Calculation of the Thermodynamic Parameters of Adsorption of the Pesticides (Rodazine) in Aqueous Solution by Natural and Modified Clays

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Abstract
The purpose from this works is to test two clays, first Bentonite and the clay of Djebel Debbagh as well as bentonite coupled with cellulose within the framework to eliminate pollution: pesticide (the Rodazine). Bentonite-cellulose is selected as the argillaceous material which has a capacity raised for the adsorption of the organic pollution used. The study is to influence the experimental parameters (pH, temperature and stirring velocity) on the power adsorbents of the clays studied with respect to the pollution used. Our works are closed by kinetic, thermodynamic modelings and the isotherms of adsorption. The results showed the practical interest of the use of clay in the field of the pollution of the water contaminated by the organic pollution.

Keywords: Adsorption, Clay, Organic Pollution

Introduction
The pesticides used in the agriculture are the substances of slightly biodegradable and very stable chemically. Its transformation in the anaerobic medium generates a transformation and an accumulation of the carcinogenic aromatic products (1). The water treatments polluted by the pesticides before their discharge in the network of cleansing this proved to be necessary. Scientific researchers of different fields (chemistry, geology, agronomy, vegetable physiology and medicine) are interested more and more in the identification and elimination of pollutants implied directly in the appearance of imbalances at the level of ecosystems which can lead them to death, such as animals and man. The elimination of these pollutions starting from the waste of industrial which is very often carried out by classical chemical treatments such as: decantation, coagulation-flocculation, oxidation,… etc (2, 3). The waste water treated by this process contains pollutions and is charged because of adding reagents. In most case, these processes are very expensive. It is necessary to think on techniques of severe effectiveness and lower costs. The techniques of adsorption were crowned success in the elimination of organic species. Currently, the activated carbon is the adsorbent most commonly employed, thanks to its adsorbent power which is very important by respecting pesticides, but the disadvantage is that the activated carbon is expensive because of its preparation which requires great investments (oxidation, crushing, sifting, activation, conditioning…) (4-6). In this context, we proposed to test competitive adsorbents with the activated carbon containing clays available in great quantity in our countries because it is easy and inexpensive exploitation. Among these adsorbents: the Bentonite-cellulose, Bentonite and the clay of Djebel Debbagh. The Bentonite is a montmorillonite clay type (7). The elementary layer of montmorillonite is formed by the octahedral layer ranging between two tetrahedral layers. The Si^{4+} ions are located inside a tetrahedron whose tops are occupied by oxygen atoms. The Al^{3+} ions are located inside octahedral whose tops are occupied by four atoms of oxygèneet of two ions hydroxyls. The elementary layers are of type 2/1 separated by molecules of water and cations exchangeable (8, 9).

Materials and Methods
The various methods of analysis that used during this study and which can be classified in two groups: On the one hand, those which make it possible to characterize the physicochemical properties of the solid phase (clays) being able to be studied on various scales with suitable methods. The study with the molecular scale is obtained by infra-red spectroscopy (IR). In addition, methods allow knowing the properties of the liquid phase (pesticide) by

the UV-Visible analysis spectrophotometry. An organic pesticide is selected to realize the tests of adsorption: Rodazine: λ max= 210 nm. To study the kinetics of adsorption of the adsorbates with 25°C, one takes a volume of 0.5 liter solution containing the dye of concentration 100 mg/l, with a mass of 1 gram of adsorbent, under agitation speed of 500 turns per minutes. The pH of the solution is followed continuously using a pH-meter, and for the evolution of the concentration of the pollution is followed by UV-visible spectrophotometry.

$$q_t = \frac{(C_0 - C_t).V}{m}$$

qt: fixed quantity of mg pollutant per gram of adsorbent, Co and Ct: the respect of the concentrations of the initial and instantaneous pollution (mg/L), V: the volume of the solution (L),

Table 1: Values of the Chemical Composition Clays Used.

% massique	Bentonite	Djabel Debbagh
SiO_2	65.2	45.23
Al_2O_3	17.25	38.31
Na_2O	3	0.66
C_aO	5	0.21
K_2O	1.7	0.08
M_gO	3.10	0.06

The Bentonite that used during our works is extracted from the layer of Hammam-Boughrara with Maghnia (Tlemcen ALGERIA). The clay of Djabel Debbaghest extracted the layer of Ain Barbar (Guelma) etles clays was provided to us at the finely crushed state, for the preparation of Bentonite – Cellulose to realize by agitation of 6:00 of Bentonite 3g with 0.6g of Cellulose and 66 ml of ethanol and 33ml of H_2O [36]. The analysis of the chemical composition by fluoressence X enabled us to determine the components of oxide clays whose contents are evaluated mass expressed as a percentage. Table 1 shows the results of analysis of the chemical composition of clays used. It arises from the examination of the results of the chemical composition that these three clays a high percentage of SiO_2 with aluminic trend. The grain size result of analysis by sedimentation shows that the Bentonite has a very fine granulometry; approximately 54% grains have a diameter lower than 2mm, followed by the clay of Djabel Debbagh with 32%. The spectra IR recorded in KBr of Bentonite, Bentonite-Cellulose and clay Djabel Debbagh (fig 1) show the various absorption bands characteristic of the clays recorded between 4000 and 400 cm⁻¹ (10-12).

