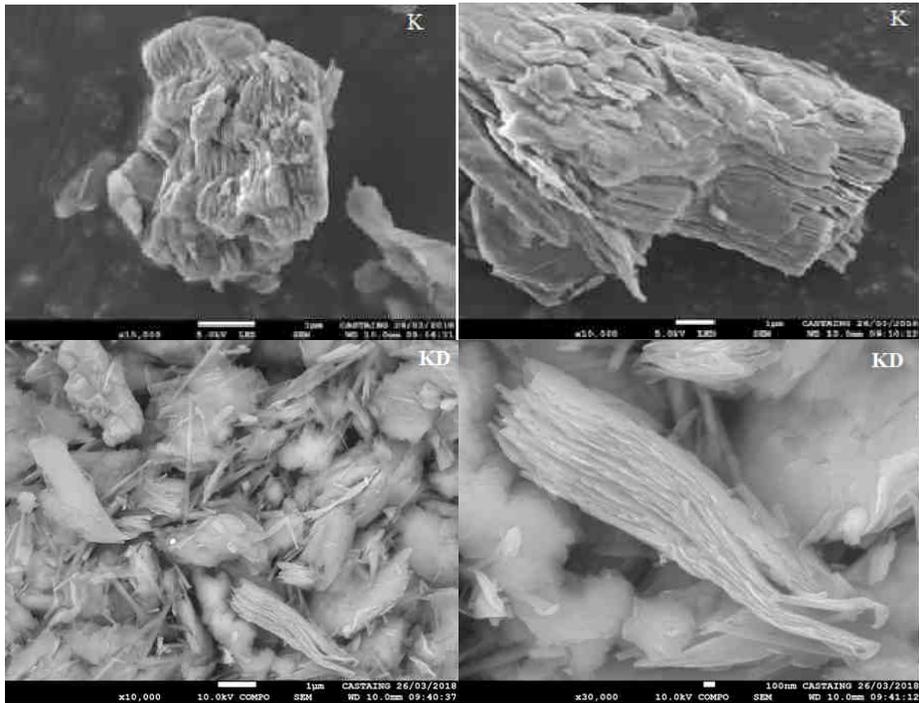


Fig. 3. Scanning electron microscopy images of unmodified kaolin (K) and DMSO-intercalated kaolin (KD)

The surface morphology of Tamazert kaolin, respected by SEM (Fig. 3), indicates the presence of well crystallized kaolinite and hexagonal particles of different sizes.

The intercalation of the clay by DMSO (KD) caused a great textural modification of our clay. Indeed, the kaolinite plates show a partial separation and disintegration of the particles, corresponding to their interaction with the organic molecules

Adsorption of BM

Effect of adsorbent concentration

The amount of adsorbed dye per unit mass of clay decreased as the solid/liquid ratio increased (Fig. 4). This decrease can be explained by the fact that the presence of a large amount of adsorbent reduces the number of adsorption sites per unit mass, which causes a decrease in adsorption. On the other hand, increasing the amount of adsorbent will scream an aggregation of the particles which results in the decrease of the total area and an increase in the length of the diffusion path. These two phenomena contribute to the decrease of the adsorbed quantity per unit mass [33, 34]. The largest amount adsorbed at equilibrium was observed at a ratio of 1 g/dm^3 , with a methylene blue removal rate greater than 97 % for both materials. Thus, 1 g/dm^3 was considered in all subsequent experiments.

