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Removal of cationic dye ''Crystal Violet'' in aqueous solution by the local clay

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Abstract

The work described herein was undertaken in order to respond to a major environmental challenge that is water pollution and its impacts on receiving media, especially those arising from industrial effluents. Our focus was particularly directed on the textile industry which releases sizeable amounts of wastewater loaded with toxic pollutants. In the course of this project we were able to develop a wastewater treatment method which turned out to be effective, affordable and easily implementable. Though various water treatments already exist, they each have their own set of disadvantages, for example adsorption over activated carbon which in spite of being effective, remains costly and generates a sludge posing by itself an environmental threat. In this perspective, the use of natural material such as clay (AT) from the Taounate area as an adsorbent is appealing since the efficient, inexpensive and readily available. Effect of the physicochemical conditions of the medium (stirring speed, temperature, pH, concentration and contact time) as well as properties of the adsorbent materials in terms of thermodynamics, kinetics and adsorption isotherms were all investigated. Once compared with adsorption models, our results enabled us to describe this adsorption as a process being spontaneous, endothermic and having pseudo-second ordre kinetics when tests were conducted with dies such as Crystal Violet (CV). The adsorption isotherm data were well described by the Langmuir models.

1. Introduction

The aquatic environment is the favorable site for receiving very complicated human and industrial wastes. This latter is causing increasing pollution, threatening the environment and human health [1]. The impurities of water are of various origins and can be classified into the following categories: suspended elements, mineral solutes, organic solutes, dissolved gases and microorganisms [2]. Although most of them can be eliminated by conventional methods, the concentration of toxic substances remaining in the water after treatment may in many cases exceed the permissible limit [3]. In this case, they are mainly organic substances such as organic dyes released in large quantities by the textile industry and are responsible for the toxicity, odor, unpleasant taste and color of the water; Causing degradation of water quality and subsequent disappearance of aquatic life. Hence, the need to treat colored effluents before being discharged into the environment [4].

Dyes are known for their stability, as well as their recalcitrant capacity, which makes them very dangerous to human health, because they have both a carcinogenic and toxic potential; this could have an effect on the direct destruction of living aquatic organisms [5-6]. Therefore, the development of a sustainable competitive process of effluent management for the dyeing industry has long been an important task for the protection of the environment. Conventional physicochemical processes for the removal of dyes from wastewater include chemical oxidation, reverse osmosis, membrane filtration, coagulation/flocculation and adsorption [7-9].

The latter is one of the most effective methods which have been successfully adopted for the elimination of the color of wastewater [10]. Among the processes for treating liquid discharges, adsorption remains a relatively used and easy to use technique. However, activated carbon is the most widely used adsorbent due to its high adsorption capacity of organic materials [11]. This adsorbent has a high cost and remains difficult to regenerate.

The search for another effective and less expensive adsorbent is therefore very advantageous for removing textile dyes such as: bituminous shales [12], zeolites [13], fly ash [14], clays [15] , Pyrophillite [16], animal bone meal [17], egg shells [18], hydroxyapatite [19], chitin-chitosan [20], corn support [21] Wood etc [22].

Concerning the problem of colored waters, we suggested contribution to the study of the Crystal Violet (CV) dye removal by the clay material (AT).

Our research team has therefore studied the subject in order to design a water treatment strategy that reconciles respect for environmental standards, technical and economic efficiency. The target of this study is hence to develop adsorbent systems which are effective in the treatment of water and particularly for the removal of textile dyes.

In this unpublished study, it was necessary to understand how the dye (CV) interacts with the adsorbent (AT) during discoloration and to describe the potential processes involved in these interactions. For this purpose, we carried out a parametric study of the adsorption, by studying the effect of several significant parameters on the decolorizing power of the material used particularly the contact time, the concentration of the adsorbent, the pH, the stirring speed and temperature. In this respect, experiments have highlighted the determining role of these parameters. For this reason, a kinetic study was accomplished and kinetic models were applied to the experimental results such as the pseudo-first order model and the pseudo-second order model. Furthermore, adsorption isotherms were carried out for the dye, their modeling was achieved by applying known models such as Langmuir and Freundlich.

2. Materials and methods

2.1. Material

The reactive dye used as an adsorbate was Crystal Violet (purity of 99%) which was supplied by Ciba Specialty Chemicals Inc. and was used without further purification. The molecular structure of the dye is shown in Figure 1 and its molar mass is 407.98 g/mol.

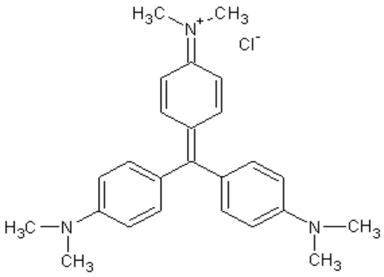


Figure 1: Chemical structure of the Crystal Violet (CV)

All chemicals used in the synthesis and adsorption experiments were used without further purification.

The crude clay used in this work is taken from a natural basin in the region of Taounate (Morocco), crushed and sieved to obtain fractions <80 µm and then dried at 105 °C for 24 hours.

