



Equilibrium, Isotherm, Kinetic and Thermodynamic Studies of Removal of Crystal Violet by Adsorption onto a Natural Clay

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ABSTRACT

This study reports the adsorption of crystal violet (CV) cationic dye on natural clay originated from Agadir region (south Morocco) through batch adsorption experiment, in order to develop a low-cost, natural, eco-friendly and alternative adsorbent for the removal of organic pollutants. Several analytical techniques (XRD, BET, TGA, TDA, TGA and FTIR) were used to characterize the studied material. The effect of different parameters were studied such as pH (3–10), adsorbent mass (0.02–0.3 g), contact time (20–120 min), initial dye concentration (100–900 mg/L), and temperature (25–65 °C) on the adsorption of CV dye. The results showed that CV adsorption on the natural clay depends on pH, initial dye concentration and temperature. The adsorption equilibrium data were fitted in Langmuir, Freundlich and Temkin adsorption isotherm models. The adsorption data obtained were well described by Langmuir isotherm model with correlation coefficients ($R^2 = 0.99$). Maximum adsorption capacity of clay was found to be 250 mg/g. Adsorption kinetics were well fitted by Pseudo-second order kinetic model ($R^2 = 0.999$). Thermodynamic study revealed that the adsorption of CV on clay is spontaneous physical sorption process, endothermic and favorable. Experimental results indicate that the clay studied is a promising adsorbent for the removal of cationic dye molecules from aqueous solutions.

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INTRODUCTION

Industrial activities are an important source of pollution causing deterioration of the environment and health. The treatment becomes an important environmental issue to avoid environmental pollution and water contamination [1]. Indeed, currently, a great number of treatment technique of domestic or industrial wastewater, are used. They differ from each other and include, for example, adsorption, electrolysis, dissolution, flotation, precipitation, ion exchanges and the liquid-liquid extraction. Among these techniques, adsorption, on which rests this study, has shown great depollution capacities of wastewater. It is also very simple and effective for the removal of certain

pollutants, particularly dyes. But its effectiveness depends greatly on the type of substrate used as adsorbent, particularly, its cost, availability and regeneration. Therefore, all these factors have stimulated a lot of research where the aim is the development or improvement of adsorption capacities of solid supports. This passes inevitably by understanding of the pollutant retention mechanism by the solid support.

This study is within this perspective, using local clay as an adsorbent for the retention of some dyes such as crystal violet (CV). In deed recent years, clays have attracted the attention of researchers because they are cheaper than activated carbon and their sheet structure gives it a very high specific surface [2-4]. CV, cationic dye, is used as a model of pollutant for adsorption studies to measure adsorption capacity of clay material.

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It causes skin burns and severe eye damage. It is therefore essential to remove this dye from water.

In this work, chemical and physical characterization of material used in this study was performed. The parameters that influence adsorption such as pollutant initial concentration, contact time, adsorbent mass, solution pH and temperature were investigated. The adsorption kinetic models, equilibrium isotherm models (Langmuir, Freundlich and Temkin) and thermodynamic parameters were also evaluated.

MATERIALS AND METHODS

Preparation of polluting solution

Crystal Violet (CV) [Cationic form, Chemical formula: $C_{25}H_{30}ClN_3$, Molar mass 407.979 g/mol) used in this work was purchased from Sigma-Aldrich and used without further purification. The molecular structure of the dye is illustrated in Figure 1. This dye is widely used in microbiology for gram stain, color indicator in assays reactions and fingerprint revelation. Stock solution of dye was prepared by dissolving accurately weighed dye in distilled water to a concentration of 1g/L. The experimental solution of the desired concentrations was obtained by successive dilutions. The concentration of CV dye was measured at $\lambda_{max} = 589.5$ nm, using UV-Visible spectrophotometer (UV 2300).

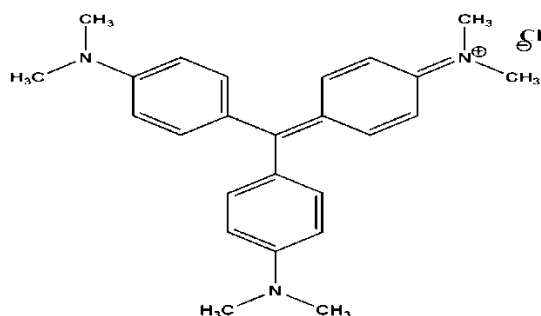


Figure 1. The structure of crystal violet (CV)

Preparation of adsorbent

The natural clay used in this study was collected from Agadir region and was crushed utilising the jaw crusher and tungsten mill, then it was sieved to obtain fragments <50 μ m.