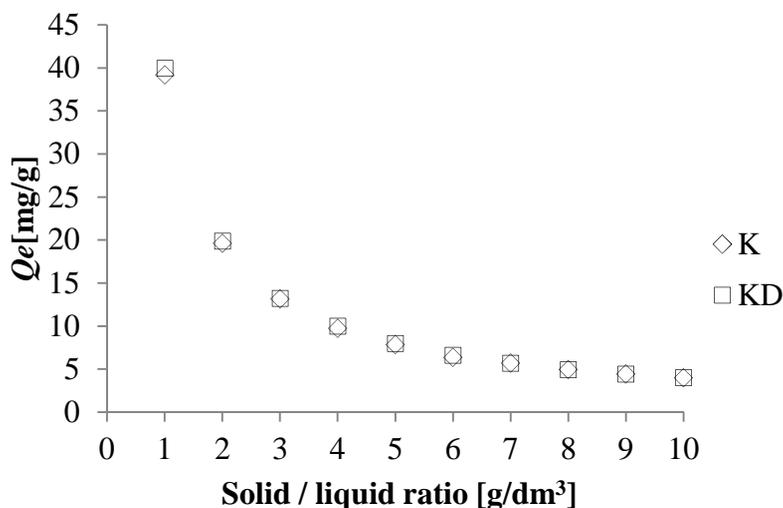


Fig. 4. Effect of solid/solution concentration on the amount adsorbed by the kaolin solids

Effects of pH

pH is one of the factors influencing adsorption, by modifying the surface charge of the adsorption. In this study we followed the effect of pH on the elimination of methylene blue by different materials, for an initial concentration of 40 mg/dm^3 . Figure 5 shows the evolution of the quantity adsorbed at equilibrium by each material as a function of the pH of the solution. The retention capacity of methylene blue increases rapidly in the range of pH from 2 to 5 and then stabilizes for both materials. The strong adsorption in this pH

range can be explained by the competitive effect between the H^+ ions and the cationic dye. For the rest of the experiment, we adjusted the pH of the solutions to 5.

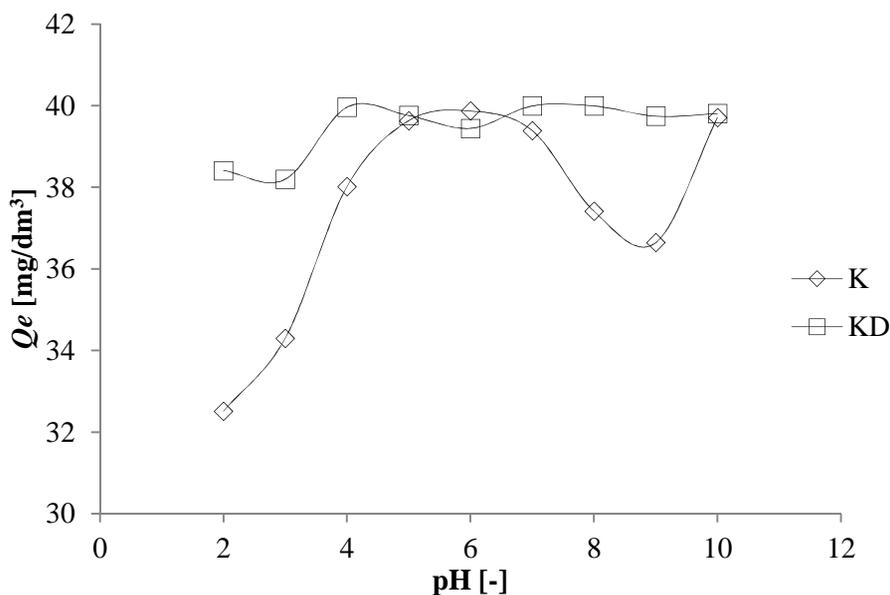


Fig. 5. Effect of pH on the adsorption of methylene blue onto the kaolin solids

Effect of contact time

In order to study the effect of time on the adsorption of methylene blue by the two materials, a series of experiments were carried out at $pH = 5$ and at time intervals ranging from 1 to 120 minutes (Fig. 6). The adsorption was quick in the first ten minutes, due to the availability of surface negatively charged sites. The curves then tend towards a landing. Equilibrium is reached after 30 minutes of contact for beyond the change was not significant.