Spectral analyses FTIR were carried out to confirm the cellulose grafting on bentonite and the presence of polyethylene glycol. Two absorption bands characterizing connections O-H located respectively between 3200 and 3800 cm⁻¹, the band of adsorption which is related to the hydroxyl groups, is shifted of 3624cm⁻¹ with 3453cm⁻¹ dans the bentonite-cellulose spectrum, this shift is DUA the formation of the interactions of hydrogen bond between the groups' hydroxyls cellulose, pololyethylene glycol and of Bentonite. Another average band is spread out between 1600cm⁻¹ is allotted to the vibrations of deformation of connection O-H of boiler feed water and to the vibrations of deformation of the connections of water molecules adsorbed between the layers. An intense band of adsorption between 900-1100 cm⁻¹, this bandeest centered towards (1030 cm⁻¹ ± 10), it characterizes the vibrations of valance of the bond Si-O.

Moreover the vibrations inflections were considered to 910 cm⁻¹ (Al-Al-OH) and 874 cm⁻¹ (Al-Fe-Oh) which were due to the association of the hydroxyl group of the Bentonite. Intensity of a band to 1454 cm⁻¹ est allotted to the vibrations of deformations of connection of CH (- CH₂) (13). Bands of vibration of these connections Si-O-M VI (M indicates Al metals, Mg and Fe located in octahedral position) in the interval 400-550 cm⁻¹ appears. The bands characteristic of impurity appear to 1034,915, and 798. They appear by shoulders which we allot to the presence of quartz. The peaks 3337 cm⁻¹ and 1153 cm⁻¹ are characteristic of grouping O-H and C-O-C in the spectrum of pure cellulose.
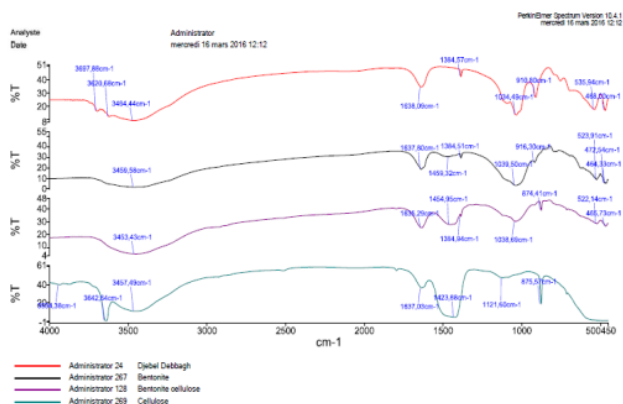

Figure 1: Spectrum Will Infra Red Clays Used

Table 2: Principal Absorption Bands Ir Cm⁻¹

Attribution	Bentonite-cellulos	Bentonite	Djabel debbagh
vOH élongation (H$_2$O)	3453	3800-3200	3690-3450
vOH déformation (H$_2$O)	1635	1650-1600	1638
vSiO élongation dans le plan	1038	1100-900	910-1092
δAl-O-H	900	900	900

Measurement of Specific Surface Area (BET)

The adsorption isotherms were carried out on a dvice Quanta-chrome NovaWin instrument with temperature 77 K. The values of the surfaces measured with the BET method are presented (Table 3). Table 3 shows that the Djabel Debbagh clay has a specific surface larger than those of bentonite–cellulose and bentonite.

X-Ray Powder Diffraction (Xrd) Analysis

Figure 2 shows the spectra that are recorded on a Bruker AXS D-8 diffractometer using monochromatic K_ radiation of 1.54 A copper. The structure of bentonite contains montmorillonite as the main constituent. The diffractogram of bentonite (Fig. 2a) also indicates the presence of quartz, cristobalite, feldspar, dolomite, calcite, and plagioclase (Table 4). Bentonite shows a diffraction peak typically at 2Θ = 7.19° corresponding to a base spacing of 12.28

A°; the presence of a cellulosic chain has increased the structure of the bentonite layer. It can be seen from Fig. 2b that the diffraction peak of the bentonite–cellulose increases. This result indicated that the cellulosic molecules were successfully intercalated in the bentonite layer spacing and separated the silicate layers of montmorillonite with a spacing of 15.32 A (Table 5). The mineralogical structure of Djabel Debbagh (Fig. 2c) is close to that determined for kaolin (Table 5). As a result, the researchers can say that this clay belongs to the type 1.1 minerals.

The researchers obtained the same peaks with differences in distances. They also found the presence of the peaks that correspond to the cellulose, which confirms the interaction of the polymer with the clay. From these findings, it can be said that the interfoliar space has more of the specific surfaces determined.

Table 3. Inter-reticular (Intercross) Distances of the Characteristic Peaks of the Different Minerals Present in the Bentonite.

Minéraux argileux	D
Montmorillonite	12.28, 4.48, 1.82
Quartz	4.25, 3.22
Cristobalite	4.03, 2.88, 2.45
Feldspath	6.42, 3.44
Plagioclase	3.75, 2.56
Dolomite	2.27
Calcite	2.27

Table 4. Inter-Reticular Distance of the Characteristic Peaks of the Different Minerals Present in the Bentonite–Cellulose Clay.

Minéraux Argileux	D
Montmorillonite	15.32, 4.45, 1.90
Quartz	4.20, 3.22
Cristobalite	4.02, 2.82
Feldspath	3.31
Plagioclase	4.01, 2.55
Dolomite	2.27
Calcite	3.02
Cellulose	3.12, 3.19

Table 5. Inter-Reticular Distance of the Characteristic Peaks of the Different Minerals Present in the Djabel Debbagh Clay.