Adsorption studies

The adsorption experiments were carried out by batch mode and the effect of various parameters (pH, mass of adsorbent, initial concentration, contact time and temperature) on the adsorption of CV on natural clay were studied. Adsorption studies were carried out using natural clay (0.06 g), added to 50 mL CV solution at

initial concentrations (100-900 mg/L) stirred to the desired time intervals (20 -120 min), in a bath at different temperatures (22-60 °C) using a thermostat. The adsorbent was removed by filtration. The absorbance of the supernatant solution was measured using a UV-Spectrophotometer (UV-visible 2300-TECHCOMP) at $\lambda_{max} = 589.5$ nm. The residual concentration was calculated using equation (1) as calibration curve:

$$C_{eq} = [(A+0.016)/39061] 408000 \text{ mg/L} \quad (1)$$

The percentage removal of dye (R %), and amount of pollutant adsorbed (q_e) were respectively calculated using following equations (1) and (2):

$$q_e = [(C_0 - C_{eq})/m] V \quad (2)$$

$$R\% = [(C_0 - C_{eq})/ C_0] 100 \quad (3)$$

Where C_0 (mg/L) is the initial concentration of dye, C_e (mg/L) is the concentration of dye at equilibrium, $V(L)$ is the volume of dye solution and m is the mass of adsorbent used (g).

RESULT AND DISCUSSION

Characterization of natural clay

In order to identify the major constituent phases of the mineral fraction of the natural clay an XRD was performed. Thereby The sample of the natural clay was analyzed by X-ray diffraction (XRD) using an Bruker Phaser diffractometer applying copper anticathode bombarded by electrons accelerated (voltage = 30 Kv, intensity $I=10$ mA) and generating wavelength radiation $\lambda_{\alpha 1} = 1.54060$ Å and $\lambda_{\alpha 2} = 1.54439$ Å with a step size of 0.0405. Data were collected over a range 10°-60°. The characteristic graph of natural clay, studied was illustrated in Figure 2. The analysis of the diffraction pater shows that the dominant peaks correspond to dolomite ($2\theta = 21.6^\circ, 24.01^\circ, 30.89^\circ, 33.46^\circ, 37.3^\circ, 41.11^\circ, 43.77^\circ, 44.85^\circ, 49.21^\circ, 50.5^\circ, 51.06^\circ, 58.92^\circ$), in compare to standards JCPDS data (36-0426) attributed to the Miller levels following: (101) (012) (104) (006) (110) (113) (021) (202) (024) (018) (116) (211). In addition, the silica was also observed with less intense peaks ($2\theta = 26.64^\circ, 35.98^\circ, 50.13^\circ, 56.80^\circ$) in compare to standards JCPDS data (33-1161) attributed to the Miller levels following (101) (110) (112) (103). Fourier transform infrared spectroscopy (FTIR) spectrum of the natural clay was acquired with a spectrometer Vertex 70 Burker. The FTIR spectrum performed (Figure 3), showed a band at 3423 cm^{-1} , medium intense, of hydroxyl group OH. The presence of a peak at 1638 cm^{-1} corresponds to the deformation of H₂O molecules adsorbed between the layers. The