2.2. Methods

Different characterization techniques have been used to identify the composition of the main constituents of the clay powder. The crystal structure of the clay powder (AT) was studied by X-ray diffractometry from the Panalytical company (X'Pert PRO diffractometer on Panalatycal powder equipped with an X'Celerator Ultrarapid scintillation detector) using radiation from Cu Kα (λ=1.54060 nm), operating at 40 kV and 30 mA. Data were collected at 2θ=10°-80°. Chemical analysis of the AT clay was performed using the X-ray fluorescence spectrometer (WD-XRF) using an AXIOS PANALYTICAL sequential spectrometer with a measurement channel based on a single goniometer covering the full range of B measurement The surface morphology of the dried clay was observed on a scanning electron microscope (Quanta 200 FEI equipped with EDX probe for surface microanalysis). Quantitative analysis of the elemental composition was investigated by X-ray energy dispersive spectroscopy (EDX). The clay powder was analyzed by Fourier Transform Infrared Spectroscopy from BRUKER (Vertex70). The IR spectrum was scanned over a wavelength range of 400-7500

cm^{-1}. The clay material was tested for adsorption of the Crystal Violet dye reagent from aqueous solutions at room temperature using the batch technique. In this case, the adsorption measurements were carried out by mixing different amounts of clay to remove the potential of the Crystal Violet (CV) dye in a series of glass beakers containing 200 ml of the colored solution at different pH using and a magnetic stirrer (Stuart). Dye solutions were prepared using ultra-pure water (MILLIPORE, direct-Q, UV3 with Pump) to prevent and minimize possible interference, samples were taken using a syringe filter from diameter 0.45µm (Minisart, sartorium stedim biotech). The effect of several variables such as the adsorbent dose (0.2-4 $g.L^{-1}$), the pH solution (4-12), the stirring speed (300-900 rpm), the contact time (0-120 min), the initial concentration of dye (5-30 $mg.L^{-1}$) and the temperature of the solution (20-60 °C) were studied.

The pH solution is adjusted by adding a few drops of HCl or NaOH (0.1 M). Thus, equilibrium was established after 10 min. At the end of the adsorption experiments, the concentration of the dye was determined by measuring the absorbance of the solution at λ=588 nm using a UV-visible spectrophotometer (Jasco V530). All experiments were performed in duplicate and mean values are presented [23].

The adsorbed amounts were evaluated from the change in solution concentration using the following equation:

$$Q(mg/g) = \frac{(C_0 - C).V}{m} \tag{1}$$

Where Q is the absorption capacity ($mg.g^{-1}$), V is the volume of the solution (mL), m is the mass of the solid (g), C_0 is the initial dye concentration in the solution ($mg.L^{-1}$) and C is the final concentration of the dye in an aqueous solution after phase separation ($mg.L^{-1}$).

The results were evaluated by various adsorption isotherms incorporating the Langmuir and Freundlich isotherms and were simulated with different kinetic models including pseudo-first order and pseudo-second order.

3. Results and Discussions

3.1. Characterization of the adsorbent

3.1.1. X-ray diffraction of clay

To identify the predominant phases of the clay mineral, X-ray diffraction mineralogical analyzes were carried out by the Panalytical Siemens 5000 diffractometer using CuKα radiation (λ=1.54060 nm), operating at 40 KV and 30 mA. Data were collected at 2θ=10°-80°. Figure 2 illustrates the results of the diffractometric analysis of the studied clay (AT) [24].

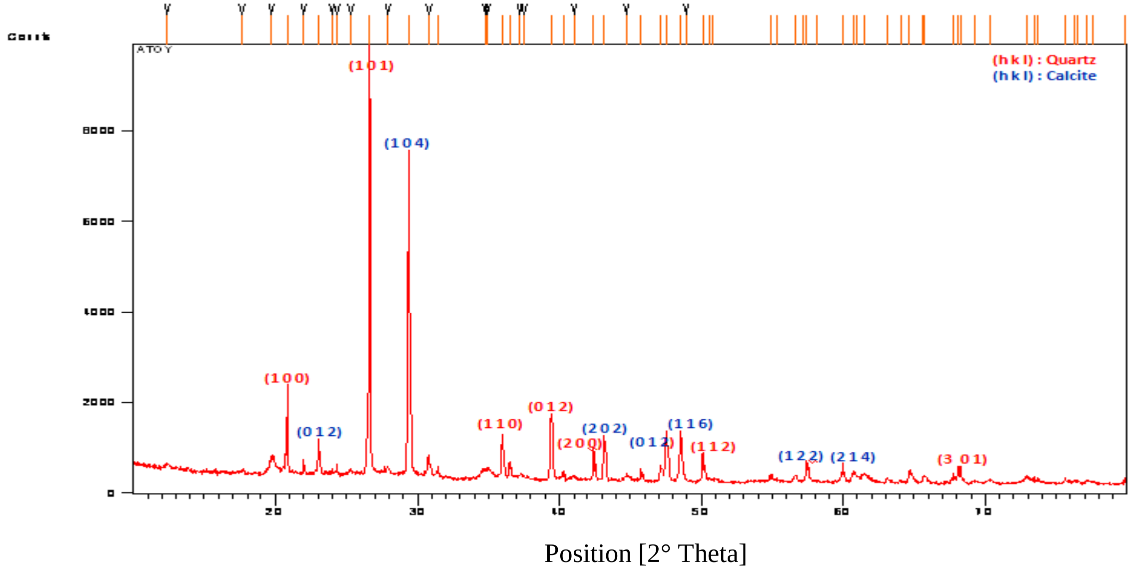


Figure 2: Diffractometric analysis of the clay AT (calcite, quartz).

The diffractometric analyzes illustrated in Figure 2, show that clay from the Taounate (AT) area consists mainly of quartz and calcite. The peaks d_{hk1} (hkl) such as: 21.3 (100); 27.7 (101); 36.2 (110); 39.9 (012); 42.7 (200); 50.2 (112) and 68.1 (301); Correspond to the quartz. The peaks 23.01 (012); 29.7 (104); 43.6 (202); 47.2 (012); 48.9 (116); 57.5 (122) and 60.01 (214) are relative to calcite [25]. The peaks 27.7 (101) and 29.7 (104) respectively exhibit a co-dominance of the revealed minerals, quartz and calcite. Allali et al., found similar results [26].