Minéraux argileux	D
Kaolinite	7.48, 3.57, 2.52
Quartz	4.21, 3.46
Muscovite	3.76, 3.23, 2.23
Feldspath	3.85, 2.96
Calcite	2.98

Table 6: Values of the Cation Exchange Capacity (cec) of the Clays Used.

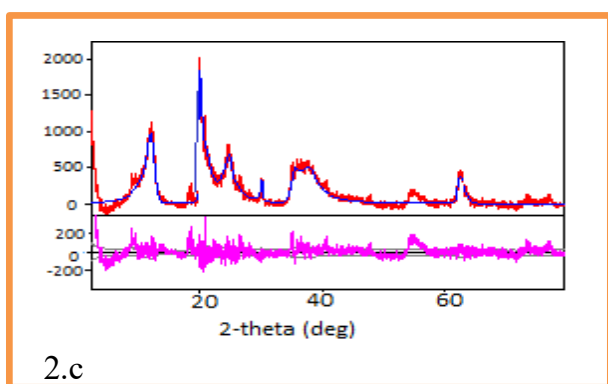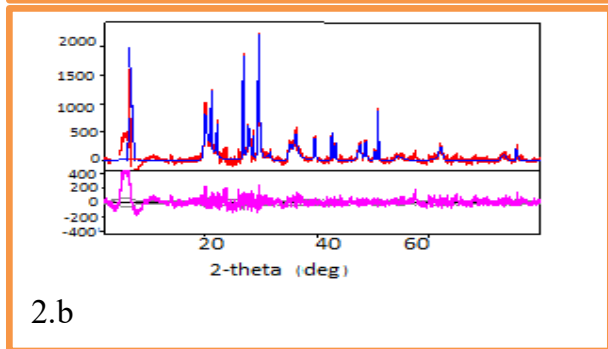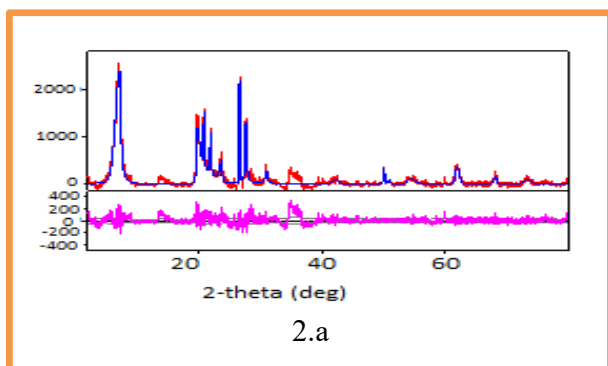| Argiles	CEC (meq/100g)
Bentonite-cellulose	91
Bentonite	80
Djabel Debbagh	37.5

2.a

2.b

2.c

Figure 2: X-ray diffractograms of Clays: (a) Bentonite, (b) Bentonite–Cellulose, and (c) Djabel Debbagh.

Cation exchange capacity (CEC)

Measurements of the CEC by cobalt chloride of the different clays show a large divergence of the CEC values obtained from (Tables 7).

1. Isotherms of Adsorption

To study the isotherms of adsorption of pesticide by Bentonite-cellulose, Bentonite and Djabel debbagh, with the volumes of 0.05L of different concentrations of pesticide going from (20 has` 300mg/l) are put in contact with amass of 0.1g of the adsorbent. The experimental conditions are similar to those of the kinetics of adsorption.

Modeling of the Isotherm of Adsorption

The last stage of the study of the isotherms consists in modeling the curve, or more precisely, giving an account by a mathematical equation of the whole of the curve. The classical models of formation of full course will be used for their simplicity of implementation. The model of Langmuir is based on the following assumptions: The only one formation lays down adsorbate on the surface of the adsorbent, the existence of sites defined of adsorption, surface is uniform with absence of interaction between the adsorbed molecules (14). The equation of Langmuir is written in the following way.

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

With: qm: capacity of adsorption to saturation (characteristic of the formation of full-course of adsorbed molecules), (mg/g) and b: Constant of equilibrium characteristic of adsorbent, depend on the temperature and the experimental conditions (l/mg). The model of Freundlich, is based on an empirical equation represents a variation of energies with the adsorbed quantity (15). This distribution of energies of interaction is explained by heterogeneity of the sites of adsorption. Contrary to the model of Langmuir, the equation of Freundlich does not envisage limit higher than adsorption what restricts its application to the diluted mediums. On the other hand, this model admits the existence of interactions between the adsorbed molecules (16). It is in the following form: $q_e = K C_e^n$

With: K: capacity of the adsorbent (l/g) and N: factor of heterogeneity.

Results and Discussions
1. Kinetic studies
The kinetics of elimination describe reaction speeds which make it possible to determine the time of contact put to reach the balance of adsorption.
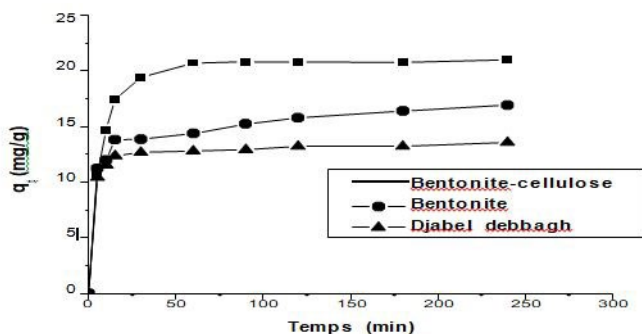
Figure 3: Kinetics of Adsorption of the Rodazine on Clays Used.