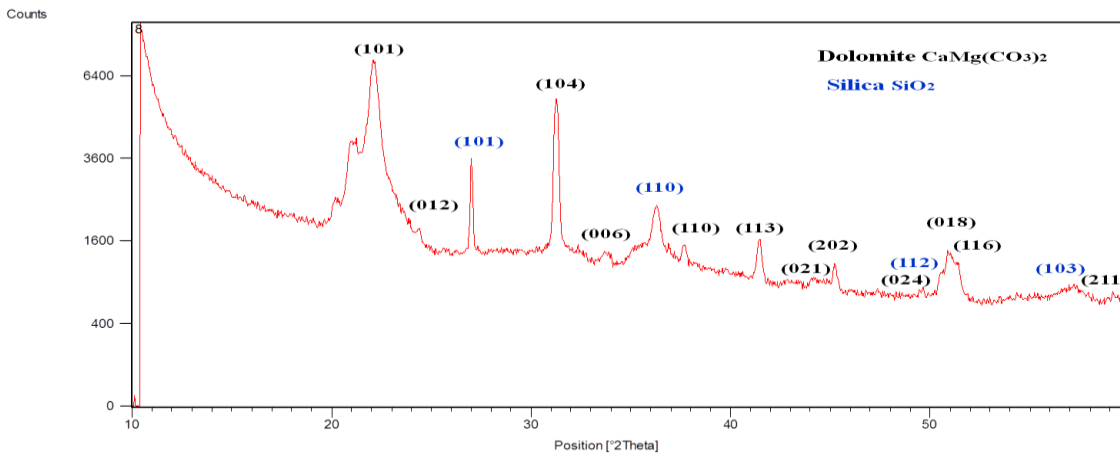


Figure 2. The XRD patterns of the natural clay

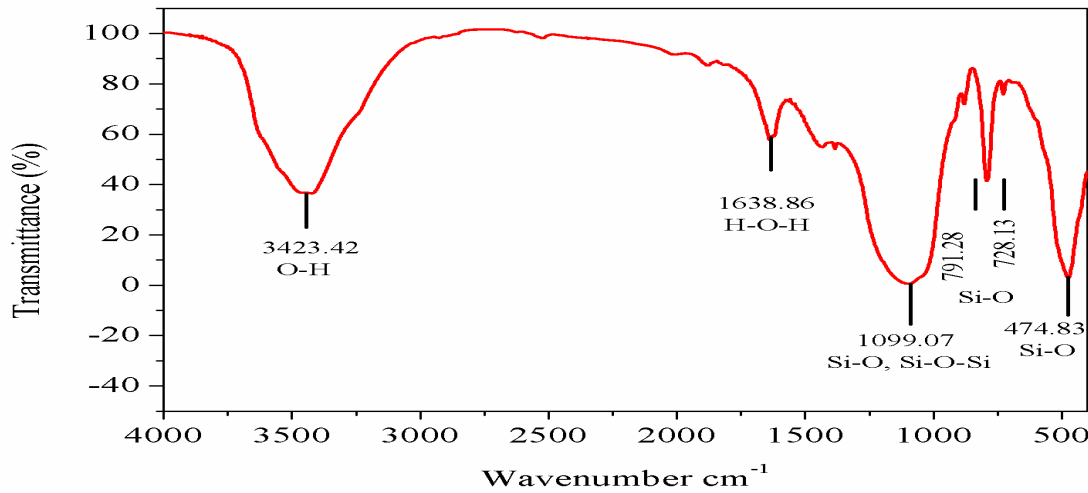


Figure 3. FTIR of natural clay

bands characteristics of the silica located in the region between 1250-700 cm⁻¹ [5]. Thus the band at 1099 cm⁻¹ is attributed to Si-O-Si stretching vibration, whereas the bands between 791-728 cm⁻¹ and at 474 cm⁻¹ are attributed to the Si-O stretching vibration [6].

The surface area of sample clay was determined by the Brunauer–Emmet–Teller (BET) method and using Quantachrome AsiQuin, Automated Gas Sorption Analyser Quantachrome Instrument Version 2.02. The specific surface area was measured, it is equal to 76.971 m²/g. The nitrogen adsorption-desorption isotherm of natural clay at 77 K are shown in Figure 4. It indicates that isotherm of type IV according to IUPAC. This isotherm is identical to that type II at low pressures. It corresponds to a medium in which mesoporous occurs capillary condensation of the adsorbate in the mesopores. The phenomenon is not reversible, generally there is a hysteresis between the adsorption and desorption curves. Thermal analysis of natural clay was carried using a SHIMADZU D 60 instrument. 9.527 mg

of dry sample was heated from room temperature (15.58 °C) to 1100 °C in dry air and at a heating rate of 10 mL/min. The results of this study are shown in Figure 5. Analysis of the TGA and TDA curves show that the loss of weight

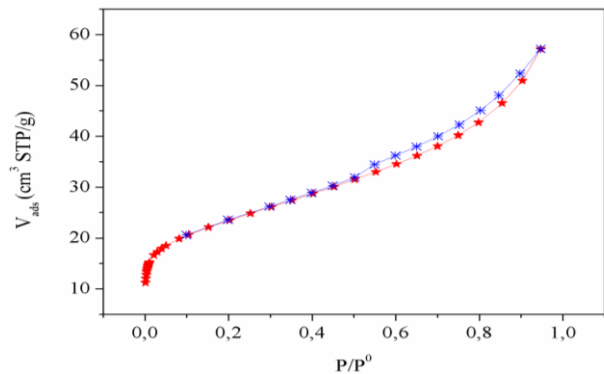


Figure 4. N₂ adsorption-desorption isotherms at 77 K for natural clay

in the natural clay occurs in three steps. The first loss between 15.58 and 100 °C corresponding to endothermic dehydration of natural clay, which is equal to 5.8 % (0.552 mg). The second between 100 and 390 °C which is equal to 2.7 % (0.257 mg), the mass loss could be associated to the elimination of adsorbed water. The third about 740 °C is an endothermic mild peak which is equal to 7.7 % (0.733 mg). The mass loss is ascribed to the two decomposition of dolomite or calcite [7, 8].