3.1.2. Fluorescence of X-rays of clay

Quantitative chemical analysis of the clay (AT) was performed using the X-ray fluorescence spectrometer (AXIOS PANALYTICAL). The results are summarized in Table 1.

Table 1: Chemical composition of the clay (AT).

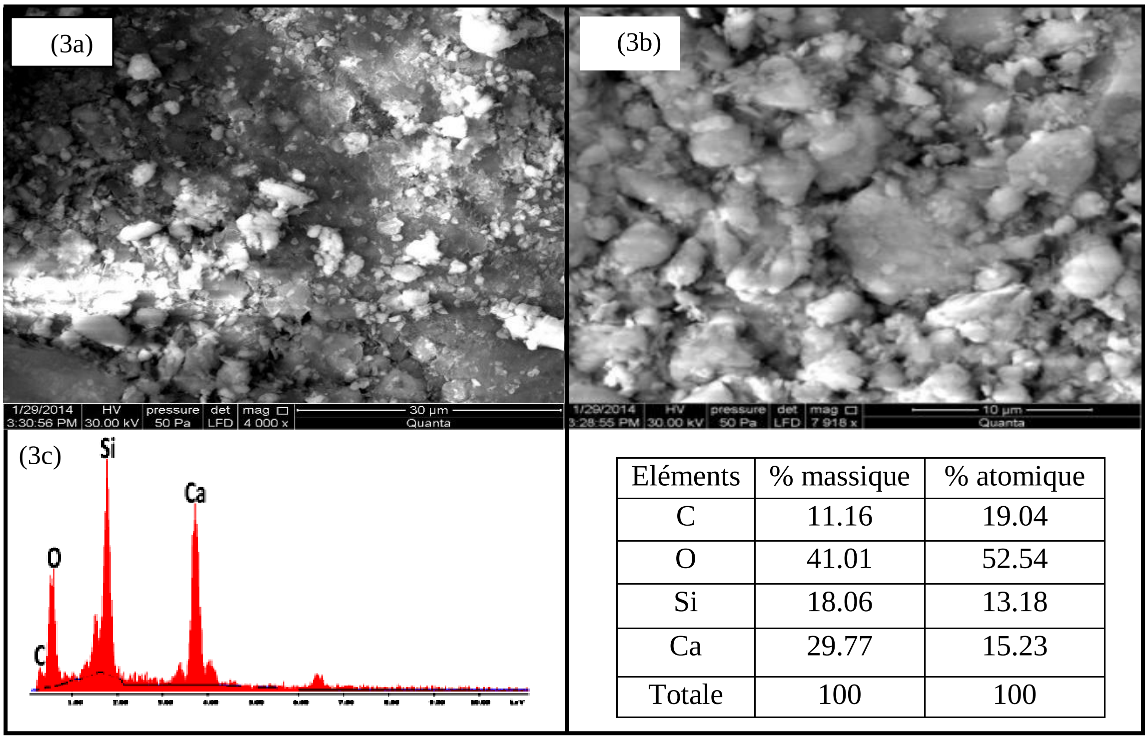
Component	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**SO_3**	**K_2O**	**Na_2O**	**MgO**	**TiO_2**	**P_2O_5**	**CaO**	**L.O.I**	**Total**
% [AT]	40.5	10.2	2.49	0.117	1.2	0.488	3.37	0.314	0.248	18.1	22.7	99.72

L.O.I: Loss on Ignition

The results of the quantitative chemical analyzes by X-ray fluorescence confirm the predominance of the two elements previously revealed by the DRX and which are quartz with the highest percentage of 40.5% and calcite with a percentage of 18.1% .

3.1.3. Analysis by Scanning Electron Microscopy of clay

Our samples were analyzed by SEM scanning electron microscopy (Quanta 200 FEI equipped with EDX probe). The use of this technique makes it possible to visualize the morphology of the clay surface. Figure 3, clarifies the results obtained by the SEM-EDX of the clay (AT).



Eléments	% massique	% atomique
C	11.16	19.04
O	41.01	52.54
Si	18.06	13.18
Ca	29.77	15.23
Totale	100	100

Figure 3: SEM microscopy coupled to EDX

The images (a) and (b) of Figure 3, show that the clay has a porous appearance which facilitates the adsorption of the materials. EDX analysis also shows the presence of the elements mentioned above, which confirms the validity of the X-ray fluorescence analysis.

3.1.4. Fourier Transform Infrared Analysis

Figure 4 presents the spectrum of the clay (AT) obtained by the Fourier transform infrared spectroscopy of the company BRUKER (Vertex 70). The IRTF spectra were scanned over a wavelength range between 400-7500 cm^{-1}. The characteristic bands of the clay are shown in Figure 4.