The parameters corresponding to the kinetic models used are reported in Table 3. The values of the coefficients of determination are extremely low, < 0.47 , for the first model. The adsorption of BM by two materials does not follow Lagergren's equation of the first order (figure not shown). The results show that the adsorption of methylene blue follows perfectly the pseudo-second-order model and that of all the materials (Fig. 7). The coefficients of determination, R^2 , tend towards 1. The calculated values, $Q_e(cal)$, also agree very well with the experimental data (Table 2). Considering the initial adsorption rate, h , DMSO-modified kaolinite adsorbs methylene blue very quickly compared to the starting material.

In adsorption from solution, diffusion from the solid-liquid interface to the interior of the solid particles plays a very important role. Whether the process of adsorption is controlled by this type of intra-particle diffusion, is tested by plotting Qt vs. $t^{0.5}$ (figure not shown). The curves were linear with regression coefficients equal to 1 (Table 3). The DMSO-modified sample promotes intraparticle diffusion of methylene blue

($K_{id} = 3.09$) compared with purified kaolinite ($K_{id} = 2.22$). The thickness of the boundary layer, C , remains constant.

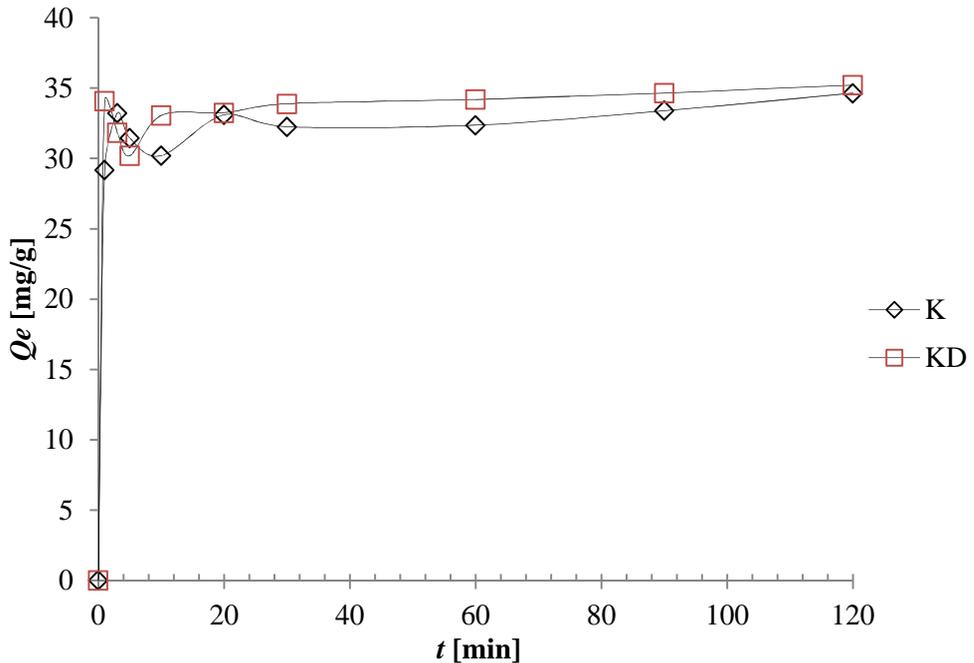


Fig. 6. Effect of contact time on the adsorption of methylene blue onto the kaolin solids

Table 3

Kinetic parameters methylene blue adsorption onto the kaolin solids

Kinetic models	Parameters	Adsorbents	
		K	KD
Pseudo-first order	$Qe(exp)$ [mg/g]	34.64	35.22
	K_1 [min^{-1}]	0.009	0.010
	$Qe(cal)$ [mg/g]	3.10	2.25
	R^2	0.47	0.42
Pseudo-second order	$Qe(exp)$ [mg/g]	34.64	35.22
	$Qe(cal)$ [mg/g]	34.25	35.09
	K_2 [$g \cdot (mg \cdot min)^{-1}$]	0.03	0.04
	h [$mg \cdot (g \cdot min)^{-1}$]	34.01	51.02
	R^2	0.99	0.99
Intraparticle diffusion model	K_{id} [$mg/g \cdot min^{-1/2}$]	2.22	3.09
	C [mg/g]	23.17	23.28
	R^2	1	1

The stagnation of C reveals that the boundary layer has no effect on the limitation of the adsorption kinetics. This implies that intraparticle diffusion is the only factor responsible for adsorption rate.