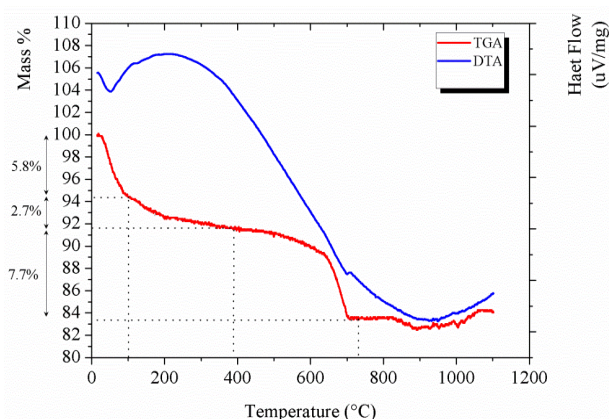


Figure 5. Thermal analysis of natural clay

Mass effect

This study is carried out by varying the mass of the adsorbent from 0.02 to 0.3 g. The concentration and temperature are maintained at 100 mg / L and 22 ± 1 °C. The effect of the mass of adsorbent on the natural clay sorption performance is given in Figure 6a. The result indicates that an increase of the mass of adsorbent leads to an increase of CV adsorption performance.

It is clear that equilibrium is reached after 0.06 g. Beyond 0.1g a slight decrease de performance is observed, which can be explained by desorption phenomenon or by agglomeration of the adsorbent particles leading a decrease in the specific surface of the clay.

Contact time effect

This study allowed determining the optimal time to reach equilibrium and kinetic model describing CV adsorption on the clay surface. It is carried out by introducing 0.06 g of adsorbent in 50 ml dye solution with concentration 100 mg/L at 22 °C and for a specified period. The obtained curve show that the adsorption capacity increases with contact time between adsorbate and adsorbent. The equilibrium was reached in about 60 min. The result is shown in Figure. 6b. We can note that the adsorption kinetic of CV on clay involves two distinct steps:

-The first step is rapid where CV dye was adsorbed by

the exterior surface of clay [8].

-The second is slow, due to the diffusion of CV molecules into the adsorbent pores, with a higher resistance which makes slower process [11].

Concentration effect

The effect of initial CV concentration under equilibrium conditions was investigated. The experiments were carried out at a fixed adsorbent dose (0.06 g in 50 mL of crystal violet solution) and at different initial CV concentrations (100 to 900 mg/L) and initial pH at 30 °C as shown in Fig.6c.

Results indicated that adsorption capacity of natural clay increased (from 78.34 to 119.5 mg/g) as the initial dye concentration increased (from 100 to 900 mg/L). The equilibrium was attained in about 700 mg/L. Beyond, the saturation is reached following the reduction of the active sites available for adsorption.

Temperature effect

The effect of temperature on the CV adsorption experiment has been investigated at different temperatures (22, 30, 40, 50 and 60 °C), by introducing 0.06 g of the clay in 50 mL of the CV solution in a thermostatic bath. Results are shown in Figure 6d. One notes that for an increase in temperature, an increase in the adsorption of CV was observed. Therefore the temperature has an effect on the solubility of the dye and the mobility to penetrate inside the sample pores at high temperature.

pH effect

The pH is a paramount factor affecting adsorption of pollutant. The effect of pH on adsorption, was carried out by adding 0.06 g of clay to 50 mL of a series of dye solutions was prepared by adjusting the pH over a range of 3–10 (0.1 M) using HCl or NaOH solutions. The pH was measured using a multi-parameter device "HANNA HI 255" with a combined pH electrode "HI 1332". Results of this study are presented in Figure. 6e. The pH of the solution changes the intensity and mode of fixing the color to the clay surface, therefore the pH influences not only the adsorbent properties, but also dye chemistry [9, 10]. Results show an increase in the adsorbed amount which increased from 77.31 mg/g (at pH 3) to 80.33 mg/g (at pH 10). This is explained by the fact that the addition of cations H^+ neutralizes the negative charges occurs in the clay surface. Thereby the adsorption of the cationic colorant on the clay is reduced due to the presence of an excess of H^+ ions in competition with dye cations for adsorption sites[11, 12].