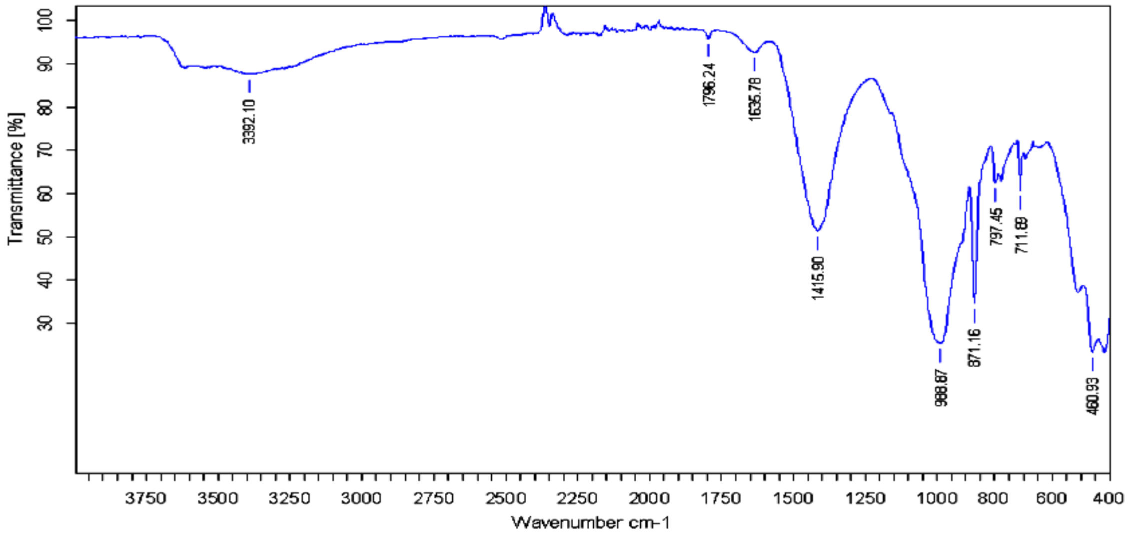


Figure 4: IRTF spectroscopy of clay (AT).

The adsorption bands observed confirms the presence of the bonds characterizing the clay (AT). Among these bands are mainly: the bands located at 3392.10 and 1796.24 cm^{-1} which correspond to the elongation vibrations of the OH group of the water of constitution, the band 1635.78 cm^{-1} which corresponds to H-OH deformation vibrations due to water molecules adsorbed between the sheets, as well as the bands 1415.90 and 871.16 cm^{-1} relating to the vibrations of CO_3 elongation. The 988.87 cm^{-1} band corresponds to the valence vibrations of the Si-O bond, the bands 797.45 and 711.89 cm^{-1} relating to the O-Si-O deformation vibrations, and the band 460.93 cm^{-1} corresponds to the Si-O-Al deformation vibrations [27-28].

3.1.5. The point of zero charge

The point of zero charge was carried out to determine the pH value for which the surface net charges of the clay (AT) is zero. The point of zero charge (PZC) of the clay AT is equal to 9.21. This behavior may be due to the fact that the surface of the clay is negatively charged at pH>PZC, which promotes the adsorption of the cationic materials. On the other hand, for pH<PZC values, the surface of the clay is positively charged and therefore capable of repelling the cations [29].

3.2. The effect's study of different parameters on the adsorption of Crystal Violet (CV).

3.2.1. Influence of contact time on the adsorption of Crystal Violet (CV)

The kinetics of the removal of Crystal Violet (CV) by clay (AT) is shown in Figure 5. The adsorption of Crystal Violet shows that after only 10 minutes of contact, the CV elimination rate (30 $mg.L^{-1}$) is almost total and exceeding 80% with an adsorption capacity of 25.984 $mg.g^{-1}$. The amount adsorbed by the adsorbent (AT) increases with increasing initial concentration of Crystal Violet (Table 2).

Table 2: Adsorbed quantity by the AT clay at various initial concentrations of the CV.

[Crystal Violet]$_0$ ($mg.L^{-1}$)		**5**	**10**	**20**	**30**
Q_{ads} ($mg.g^{-1}$)	**AT**	3.624	7.94	16.784	25.984
% Elimination	**AT**	72.48	79.44	83.92	86.613

We notice in Figure 5, that relatively speed elimination takes place at the beginning of the treatment followed by a relatively long elimination during which the adsorption process continues until reaching equilibrium (the establishment of the plateau). These results give us a quick overview of the clay adsorbent (AT) effectiveness and the estimated contact time is about 15 min.

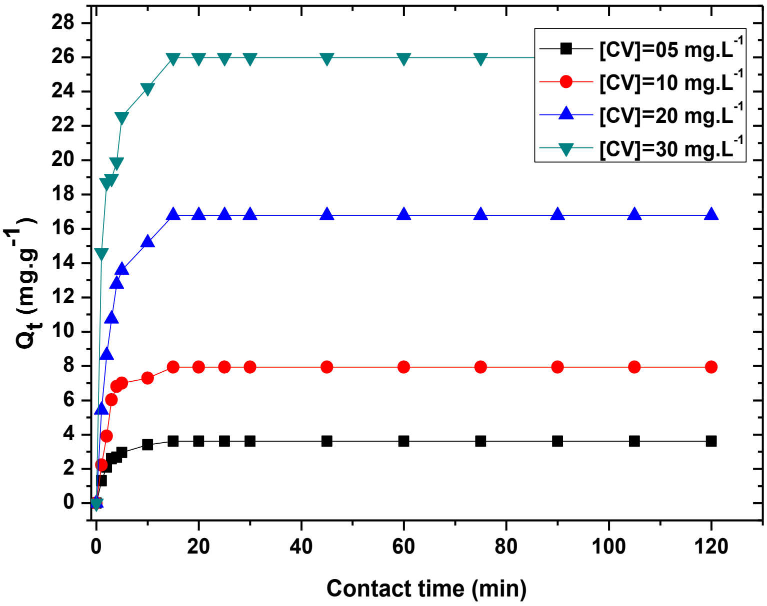


Figure 5: Influence of contact time on the adsorption kinetics of Crystal Violet (CV) on clay (AT). Conditions: (T = 20 °C, [AT] = 1.0 g.L^{-1}, V $_{\text{stirring}}$ =500 rpm).

From these results, we can deduce that the adsorption of Crystal Violet (CV) on the clay (AT) is done in three stages [30]:

1. Relatively speed adsorption of the CV dye in solution due to the presence of the free sites on the adsorbent particles surface, which translates the linear increase of the adsorption capacity over time. This step lasts 10 min under the operating conditions undertaken.
2. Reduction of the adsorption rate reflected by a very small increase in the adsorption capacity due to the decrease in the quantity of CV dye in solution and the number of sites available for adsorption. This stage lasts 10 to 15 minutes.
3. Stability of the adsorption capacity is observed; this is probably due to the almost total occupation of the available adsorption sites: the establishment of the level therefore reflects this stage.