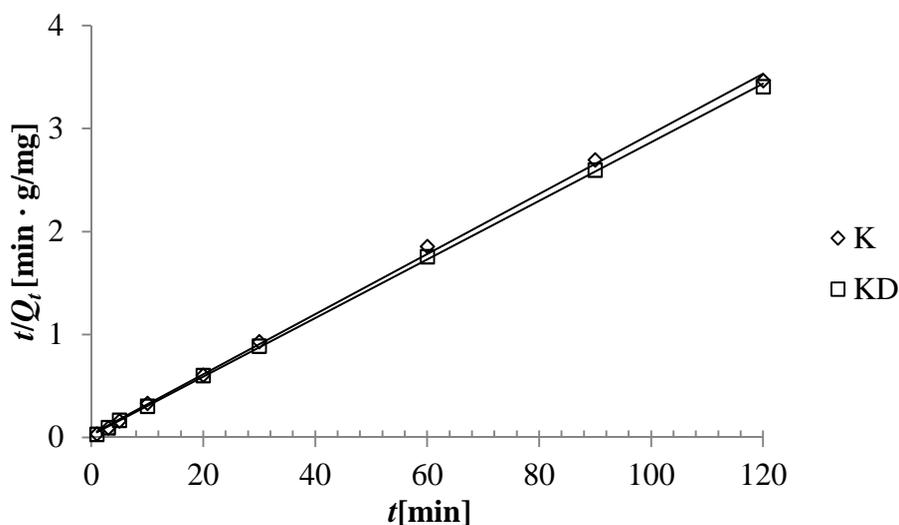


Fig. 7. Application of the pseudo-second model

Adsorption equilibrium

Isotherms

Using the classification of Giles et al. [35], the adsorption isotherms of methylene blue are of L type (figure not shown). The L shape means that there is no strong competition between the solvent and the sorbate to occupy the sorbent surface sites. The initial curvature of the L curve shows that the contaminant has a high affinity for the surface. The adsorption isotherms of BM by kaolinite indicate that the adsorbed quantity increases with increasing temperature. This suggests an endothermic effect. This increase can be attributed to an increase in the number of available active surface sites or to an increase in the mobility of methylene blue cations [33].

On the other hand, for the adsorption isotherms of methylene blue by DMSO-modified kaolinite, the opposite effect is observed. Indeed, the rise in temperature causes a decrease in the amount adsorbed at equilibrium. This shows that the adsorption of this dye is favoured at low temperature during the adsorption of the cationic dye (methylene blue) by the kaolinite intercalated by DMSO [36]. The adsorption process was exothermic. Whatever the initial concentration and whatever the temperature, the adsorbed quantities at equilibrium of the BM by the modified kaolinite (KD) are greater than those of the starting material (K).

Fitting the models to the experimental data

The parameters of the models used to describe the equilibrium between BM and kaolinitic solids are listed in Table 4.

The Langmuir model does not describe all the experimental isotherms because the R^2 values are relatively low. According to Table 4, the fit of the experimental data according to the Freundlich model appears better compared to that of Langmuir. The coefficient of determination is ≥ 0.87 . This suggests that there are different types of adsorption sites of

different energy, distributed according to an exponential law depending on the heat of adsorption. This distribution of interaction energies is explained by the heterogeneity of the sites. The adsorption capacity K_F increases with the temperature for both materials. The coefficient n varies with the temperature; it characterizes the intensity of the adsorption. Whatever the sample, $n > 1$ indicates a favourable adsorption process. Adsorption is not always a simple process, because different interactions can be at the origin of the association of a chemical (adsorbate) with a solid (adsorbent). These interactions can be electrostatic, Van der Waals type, hydrogen bond, polar, ion exchange.