At the conclusion of these experiments which is represented on figure 3 shows that the evolution of the curves of elimination of the adsorbate by clays can be broken up into three phases: first is very fast, followed by second of average speed, to reach the stage of saturation. This phenomenon can be explained in first stage by the existence of the sites of adsorption easily accessible, followed by diffusion towards less accessible sites of adsorption before reaching a balance of adsorption where all the sites become occupied. For Bentonite-Cellulose, fixing is fast being explained by the great affinity of the support and the active sites on surface has opposite the adsorbate used (17, 18). The comparison of three clays easily enables us to conclude that the Bentonite-Cellulose presents a power adsorbing higher than Bentonite and clay Djabel Debbagh. In parallel under investigation kinetic of adsorption of the pollution on these clays, we followed the variation of the initial pH of the solutions represented on figure 4.
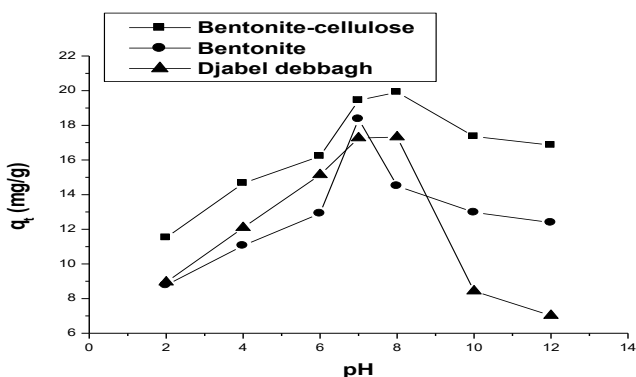

Figure 4: Evaluation of the ph of the Rodazine in the Presence of Clays Used.

According to these results, it arises that the adsorption of pesticide on clays strongly depends on the pH. The maximum of adsorption of pesticide on clays is obtained with pH ranging between 6 and 8. With pH superiors with 8 and lower than 6, the quantity of dye adsorbed decreases. Kaoua and collar, explained the influence of the pH on the variation of the rate of elimination of the pesticide by the bonding strengths which intervene in the formation of the complex molecule clay and which gather:
* Coulomb forces: between a negatively charged surface and pos-

itively charged compounds.
* forces of Van Der Waals: with the interactions ion-dipole, between the surface of material and the organic compounds (19).

2. Influence of the Temperature
To study the influence of the temperature on the kinetics to adsorbate by the various types of clays, the experiments were carried out in an active interval of temperature of 10°C at 50°C, in a bath water boiler. Therefore, results presented on the following figure:
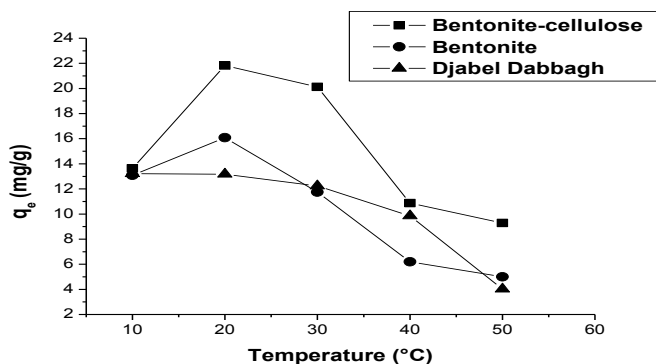

Figure 5: Influence of the Temperature on the Kinetics of Adsorption to the Equilibrium of the Rodazine with Clays Used.

According to figure one we notice that the increase in the temperature in the studied interval causes a reduction in the capacity of adsorption of the adsorbates on clays with equilibrium. Reduction in adsorption in the interval of temperature 10 - 50°C, means that the process of adsorption of the pesticide by these clays used, is exothermic.

3. Influence Agitation Speed
To study the influence agitation speed on the kinetics of adsorption of the adsorbate on clays, we choose an interval this stirring velocity going from 0 to 1000 turns per minutes. According to the results that illustrated on the following.
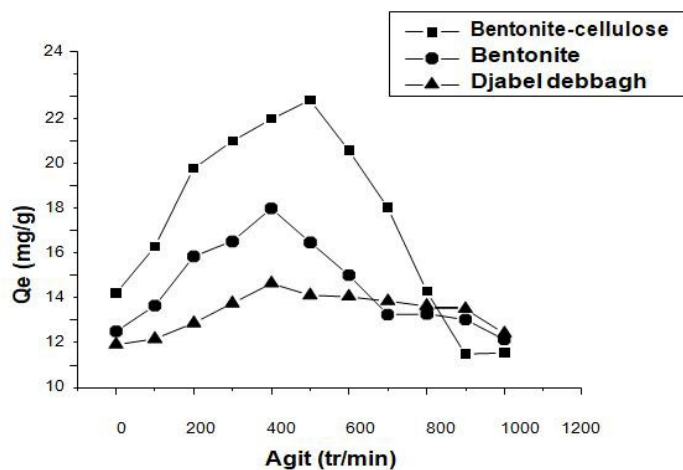

Figure 6: Effect the Agitation Speed on the Kinetics of Adsorption of the Rodazine by Clays.