3.2.2. Influence of the stirring speed on the adsorption of Crystal Violet (CV)

Figure 6 shows the variation in the adsorbed quantity of Crystal Violet at equilibrium Q_e (mg.g^{-1}) on AT, as a function of the stirring speed which varies from 300 to 900 rpm. In all experiments conducted for the stirring effect, the initial Crystal Violet concentration was 20 mg.L^{-1}, the dose of the AT clay was 1.0 g.L^{-1}. It is noted that the quantity of the Crystal Violet dye adsorbed at equilibrium is independent of the degree of stirring in the range studied. The difference between the amounts adsorbed at 300 and 600 rpm is negligible.

3.2.3. Influence of temperature on the adsorption of Crystal Violet (CV)

Figure 7 shows the influence of the temperature on the adsorption of the dye. It is observed that the increase in the temperature in the range studied (20 to 60°C.) for the CV results in an increase in the adsorption quantity Q_e (mg.g^{-1}) of Crystal Violet by the clay (AT). This means that the interaction of the adsorbent (AT) and the adsorbate (CV) is endothermic in nature. Thus, it is interesting to note that the contribution of heat plays an important role in the kinetics of retention of the dye and the elevation of the temperature favors the adsorption of CV on AT.

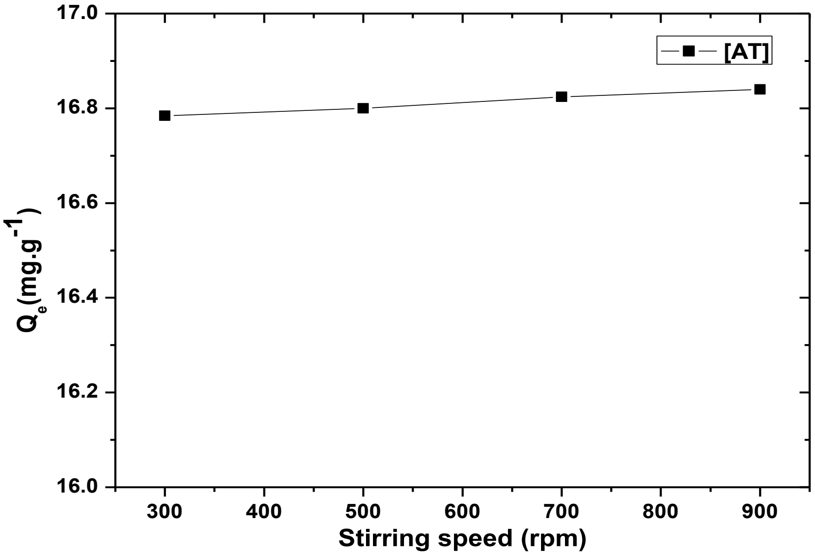


Figure 6: Stirring effect rate on the adsorbed quantity of Crystal Violet (CV) at equilibrium on the clay (AT). Conditions: (T = 20 °C, [AT] = 1.0 $g.L^{-1}$, [CV] = 20 $mg.L^{-1}$).

Moreover, temperature has major effects on the adsorption process: the increase in temperature is known to increase the diffusion rate of the adsorbate molecules through the outer boundary of the layer and into the internal pores of the adsorbent. Particle of the adsorbent is due to the decrease in the solution viscosity. Furthermore, a change in temperature may change the adsorbent equilibrium capacity for a given adsorbate [31].

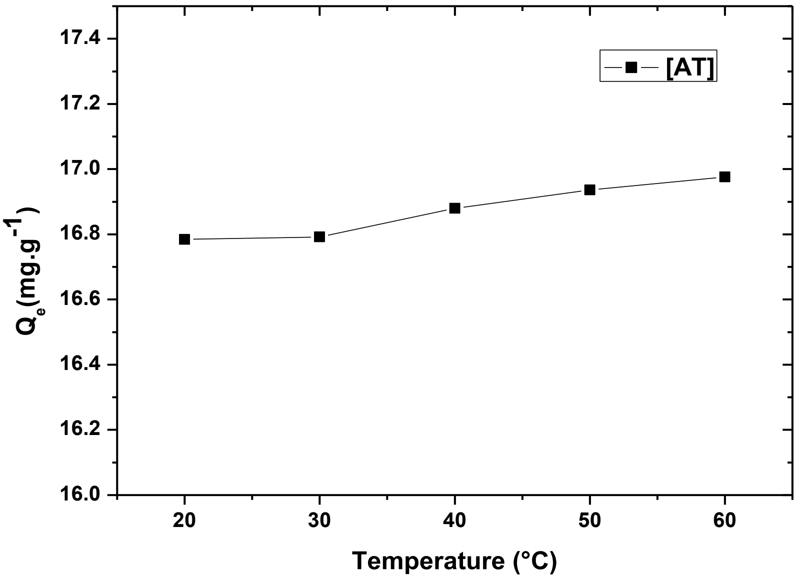


Figure 7: Evolution of the Crystal Violet (CV) adsorbed quantity on the clay surface (AT) as a function of temperature. Conditions: ([CV] = 20 $mg.L^{-1}$, [AT] = 1.0 $g.L^{-1}$, $V_{stirring}$=500 rpm).

3.2.4. Influence of the adsorbent dose on the adsorption of Crystal Violet (CV)

The study of the influence of the clay material mass on the adsorption capacity of the Crystal Violet (CV) dye led us to vary the adsorbent initial amount while retaining the initial concentration of the adsorbate (CV) in solution. The initial CV concentration in this study was set to 20 $mg.L^{-1}$ and the AT dose ranged from 0.5 to 4.0 $g.L^{-1}$. The results of Figure 8 show that the number of adsorption sites increases if the dose of the solid in the solution is high. It is observed that the percentage of adsorption increases with the increase in the mass of the adsorbent (AT) up to saturation of the active sites of the adsorbate (CV).