The point of zero charge of natural clay (pH ZPC) was determined as described by Al-Harashseh et al [15]. The result was depicted in Figure. 6f. The pH_{ZPC} of

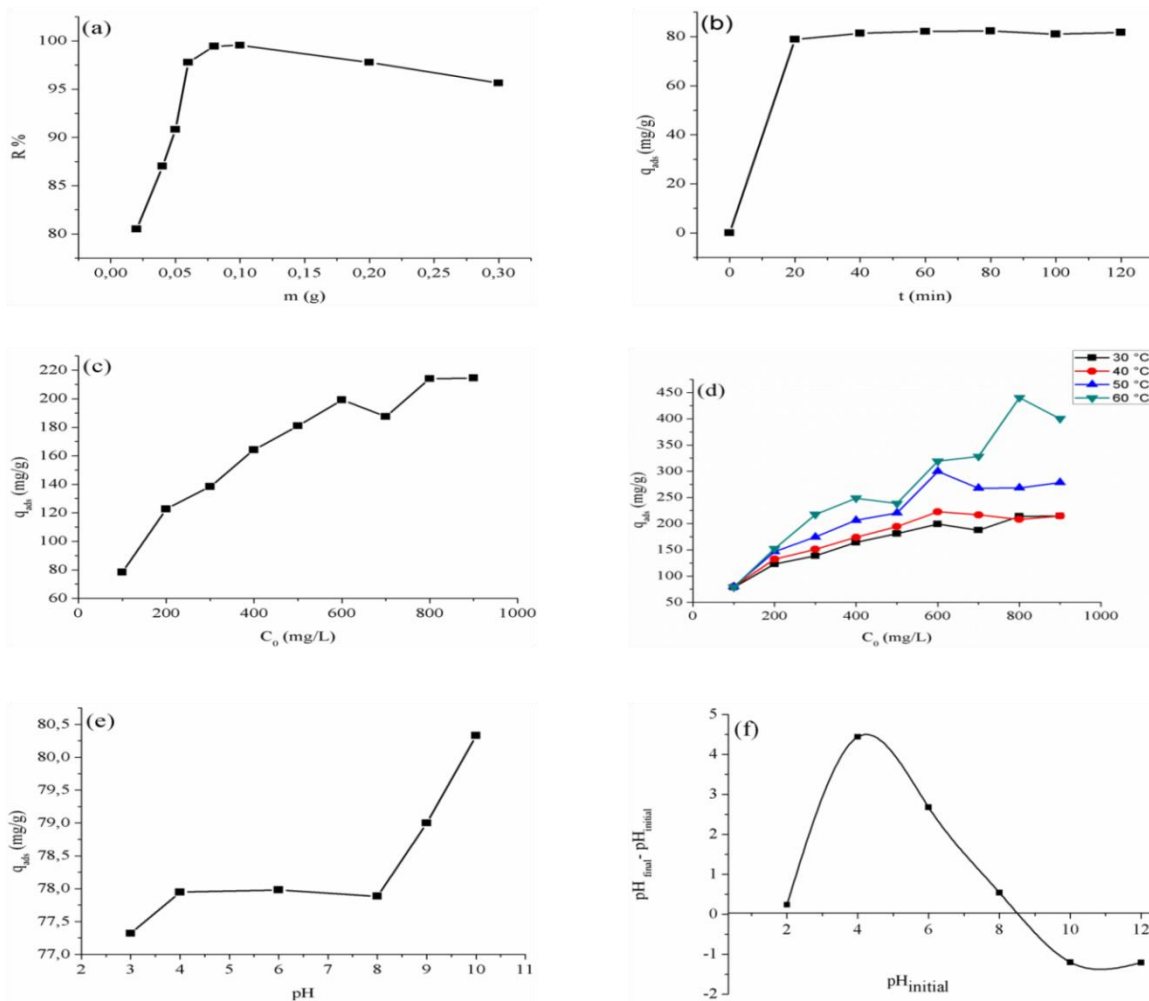


Figure 6. Influencing parameter on the adsorption of CV on clay: (a) effect of adsorbent mass, (b) effect of contact time, (c) effect of the concentration of adsorbate, (d) effect of the temperature, (e) effect of pH and (f) the zero of point charge of natural clay.

natural clay is 8.49, which means that the surface of the adsorbent will have a positive charge below 8.6, resulting in better adsorption of the anionic dye by the phenomenon of electrostatic attraction. Whereas above the pH ZPC the adsorbent surface becomes negatively charged, resulting in an increase of the adsorption of the cationic dye, this explains the increase in the adsorption of crystal violet in basic medium.

Adsorption kinetics

The study of adsorption kinetics we can understand the mechanism of adsorption process, migration mode the solute from the liquid phase to the solid phase, molecular and pore diffusion [13].