We observe that the greatest capacity of adsorption is to balance and obtaine with a agitation speed 400 and 500 trs/min, which ensures a good diffusion of the adsorbate towards clays. In the case of raised agitation speed, we notice a reduction in the capacity of adsorption. Whereas, for the absence agitation speed, we note a very significant reduction in the capacity of adsorption (20, 21).

4. Determination of the Thermodynamic Parameters

To determine the parameters we used the relation Gibbs-Helmholtz:

$$\Delta G = -RTLnK_c$$

$$\Delta G = \Delta H - T\Delta S$$

$$LnK_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

with

$$K_c = \frac{C_e}{(C_0 - C_e)}$$

Kc: Constant of balance
ΔG: free enthalpy (joule/mole)
ΔH: The enthalpy (joule/mole)
ΔS: The entropy (joule/mole. K)
T: Absolute temperature (K)
Co: Initial concentration of the adsorbate
Ce: Concentration with the balance of the adsorbate
R: constant of perfect gases (8,314 Joule/mole K).

Heats of adsorption ΔH and the entropies ΔS of the adsorbate on clays are graphically given while carrying LnKc according to the reverse of the temperature in Kelvin degree (22, 23).
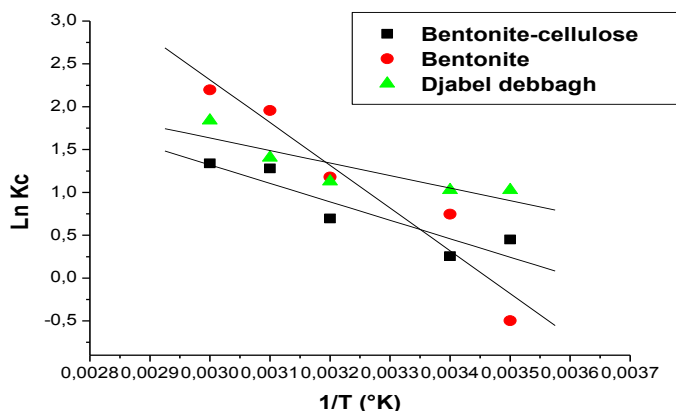

Figure 7: Determination of the Enthali and the Entropies of the Adsorption of the Rodazine on Clays.

According to figure 7 we obtained lines with good coefficients of correlation, which allow us calculer ΔH and ΔS of adsorption of the adsorbate on clays. The results of the thermodynamic parameters are gathered in table 8.

Table 8: Value of the Free Enthalpy of l'adsorption of l'adsorbat on Clays.

Adsorbants	ΔH (kJ/mole)	ΔH (kJ/mole)	R²
Bentonite cellulose	-17.90	64.75	0.92
Bentonite	-41.48	143.68	0.96
Djabel debbagh	-12.15	50.06	0.88

The negative values of the free enthalpy ΔG given on table 9, show that the process of adsorption of the adsorbate on clays is a spontaneous process. The constant speed of adsorption of the adsorbate on clays for the first, pseudosecond order, and second order are graphically given. For each couple adsorbing adsorbate we calculated the constants speeds for the first, pseudonym second order and the second order starting from the right-hand sides obtained. According to the results indicated on tables 10, 11, 12 we notice that the model of pseudonym second order is most reliable to determine the order of the kinetics of adsorption of the dye by Bentonite-Cellulose, Bentonite and clay Djabel Dabbagh who represents a good coefficient of correlation (R 2 = 0.99). In the same way and according to the values that shown in the table 13, one notices that this computed value by the model of pseudonym second order is very close has that to determine in experiments what still justified that the kinetics of adsorption of the pesticide used by clays are of pseudonym second order. Several studies found that the kinetics of adsorption of the pesticides on the argillaceous supports obey the pseudonym second order (24, 25).
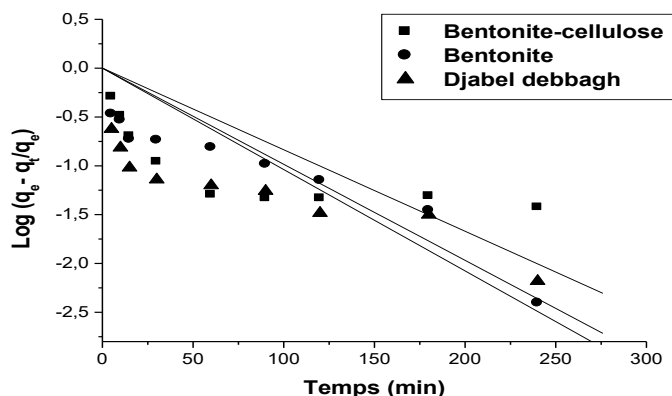

Figure 8: Determination of the Constants First Order Speed of Adsorption of the Rodazine on Clays.

Table 9: Constant First Order Speed.