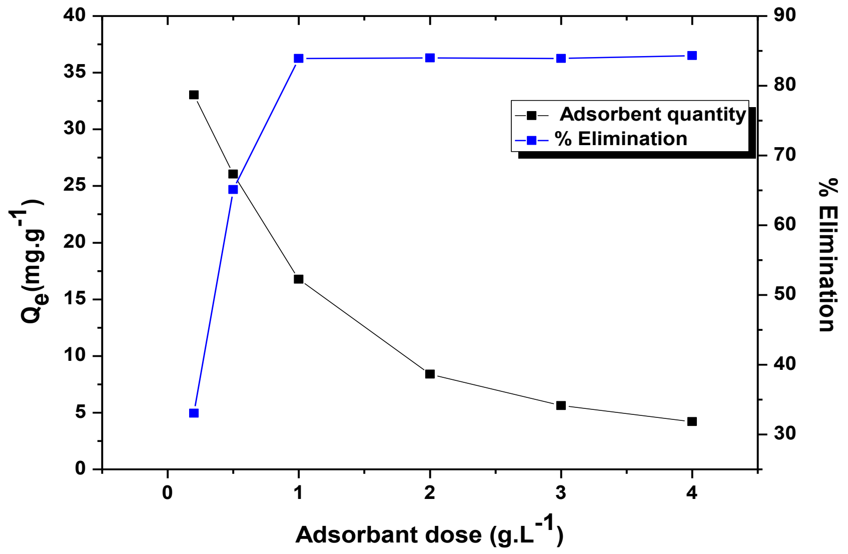


Figure 8: The percentage elimination of CV as a function of the adsorbent dose (AT). Conditions: (T=20 °C, [CV] = 20 mg.L^{-1}, V $_{\text{stirring}}$=500 rpm).

3.2.5. Effect of pH on the adsorption of Crystal Violet (CV)

The pH is an important parameter because it has a major effect on the protonation and deprotonation of the adsorbent and the functional groups of the adsorbate, conditioning their electrostatic interaction [32]. In this respect, the adsorption of the cationic dye Crystal Violet is a phenomenon which is strongly influenced by the pH of the solution; this is due to the involvement of mechanisms which in turn are highly pH dependent, such as ion exchange, complexation, or retention by electrostatic forces [33].

The adsorption behavior of the Crystal Violet (CV) dye on the adsorbent (AT) was studied over a wide pH range (4-12), adjusting the solutions to the desired values by adding HCl (0.1N) and NaOH (0.1N), while keeping the concentration of the CV (20 mg.L^{-1}), the temperature (20 °C.) and the mass of the AT adsorbent (1 g.L^{-1}). Figure 9 shows a slight increase in the adsorbed amount of the dye (CV) by the clay (AT) with the pH of the solution. The point of zero charge (PZC) of the clay AT is equal to 9.21. Indeed, at acidic pH, the cationic dyes are in competition with the H^+ ions present in high concentration in the solution. These hydronium ions are thus more adsorbed than the cationic dyes because of their high mobility. On the other hand, in the basic pH the cationic dyes are eliminated by the OH^- ions. Moreover, when the pH increases, there is a decrease in the H^+ cations, which explains the increase in the adsorption amount of the Crystal Violet.

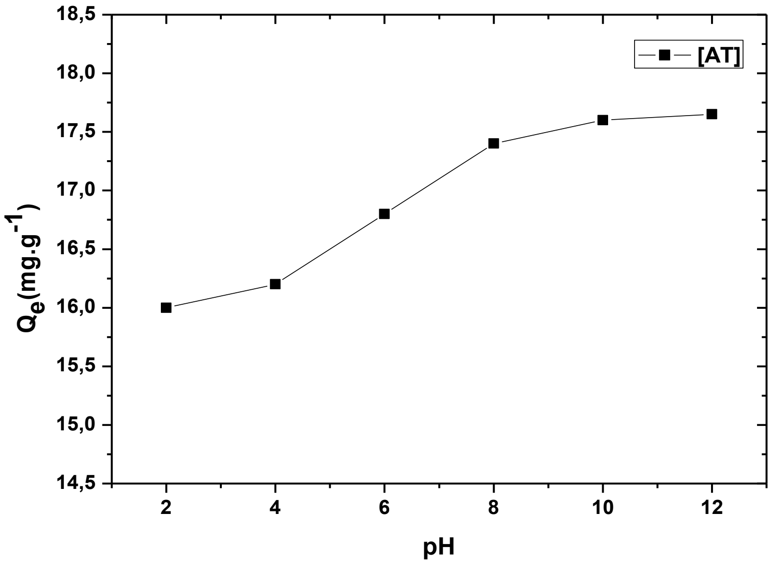


Figure 9: Influence of the pH on the adsorption capacity of Crystal Violet (CV). Conditions: (T=20°C, [CV]=20mg.L^{-1}, [AT]=1g.L^{-1}, V $_{\text{stirring}}$=500 rpm).

3.2.6. Adsorption Kinetics

To determine the adsorption rate constants, kinetic data are analyzed using the kinetic models already cited in the bibliographic study, namely the pseudo-first order model proposed by Lagergren and that of the pseudo-second order. The most representative model of the data is discussed on the basis of the value of the correlation coefficient R^2.