Table 4

Isotherm parameters for the BM adsorption at different temperatures

Isotherms models	Parameters	Adsorbents					
		K			KD		
		298 K	313 K	323 K	298 K	313 K	323 K
Langmuir	Q_e [mg/g]	147.43	179.35	194.88	209.43	187.61	143.06
	Q_m [mg/g]	212.77	178.35	204.08	243.90	212.77	147.06
	K_L [dm ³ /mg]	0.013	0.035	0.054	0.016	0.021	0.038
	R^2	0.309	0.949	0.973	0.668	0.815	0.963
	E [%]	34.57	25.92	33.34	44.64	39.65	40.63
Freundlich	K_F [dm ³ /g]	12.258	23.512	23.122	22.087	24.829	23.310
	n	2.156	3.225	2.463	2.840	3.104	3.209
	R^2	0.894	0.869	0.915	0.873	0.873	0.961
	E [%]	21.35	19.29	18.92	29.48	25.73	14.21
Redlich-Peterson	M [mg/g]	0.006	0.306	0.763	733.809	0.047	0.322
	β	0.301	0.577	0.632	0.313	0.438	0.635
	K_{RP} [dm ³ /mg]	12845	14355	18528	135539	12459	68946
	R^2	0.988	0.994	0.976	0.980	0.975	0.972
	E [%]	13.53	6.85	20.21	29.01	26.44	13.19

The adsorption phenomenon for this type of system is therefore very complex. Models with two parameters to adjust, such as those of Langmuir and Freundlich, would not be able to explain the equilibrium relationships. For this reason, we used the Redlich-Peterson model to describe experimental isotherms. From the values of the coefficient of determination, R^2 , we can affirm that the Redlich-Peterson equation very suitably describes the BM adsorption isotherms by the two materials (Fig. 8). Whatever the temperature $R^2 \geq 0.970$ (Table 4).

The K_{RP} values showed that the adsorption capacity increased with increasing temperature for the purified kaolinite and decreased for the intercalated kaolinite. Similar behaviour has also been observed with experimental isotherms. The maximum amount absorbed, M , evolves in the same direction as K_{RP} . The surface heterogeneity factor, β , depends on the surface properties, the degree of crystallinity and the distribution of the active sites. The value of this parameter is < 1 for all solids. This result is a sign of favourable adsorption.