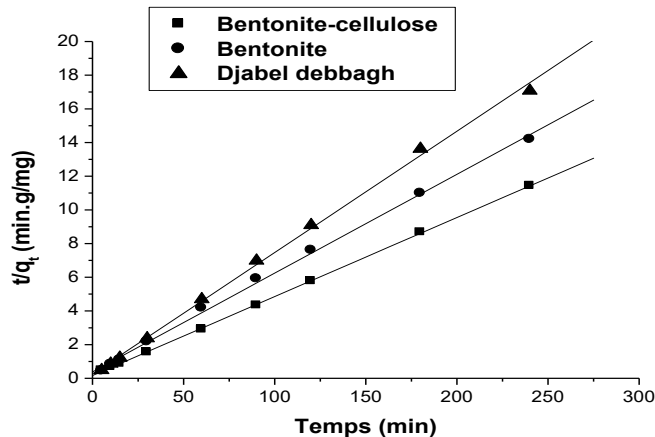| Adsorbate	Adsorbing	Kv(mn⁻¹)	R²
Rodazine	Bentonite-cellulose	0.019	0.78
	Bentonite	0.023	0.96
	Djabel debbagh	0.024	0.94

Figure 9: Determination of the Constants Speed of the Pseudonym Second Order of the Adsorption of the Rodazine on Clays.

Table 10: Constant Speed of the Pseudoseconde Order.

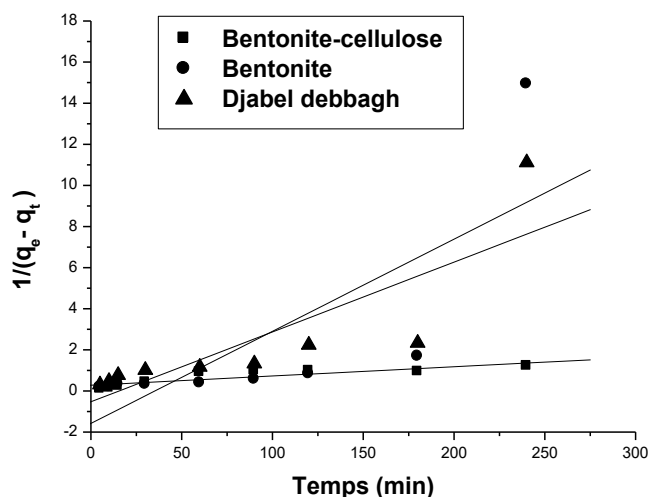| Adsorbate	Adsorbate	qe (mg/g)	K' (min'1.g/mg).	R²
Rodazine	Bentonitecellulose	21.31	0.006	0.999
	Bentonite	17.04	0.005	0.998
	Djabeldebbagh	13.88	0.003	0.999

Figure 10: Determination of the Constants Speed of the Second order of Adsorption of the Rodazine.

Table 11: Constant Speed of the Second Order Clays.

Adsorbate	Adsorbing	Kv(mn⁻¹)	R²
Rodazine	Bentonite-cellulose	0.019	0.78
	Bentonite	0.023	0.96
	Djabel debbagh	0.024	0.94

Table 12: Comparison of Quantity Adsorbee of the Adsorbate to Balance on Clays Between the Experiment and the Models Use.

Adsorbate	Adsorbing	q_e exp (mg/g)	qe cal (mg/g) pseudo second ordre	qe cal (mg/g) second ordre
Rodazine	Benton-ite-cellulo	21.821	21.31	3.585
	Bentonite	16.983	17.04	0.632
	Djabel deb-bagh	13.643	13.88	1.898

5. Determination of the Coefficients of Diffusion of Adsorption of Adsorbates on Clays.

5.1 Models Diffusion

With the aim of selecting the models best adapted to the mechanisms of diffusion intervening in the adsorption of the adsorbate on clays used we used the models established respectively by Sphan and Schlunder [31], for the external diffusion Morris , Weber and Urano Tachikawa for the diffusion intraparticulaire $dCt/dt = \beta_L S$ (Ct-Cs) Where S represents the specific surface of the adsorbent and βL the external coefficient of transfer. The concentration of the aqueous solution on the surface of the adsorbent is regarded as negligible at the moment T = 0 (Cs→0). Under these conditions operational, for t→0, Ct→Co. The previous equation can be reduced, for the first of contact, with: $dCt/dt = \beta_L S$ Co The coefficient speed of diffusion BLS can be obtained by determination of the slope at the origin of the Ct/Co curve according to time. To determine the coefficients of diffusion BLS of adsorption of adsorbate on Bentonite-Cellulose, Bentonite and Djabel Dabbagh have 25°C can be obtained by determination of the slope at the origin of the Ct/Co curve according to time. We notice on figure 11 a fast fall of the report of the concentration, and the time necessary to reach balance is shorter. The values of coefficient of diffusion in several cases are confirmed by the low values of the coefficient of correlation (table 14).
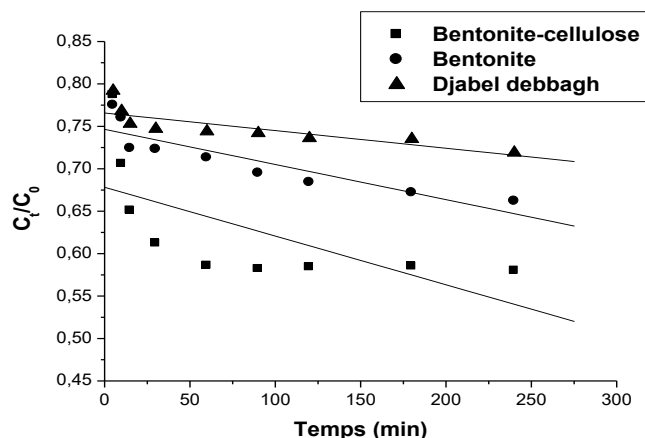
Figure 11: Determination of the Coefficients of the External Diffusion of Adsorption of the Rodazine on Clays Used.