- Pseudo-first order model (Lagergren equation)

The pseudo-first order kinetics model is the most suitable for the lowest concentrations of solute. This model presented by the Lagergren relation [89], based on the adsorbed amount and on the first equation of velocity established to describe the adsorption kinetics in a liquid/solid system. This pseudo-first order model is represented by the following relation [34-35]:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (2)$$

Were, q_t: quantity of adsorbate adsorbed at time t ($mg.g^{-1}$); q_e: adsorbed amount at equilibrium ($mg.g^{-1}$); K_1: adsorption rate constant of the pseudo-first order model (min^{-1}); t: time (min).
If the Lagergren relation is satisfied, carrying ln (q_e-q_t) as a function of time, we must obtain a line of slope -K_{ads}.
The parameters of the Lagergren model and the correlation coefficients are not satisfactory for the clay material (AT). This confirms that the Lagergren model does not apply in this case. Then the adsorption of the CV on AT does not correspond to the kinetics of the pseudo-first order.

- Pseudo-second order model

The pseudo-second order reaction rate depends on the amount adsorbed to the surface of the adsorbent and the adsorbed amount at equilibrium. The pseudo-second order model can be represented in the following form [36-37]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

Where: K_2 is the adsorption rate constant of the pseudo-second order model ($g.mg^{-1}.min^{-1}$).
If this equation is satisfied, by plotting t/qt as a function of t, we must obtain a line of slope $1/q_e$ and ordinate at the origin equal to $1/(K_2\, q_e^2)$.
Figure 10 shows that the curves are linear throughout the range of concentrations studied for this model.

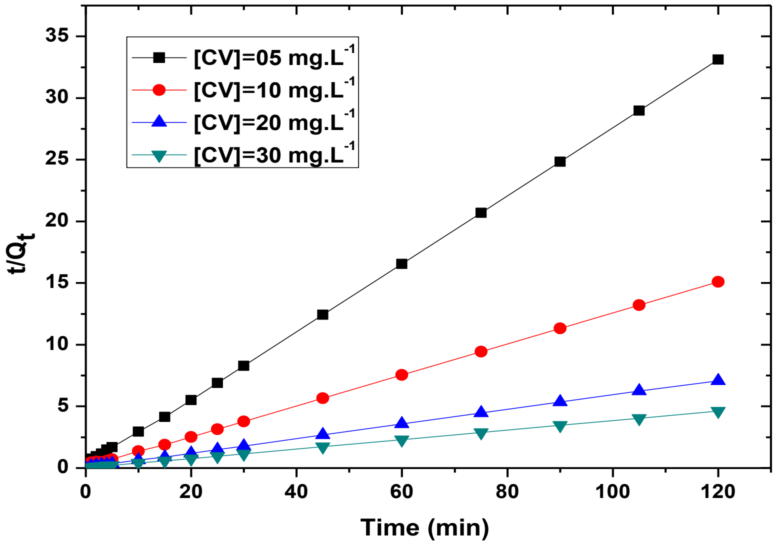


Figure 10: Pseudo-second order model for the adsorption of Crystal Violet (CV) on the clay adsorbent (AT). Conditions: (T=20 °C, [CV] = 20 $mg.g^{-1}$, [AT] = 1.0 $g.L^{-1}$, $V_{stirring}$ =20 °C).

Table 3 summarizes the pseudo-second order rate constants K_2 and the correlation coefficients R^2. We can observe that the pseudo-second order model is adequate to describe the adsorption kinetics of the Crystal Violet dye by the clay adsorbent studied since the coefficient of correlation is high (R^2=0.99). Similarly, the values of q_e calculated by the pseudo-second order model are very close to those determined experimentally, which confirms this result. Several studies confirm that the adsorption of the dyes on the argillaceous supports obey the pseudo-second order model [38].

Table 4: Parameters characterizing the adsorption kinetics of the CV on the adsorbent AT.

C_0 (CV) ($mg.L^{-1}$)	Q_{exp} ($mg.g^{-1}$)	Kinetics of 2nd order		
		K_2 ($g.mg^1.min^{-1}$)	Q_{cal} ($mg.g^{-1}$)	R^2
[CV]=05 mg.L^{-1}	3.624	1.235	3.66	0.999
[CV]=10 mg.L^{-1}	7.944	1.19	8.06	0.999
[CV]=20 mg.L^{-1}	16.976	0.93	17.24	0.999
[CV]=30 mg.L^{-1}	25.984	1.81	26.31	0.999

3.2.7. Adsorption Thermodynamics

The adsorption reaction of coloring molecules on a surface implies a variation of the Gibbs energy between the initial state and the final state. The feasibility of a reaction is defined as ΔG° ($kJ.mol^{-1}$), which corresponds to the variation of free enthalpy (variation of energy at constant pressure). In this case, a thermodynamic system always evolves spontaneously towards a lower energy level and for a reaction to be possible in isolation ΔG° must have a negative value. The values of ΔH° and ΔS° were calculated using the following Van't Hoff equation:

$$lnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

Where R: perfect gas constant (R=8.314 $J.mol^{-1}.K^{-1}$), and T: absolute solution temperature (K), K_d: distribution coefficient. Where Q_e: amount of adsorbed on the solid at equilibrium ($mg.g^{-1}$), and C_e: equilibrium concentration ($mg.L^{-1}$) The values of ΔH° and ΔS° were calculated from The slope and the interception of the plot of lnK_d as a function of 1/T. ΔG° can be calculated using the relationship below:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

The energy of Gibbs is composed of two terms clearly cited as follows: an enthalpy term H which expresses the energies of interactions between the molecules and the adsorbent surface, and an entropy term S which expresses the modification and arrangement of the molecules in the liquid phase and on the surface. The entropy variation ΔS° is a measure of the disorder. The spontaneous transformations are in the direction of an increase of the disorder. The adsorption phenomenon is always accompanied by a thermal process either exothermic (ΔH°<0) or endothermic (ΔH°> 0) [39]. The values of the free enthalpy of adsorption, the heat of adsorption and the entropy are grouped in Table 5.