Pseudo first-order and pseudo second-order kinetic models were applied. The pseudo first order was developed by Lagergren [14], is defined by the following equation

The pseudo second order was developed by Ho H

[15], is expressed by the following equation:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2} \cdot 303 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg/g), k_1 and k_2 are the rate constant of the pseudo-first-order adsorption (min^{-1}) and the pseudo-second-order ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) respectively.

The results obtained are shown in Figures 7a and 7b. The kinetic parameters are summarized in Table 1. From the results shown in the table, the adsorption of CV could be best described by the pseudo second order model, with the correlation coefficient ($R^2 = 0.999$) higher [10, 16, 17], thereby the calculated q_e values also agree very well with the experimental data ($q_e = 82.132$).

Table 1. Kinetic model parameters for CV adsorption to natural clay

Pseudo premier ordre			pseudo second ordre		
q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$)	R^2
0.00127057	0.073696	0.409	83.3333	0.072	0.999

Adsorption isotherms

Equilibrium isotherms and adsorption properties describe the interaction between adsorbate and adsorbent. Langmuir [18], Freundlich [19] and Timken models were applied to describe the adsorption of CV on natural clay. The adsorption isotherm was carried for different concentrations and different temperatures ranging from 100 to 900 mg/L and from 30 to 60 °C respectively. The mass of adsorbent is maintained in 0.06 g, for 60 minutes and initial pH of the dye.

Langmuir model (Figure. 8a) assumes monolayer adsorption onto adsorbent surface containing a finite number of identical adsorption sites [20]. It can be expressed by the following equation :

$$C_e/q_e = C_e/q_m + 1/K_L q_m \quad (6)$$

Where Q_m and K_L are the maximum adsorption capacity (mg/g) and the Langmuir constant (L/mg) respectively. Dimensionless equilibrium parameter separation factor R_L [21] that characterizes adsorption is defined by the following equation:

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

Adsorption is favorable if R_L values follows $0 < R_L < 1$, where as $R_L > 1$ (unfavorable), $R_L = 1$ (linear), $R_L = 0$ (irreversible).

In the Freundlich isotherm (Figure. 8b) assumes heterogeneous surface energies and nonuniform distribution of the heat of adsorption over the adsorbent surface [20]. It is defined by (Eq.8):

$$\ln q_e = \ln K_F + \ln C_e/n \quad (9)$$

Where K_F ($(\text{mg} / \text{g}) (\text{L} / \text{mg})^{1/n}$) is the Freundlich isotherm constant and $1/n$ is the intensity of adsorption.

The model of Timken (Figure. 8c) can be expressed by the following equation:

$$q_e = B \ln K_T + B \ln C_e \quad (9)$$

Where B is a constant related to the heat of adsorption (J/mol) and K_T is the Temkin constant (L/mg). The resulting parameters for three isotherms are tabulated in Table 2. The data obtained for the Langmuir, Freundlich and Temkin isotherms indicates that the Langmuir model best describes the adsorption of CV on natural clay, consequently dye molecules can be adsorbed in monolayer coverage, without any dye-dye interactions. The equilibrium experimental adsorption capacities of CV is in excellent agreement with adsorption capacities generated Langmuir isotherm, and confirming the best fit of Langmuir model with practical data. In contrast, Freundlich and Temkin models do not describe the adsorption data. The values of the separation factor (R_L) for all temperature ranges (from 295.15 K to 333.15 K) were $0 < R_L < 1$ indicating the favorable adsorption isotherm.

Thermodynamic study

Thermodynamic studies were carried out to determine the nature of adsorption process. Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) can be determined by tracing $\ln K_d = f(1/T)$ or were calculated using the following equation (10-11-12) [22, 23]:

$$K_d = C_{\text{ads}}/C_e \quad (10)$$

$$\Delta G^\circ = -RT \ln K_d \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

Where, K_d is the equilibrium constant. C_{ads} and C_e are the equilibrium concentrations (mg/L) of the dye on the adsorbent and in the solution respectively. T is the temperature in Kelvin and R is gas constant (8.314 J/mol K).