Table 13: Value of the Coefficients of External Diffusion.

Adsorbate	Adsorbing	βLS (cm^{-1}) 10^{-3}	R^2
Rodazine	Bentonite-cellulos	0.6	0.656
	Bentonite	0.4	0.897
	Djabel debbagh	0.2	0.814

In this case of a diffusion intraparticulaire, Morris and Weber consider that the evolution of the concentration of the aqueous solution in the solid phase is a law in t 0.5:

Q = K t $^{0.5}$ with: Q: quantity of aqueous solution adsorbed per unit of mass of the adsorbent (mg/g) at time t, t: time (min), K: coefficient speed of diffusion intraparticulaire (mg.g-1 .min$^{0.5}$), the determination of the slope at the origin of the curve. Q = F (t $^{0.5}$) will make it possible to have access to at the speed of diffusion intraparticulaire. Urano Tachikawa envisages in its model of diffusion intraparticulaire, a linear variation of the function
F (qt/qe) = - Log [1 (qt/qe)^2 = 4Π^2Di/2.3d^2 t

the alignment of the points representative of the function will make it possible to conclude on the application from the model to the experimental results. qt: quantity of the adsorbate to time t (mg/g), qe: quantity of the adsorbate with balance (mg/g), D: average diameter of the particles of adsorbent, Di: coefficient of diffusion intraparticulaire (m^2 .min^{-1}).

For the diffusion intraparticulaire we modelled our experimental results with two models those of Morris and Weber (figure 12, table 15) and of Urano and Tachikawa (figure 13, table 16). According to the coefficients of correlation of the two studied models, one can say that the stage of the diffusion intraparticulaire is the limiting stage. This result suggests the transfer of the adsorbates through the boundary layer in solution towards interfoliaceous space constituting the structure of clays used is regarded as a determining stage of the phenomenon of adsorption.
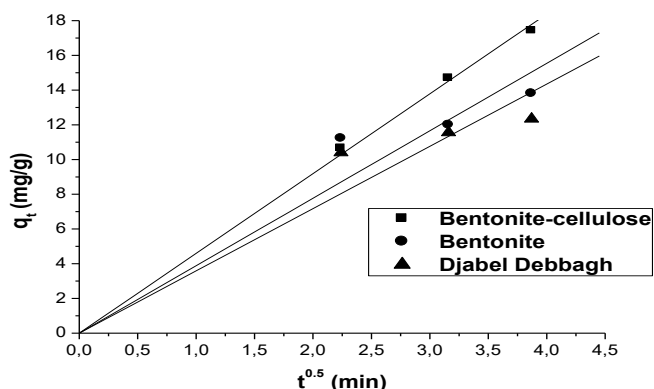

Figure 12: Determination of the Coefficients of the Diffusion Will Intra Particuliaire of the Adsorption of the Rodazine on the Clays Used According to the Model of Morris and Weber.

Table 14: Value of the Coefficient Intraparticulate Diffusion According to the Model of Morris and Weber.

Adsorbate	Adsorbate	K (mg^{-1}.min0.5)	R^2
Rodazine	Bentonite-cellulos	4.595	0.999
	Bentonite	3.885	0.955
	Djabel debbagh	3.587	0.999

Table 15: Value of the Coefficients of Intraparticulate Diffusion According to the Model of Urano and Tachikawa.

Adsorbate	Adsorbate	Di 10^{-15} (m^2.min^{-1})	R^2
Rodazine	Bentonite-cellulose	2.203	0.998
	Bentonite	2.535	0.956
	Djabel debbagh	4.358	0.999

5.2 Equilibrium of adsorption
To measure the isotherms of adsorption of the pesticide by Bentonite-Cellulose, Bentonite and Djabel Debbagh with 25°C, the duration of setting in contact solution adsorbent was fixed at 5h, time beyond which one is as sured that it there is no cative variation signify concentration of the pesticide to balance. This time of balance was selected on the basis of result of the kinetics of adsorption of the pesticide by clays used obtained which is about 4h.
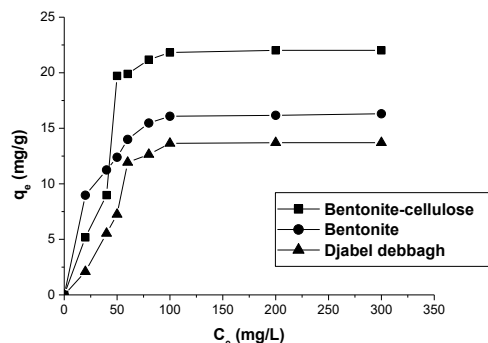

Figure 13: Isotherms of Adsorption of the Rodazine by Clays With 25°C.

According to Figure13, we observe that the isotherms of adsorption of the Rodazine on bentonite-cellulose, bentonite and djabel debbagh, have the same pace: the quantity of the dye increases quickly concentrations in solution, then attenuates to reach a plate trained correspondent with a saturation of the sites of adsorption, and representing an adsorption into full-course. The isotherm is obtained according to the classification of Gilles (26). The modeling of the isotherms of adsorption of the pesticide on clays by the model of Langmuir [34] which is written in the following way.