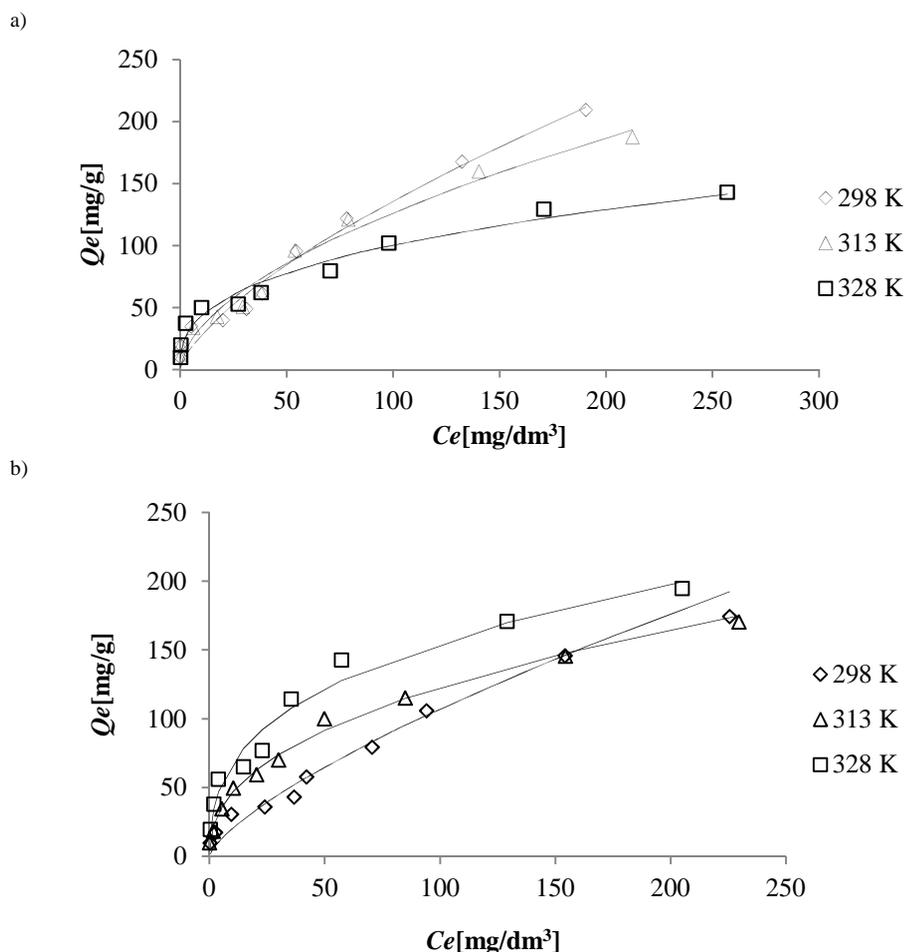


Fig. 8. Adsorption isotherms of BM, according to the experimental data and RP model: a) DMSO-intercalated kaolin, b) unmodified kaolin

Thermodynamic parameters

The thermodynamic quantities ΔH° , ΔS° and ΔG° are given in Table 5. In the case of a physisorption, the variation of the free energy is between 0 and 20 kJ/mol [37], as for the chemisorption it is in the range 80-400 kJ/mol [38]. From these thermodynamic values, it can be said that Tamazert kaolin has changed its behaviour with respect to the elimination of methylene blue after intercalation with DMSO. Indeed, before intercalation the physisorption was endothermic ($\Delta H^\circ > 0$) disordered ($\Delta S^\circ > 0$) and spontaneous ($\Delta G^\circ < 0$). The Gibbs energy increases with temperature, which has the effect of accentuating this spontaneous character. After the modification, the physisorption became exothermic ($\Delta H^\circ < 0$) ordered ($\Delta S^\circ < 0$) and not spontaneous ($\Delta G^\circ > 0$). This non-spontaneity increases with the rise in temperature.

Table 5

Thermodynamic parameters for adsorption of methylene blue by different materials

Samples	BM					R^2
	ΔH°	ΔS°	ΔG° [kJ/mol]			
	[kJ/mol]	[kJ/(mol · K)]	298 K	313 K	328 K	
K	10,445	0,036	-0.205	-0.741	-1.277	0.990
KD	-2.597	-0.056	14.114	1.955	15.797	0.999

Conclusion

The chemical treatment with DMSO caused a considerable modification of our clay. Indeed, X-ray diffraction and Fourier transform infrared confirmed the insertion of DMSO into the interfoliar space. XRD showed an increase in the basal spacing of the 001 planar plane reflection, from 7.16 to 11.22 Å, which is an intercalation rate of 98 %.

Scanning electron micrographs showed partial separation and disintegration of kaolinite particles after intercalation of Tamazert kaolin with DMSO. It has been found that the adsorption process mainly follows pseudo-second-order kinetics and intraparticle diffusion. The isotherms were better adjusted by the Redlich-Peterson model ($R^2 > 0.972$). Isotherms and thermodynamic data show a change in the behaviour of kaolin via elimination of methylene blue. The adsorption was initially ordered spontaneous endothermic disordered and after intercalation it became non spontaneous exothermic ordered.

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