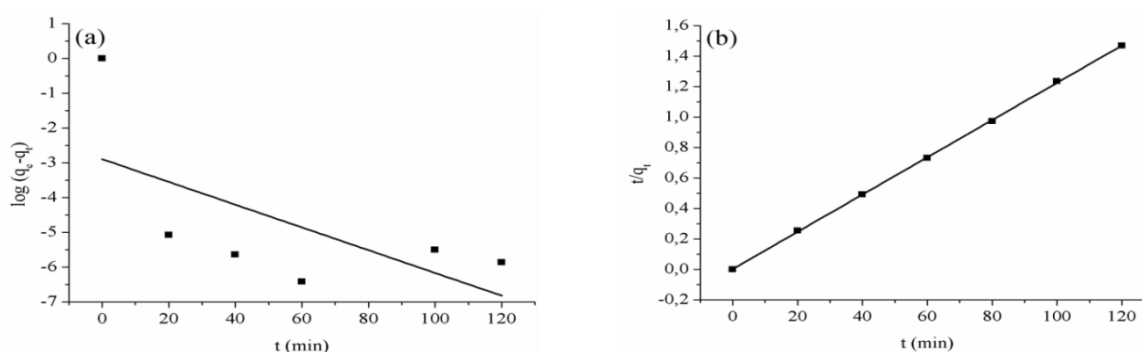


Figure 7. Kinetic of CV adsorption on natural clay at 22 °C: (a) the Pseudo-First-Order, (b) the Pseudo-Second-Order

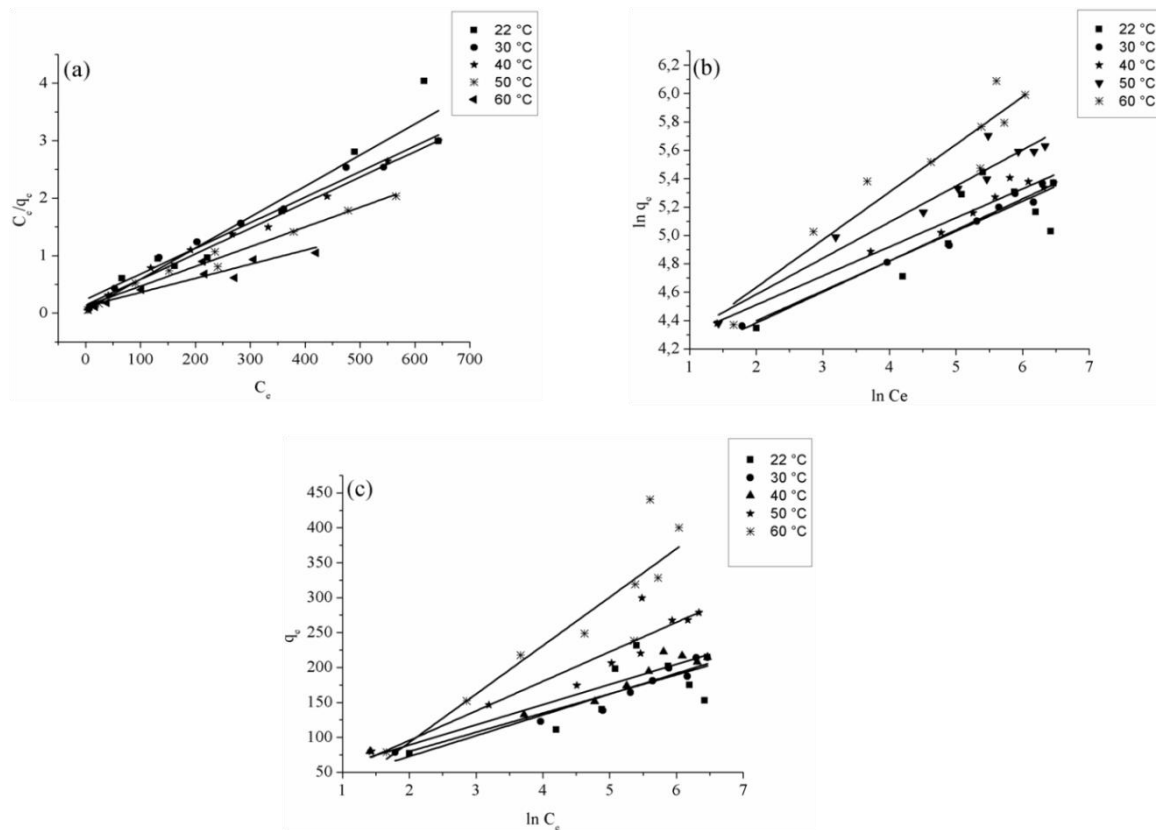


Figure 8. Adsorption isotherms of CV onto natural clay: (a) Langmuir isotherm, (b) Freundlich isotherm, (c) Temkin isotherm.