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

With: qe: Quantity of adsorbate adsorbed per gram of adsorbent to balance (mg/g), Ce: Concentration in adsorbate in the solution with equilibrium (mg/L) .qm: Capacity of adsorption to saturation (characteristic of the formation of full-course adsorbed molecules), (mg/g) Constant b: of equilibrium characteristic of adsorbent, depend on the temperature and the experimental conditions (L/mg), was carried out with the linearized form This Ce /qe = F (Ce).
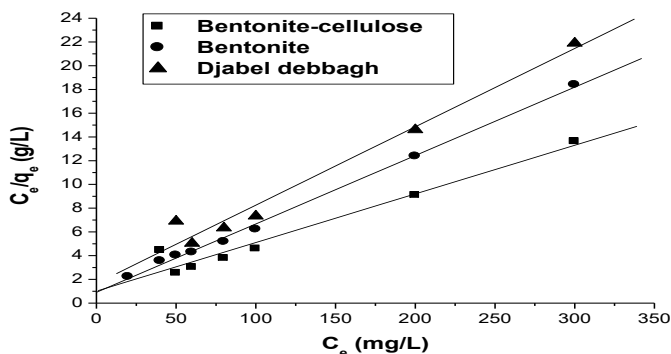

Figure 14: Modeling of the Isotherms of Adsorption of the Rodazine by Clays According to the Model of Langmuir.

According to Figure 14, we notice that the linearization of the isotherms of adsorption of the dye by clays is satisfactory with good coefficients of correlation. We can say that the model of Langmuir is adequate for a good description of these isotherms of adsorption. Values of qm obtained (TABLE 17) for the pesticide, idiot firment the trend observed previously while following the order of affinity of the pesticide on Bentonite-Cellulose, Bentonite and Djabel Debbagh.

Table 16: Constant of the Model of Langmuir.

Adsorbate	Adsorbing	qm(mg/g)	b (l/g)	R²
Rodazine	Bentonite-cellulose	24.426	0.040	0.977
	Bentonite	17.361	0.063	0.999
	Djabel debbagh	15.151	0.04	0.987

The model of Freundlich [35], is based on an empirical equation which represents a variation of energies with the adsorbed quantity, it is in the following form: qe = K C e n with: qe: Quantity of

adsorbate with balance. It Concentration of the adsorbate in the solution with balance. K: Constant of Freundlich (L/g) .n: Intensity of adsorption, n generally lies between 0 and 1, for n = 1, the isotherm is linear. The test results of modeling of the isotherms of adsorption of the pesticide by clays, according to the model of Freundlich, are represented on the fig. 15. According to the coefficients of correlation R 2 presented on Table 18, we deduce that the model of Freundlich is not adequate to model the isotherms of adsorption of the pesticide on Bentonite-Cellulose, Bentonite and Djabel Debbagh in all the field of the studied concentrations (26-39).
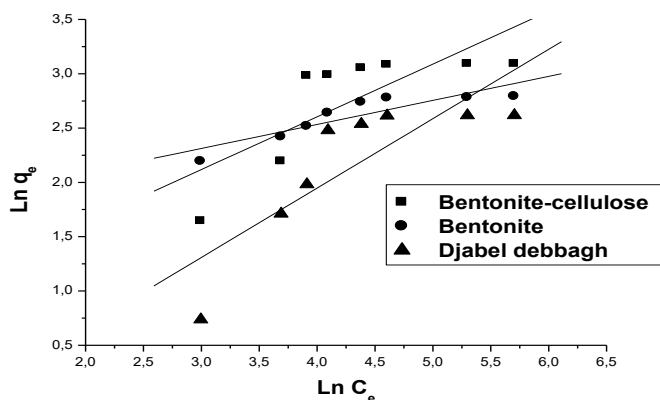

Figure 15: Modeling of the Isotherms of Adsorption of the Rodazine by Clays According to the Model of Freundlich.

Table 17: Constants of the Model of Freundlich.

Adsorbate	Adsorbate	n	K (l/g)	R²
Rodazine	Bentonite-cellulose	0.486	1.936	0.778
	Bentonite	0.221	5.199	0.894
	Djabel debbagh	0.639	1.837	0.833

Conclusion

The kinetics of adsorption of this pollution on Bentonite-cellulose, Bentonite and Djabel Dabbagh show that these clays are good adsorbents of pollution in aqueous solution. These kinetics are influenced by the studies of parameters: the temperature and agitation speed. The kinetics of adsorption of this pollution used on various clays, made it possible to select bentonite-cellulose like adsorbing with respect to the studied pollution. The kinetics of adsorption of the adsorbate (Rodazine) on clays (Bentonite-cellulose, Bentonite and Djabel Dabbagh) are of the same order (pseudo second order). The adsorption of pollution on these clays is a spontaneous and exothermic process characterized by a disorder of the adsorbent solution surface. The low values of the heat of adsorption confirm well that the interactions of various clays with pesticide are nature's physical in aqueous solution so it is a physical adsorption. The study of the diffusional mechanisms via the exploitation of the experimental data of kinetics by the two models of external diffusion and intraparticulaire, highlighted the preponderance of the diffusion intraparticulaire. The isotherms of adsorption of the

pesticides by clays are described satisfactorily by the model of Langmuir, wherea the model of Freundlich cannot describe our experiment al results on all the area of concentration studied.

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