Table 5: The adsorption process of thermodynamic parameters of Crystal Violet (CV) on AT and at various temperatures. Conditions: ([CV] = 20 $mg.L^{-1}$, [AT] = 1.0 $g.L^{-1}$, $V_{stirring}$ =500 rpm).

	ΔH° ($kJ.mol^{-1}$)	ΔS° ($J.mol^{-1}.K^{-1}$)	ΔG° ($kJ.mol^{-1}$)				
			20°C	30°C	40°C	50°C	60°C
AT	34.67	14.90	-4.33	-4.48	-4.63	-4.78	-4.93

Negative values of ΔG° indicate the feasibility and spontaneity of the adsorption process. On the other hand, the positive value of ΔH° indicates that the reaction is endothermic, which explains why the adsorbed amount increases with increasing temperature (Table 5).

3.2.8. Adsorption isotherms

The study of the adsorption isotherms of the dye Crystal Violet (CV) by the clay (AT) consists in modeling the curve or more precisely, to account by a mathematical equation of the whole curve. The classical models of Langmuir and Freundlich characterizing the formation of a monolayer will be used for their simplicity of implementation. The experimental conditions are similar to those of the adsorption kinetics.

The values of the various parameters calculated for each model used are grouped in Table 6. The values of the correlation coefficients make it possible to estimate the agreement between the experimental data and the data modeled according to each model.

- Isotherm of Langmuir

In the case of monolayer adsorption [40], Weber's equilibrium representation is [39]:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \qquad (6)$$

Where, C_e: concentration at equilibrium ($mg.L^{-1}$) and Q_e: adsorbed quantity at equilibrium ($mg.g^{-1}$), Q_{max}: maximum adsorbed amount at saturation of the monolayer or maximum adsorption capacity ($mg.g^{-1}$), and K_L: temperature-dependent adsorption equilibrium constant ($L.mg^{-1}$) If the Langmuir equation is satisfied, we must obtain by placing our experimental points in $1/Q_e = f(1/C_e)$ or $C_e/Q_e = f(C_e)$, a straight line whose slope and ordinate at the origin allow us to determine Q_{max} and K_L.

The experimental results of CV adsorption isotherms on AT are modeled by the Langmuir relation. If the Langmuir equation is satisfied, we must obtain by placing our experimental points in $1/Q_e = f(1/C_e)$ or $C_e/Q_e = f(C_e)$ coordinates, a straight line whose slope and origin allow us to determine Q_{max} and K_L.

The correlation coefficient is good (≥ 0.99) showing good linearity for the adsorbent used.

- Freundlich Isotherm

Proposed by Freundlich in 1906 [41], this is the first empirical equation known to describe the adsorption of substances on coal. It is now almost as widely used as the Langmuir equation. The adsorption of phenol on numerous supports such as activated carbon, polymers, argues or TiO_2 [42-43] for example, was recently described by the Freundlich equation. This equation is an empirical model based on adsorption on heterogeneous surfaces. It is used in the case of possible formation of more than one adsorption monolayer on the surface and the sites are heterogeneous with different binding energies. The isotherm is expressed by the equation:

$$q_e = K_F.C_e^{1/n} \qquad (7)$$

The equation can be linearized as follows:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \qquad (8)$$

K_F ($mg.g^{-1}(mg.L^{-1})^{-1/n}$) is the Freundlich adsorption constant and n is a constant dependent on the nature of adsorbate and temperature.

The Freundlich model has been applied to the experimental results of CV adsorption isotherms on AT. The results of the Freundlich parameters are reported in Table 6, the correlation coefficient of Freundlich is 0.89 showing poor linearity for the adsorbent used. It is generally asserted that for the values of $n_f < 1$, the adsorption is low. If the values of n belong to the interval 1 to 2, the adsorption is moderately difficult.

The value of the parameter n of the obtained Freundlich equation ($n_f < 1$) shows that the clay (AT) is a weak Crystal Violet (CV) adsorbent.

The estimated parameters of the adsorption isotherms of Langmuir and Freundlich for the adsorption of the Crystal Violet dye using the clay adsorbent (AT) are summarized in Table 6.

Table 6: Parameters of the Langmuir and Freundlich model.

	Langmuir				Freundlich		
	Q_{max} (mg.g^{-1})	**K_L (L.mg^{-1})**	**R_L(L.mg^{-1})**	**R^2**	**K_f(mg.g^{-1})**	**n_f**	**R^2**
AT	17.05	2.891	0.0155	0.999	255.172	0.372	0.89

The essential characteristic of the Langmuir isotherm can be expressed by the non-dimensional parameter of Hall, called the equilibrium parameter, R_L, which takes the form:

$$R_L = \frac{1}{1 + K_L C_0} \tag{9}$$

Where, C_o: initial concentration (mg.L^{-1}), and K_L: adsorption equilibrium constant of Langmuir (L.mg^{-1}), and R_L: adsorption isotherm parameter, according to criterion next: Favorable if $0 < R_L < 1$, and linear if $R_L = 1$, and unfavorable if $R_L > 1$. The value of the calculated Hall parameters is grouped in Table 6. The results obtained show that CV adsorption isotherms on AT are favorable.

Conclusion

The present study shows that the aqueous solution of the Crystal Violet (CV) dye could be removed by the batch technique which has been used under various environmentally friendly conditions to produce quantitative adsorption using the AT adsorbent. In this respect, it has been demonstrated that the adsorbed amount of dye increases with increasing parameters such as temperature, pH solution, concentration and adsorbent amount. Furthermore, the adsorption process was judged to be endothermic, meaning that the increase in temperature increased the adsorption capacity. Kinetic study of the CV dye on the clay substrate (AT) obeys the pseudo-second order model. The Langmuir model describes well the adsorption process of the CV on the clay AT.

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