TABLE 2. Parameters characteristics of adsorption isotherms

Isotherms	Parameters	Temperature (k)				
		295.15	303.15	313.15	323.15	333.15
Langmuir	K_L (L/mg)	0.094	0.016	0.028	0.024	0.017
	Q_m (mg/g)	200	250	250	333.333	500
	R^2	0.934	0.984	0.992	0.982	0.895
	R_L	0.011	0.061	0.037	0.044	0.06
		-	-	-	-	-
Freundlich	K_F	0.095	0.372	0.26	0.294	0.367
	(mg/g). (L/mg) ^{1/n}	53.35	51.67	60.4	58.85	52.56
	n_F	4.761	4.587	4.901	3.937	2.985
	R^2	0.694	0.979	0.971	0.941	0.902
Timken	K_T (L/mg)	3.18E+36	0.153	5.051E-10	14650719	1.345E+54
	B (J/mol)	0.02	0.031	0.032	0.02	0.011
	R^2	0.572	0.931	0.934	0.883	0.817

The results obtained are tabulated in Table 3. The negative values of ΔG° (from -6,01 to -1,24 kJ/mol) corresponding to temperatures 22-60 °C indicated the adsorption of CV on natural clay is spontaneous [27] and physisorptive process because ΔG° values fall in the range of -20 to 0 kJ/mol [28]. The positive value of the enthalpy (ΔH°) showed endothermic nature of the adsorption and the positive value of ΔS° (127,04 J mol⁻¹ K⁻¹) confirmed the increase in randomness at the

TABLE 3. Thermodynamic parameters of the adsorption of CV on natural clay

ΔH°	ΔS°	ΔG°				
(KJ/mol)	(J/mol.K)	295.15K	303.15K	313.15K	323.15K	333.15K
36.40	127.04	-1.244	-2.122	-3.043	-4.823	-6.01

CONCLUSION

The present study investigated the adsorption of crystal violet dye onto natural clay from the region Agadir (Morocco). The obtained results show that

- the adsorption may reach 94.66% of the total adsorption capacity in 20 min,
- removal of CV onto the natural clay is best at basic pH and at high temperatures
- the adsorption capacity increased with increasing the mass of natural clay
- the adsorption Langmuir isotherm has been demonstrated to give the best correlation for the adsorption of crystal violet onto natural clay with a maximum removal capacity of 250 mg/g.
- the pseudo second-order kinetic model was more favourable for the present system.
- thermodynamic results indicated the adsorption process is spontaneous, physiosorption and endothermic.

The various results obtained from this study indicated that the adsorbent chosen for the study was efficient and could be used for the removal of CV from the aqueous solution in a batch system. In addition the studied clay is abundantly and locally available, it can be considered as an economical adsorbent for industrial dye effluents

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چکیده

در این مطالعه، به بررسی جذب سطحی رنگدانه کاتیونی کریستال ویوله (CV) روی خاک رس طبیعی نشات گرفته از منطقه آگادیر (جنوب مراکش)، پرداخته است که این امر از طریق آزمایش جذب ناپیوسته به منظور تهیه جاذبی ارزان قیمت، طبیعی و دوستدار محیط زیست برای حذف آلاینده های آلی صورت گرفت. چندین روش تحلیلی (FTIR، TGA، TDA، BET، XRD) برای تعیین خصوصیات مواد مورد مطالعه، استفاده شد و اثر پارامترهای مختلف در جذب رنگدانه CV مانند پی اچ ۳-۷، جرم جاذب (۰/۰۲-۰/۳ g)، زمان تماس (۲۰-۱۲۰ min)، غلظت رنگ اولیه (۹۰۰-۱۰۰ mg/L) و درجه حرارت (۲۵-۶۵°C) مورد بررسی قرار گرفت. نتایج نشان داد که جذب CV بر روی خاک رس طبیعی به pH، غلظت رنگدانه و درجه حرارت بستگی دارد. داده های تعادلی جذب سطحی، در مدل ایزوترم لانگمویر، فروندلیچ و تیمکن برازش شده و با توجه به مدل ایزوترم لانگمویر با ضرایب همبستگی ۰/۹۹ به خوبی تشریح شدند. حداکثر ظرفیت جذب از خاک رس، مقدار ۲۵۰ mg/g بدست آمد و سینتیک جذب به خوبی توسط مدل جنبشی شبه-درجه دوم برازش داده شد. مطالعه ترمودینامیکی نشان داد که جذب CV بر روی خاک رس یک فرآیند جذب فیزیکی خود بخودی، گرماگیر و مطلوب است. نتایج تجربی نشان می دهد که این خاک رس، جاذب امیدبخشی برای حذف مولکولهای رنگدانه کاتیونی از محلول های آبی است.