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Removal of acetamiprid from aqueous solutions with low-cost sorbents

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ABSTRACT

The capacities of three Algerian clays as sorbents to remove acetamiprid insecticide from aqueous solutions were studied using a batch technique at room temperature. These clays were characterized using different methods, i.e. the X-ray fluorescence, FTIR spectroscopy, cation exchange capacity, and the specific area measurement. The static adsorption tests showed that the pH of the insecticide solutions, its temperature and agitation speed affect the adsorption process. Studies on acetamiprid retention showed that it is mainly influenced by the physicochemical properties of the clays used. Indeed, the adsorption results perfectly agree with the pseudo-second-order model, with very high regression coefficients (R^2). The pH and temperature increase influences negatively the adsorption operation. A positive ΔG value indicates that the removal process is non spontaneous with clays. The adsorption isotherm data follow the Langmuir equation in which parameters were calculated. In addition, results show that insecticide sorption on clays is an exothermic process and is higher with bentonite clay than with other clays. Therefore, the bentonite can be chosen as the material which presents a high adsorption capacity.

Keywords: Acetamiprid; Insecticide; Clays; Bentonite; Adsorption; Isotherms

1. Introduction

Pesticides have become one of the most frequently occurring pollutants in nature. Great concern has been developed about possible effects of such substances on human health and on the environment [1,2].

A large number of these chemicals, such as dichlorodiphenyltrichloroethane, technical hexachlorocyclohexane, and drin pesticides (aldrin, dieldrin and endrin), were widely used throughout the world, during the second half of the past century, to control malaria as well as for seed dressing to afford protection of stored grains against insect pests. However, Neonicotinoids are a type of synthetic insecticides that act on the central nervous system of insects and cause paralysis and death. Their broad spectrum of efficiency, good systemic properties, and low toxicity to warm-blooded animals make neonicotinoids the most widely used insecticides worldwide in recent years. Moreover, these compounds are the fastest growing type of insecticides introduced to the market due to their selective activity against numerous pest insects and their versatility for a wide range of agricultural practices. Neonicotinoid insecticides including imidacloprid, acetamiprid, and thiamethoxam are classified as II or III by WHO/EPA regulations. All

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neonicotinoid insecticides have similar chemical structures and the same mode of action [3–5]. The majority of these compounds is applied directly to the soil or sprayed over crop fields and hence they are released directly into the environment. These insecticides can therefore contaminate surface water directly through spray drift or run-off and also via drainage from treated soils. Increasing pesticide application and improper wastewater disposal methods have become a particular concern for the freshwater (surface and groundwater) as well as for coastal and marine environments [6].

In order to evaluate the environmental impact of neonicotinoid insecticides, numerous studies have reported contamination of water resources by these chemicals [7–13]. Advanced pesticide removal methods are usually needed to meet environmental quality requirements and improve the ecological system. These include combinations of biological, chemical, and physical processes. Adsorption has evolved into one of the most effective physical processes for pesticide removal because this technique uses equipment that is readily available, easy to use and not energy-intensive, and also because the treatment is cost-effective [14–18]. Though activated charcoal is undoubtedly an effective adsorbent for treating pesticide contaminated water, the high cost associated with it limits its large-scale application [19]. Thus in search of an effective and low-cost adsorbent, researchers have evaluated several naturally occurring materials like clays, especially montmorillonite and other adsorbents such as zeolites [19,20]. Thus, the aim of this paper is to study the effect of operating factors on the removal of neonicotinoid insecticides “acetamiprid” from aqueous solutions using natural clays from Algeria. The usefulness of clay materials originates essentially from their chemical and mechanical stabilities, and their various surface and structural properties. The effect of several physicochemical parameters, such as the pH of insecticide solution, contact time, temperature, and agitation speed and pesticide concentration, was investigated to better describe the adsorption process.

2. Materials and methods

2.1. Adsorbent materials

Three natural clays from Algeria were used in this study. The bentonite used in this work was extracted from the deposit of Hammam–Boughrara, in Maghnia (Tlemcen). It was supplied to us by the company (ENOF) of Maghnia (Tlemcen). The kaolin came from the deposit of Tamazert (Mila), and the clay of Djebel Debbagh was extracted from the deposit of Ain Barbar (Guelma), and supplied to us by the ceramics company of Ghazaouet (Tlemcen). The three natural clays were finely crushed.

Clay mineral compositions were investigated by X-ray fluorescence in the laboratory of quality control on cement works of Saida by the spectrometer of the pat of OXFORD-MDX 1000.

The specific area of the clay adsorbents was calculated by the Brunauer, Emmett and Teller (BET) equation using the adsorption data in the relative pressure. The isotherms of adsorption–desorption of nitrogen to 77 K were determined using the Micromeritics ASAP 2010 apparatus. The adsorbent samples were degassed at 250°C prior to the adsorption measurements.

Cation exchange capacity (CEC) of the clays was estimated using the displacement method of exchangeable cations by cobalt chloride. An amount of 1 g of clay was put in contact with 15 mL of cobalt chloride solution (0.05 N), and the mixture was shaken during 4 h, then centrifuged during 20 min, the cobalt (II) in the supernatant was assayed using a UV–visible spectrophotometer, and its final concentration was determined from a calibration line based on standard solutions, at a maximal wavelength of 470 nm.

The chemical composition, specific area, and CEC of clays are summarized in Table 1.

2.2. Reagents and equipment

The Neonicotinoid insecticide “Aceplan” was marketed in a powder form by the rival company in France; it was used without purification. The chemical structure of the activate ingredient of the acetamiprid insecticides is given in Fig. 1.

Before proceeding to the adsorption kinetics, it was essential to realize experiments to determine the maximal wavelength of which pesticide absorbance is maximal. The use of UV/Vis spectrophotometer, allowed us to find that absorbance is at wavelength 245 nm, using 1 cm square cells of quartz (Fig. 2).

3. Batch adsorption experiments

The adsorption tests were carried out using the batch technique, at room temperature (25°C). The batch adsorption process was selected due to its simplicity and reliability.

In each experiment, 300 mL of insecticide solution with a concentration of 100 mg/L was continuously stirred at 500 rpm with 1 g of clay at ambient temperature and natural pH of insecticide solution (pH = 7.03). The contact time ranged from 5 to 60 min, and the insecticide concentrations in the solution were

Table 1
Chemical analysis, specific area, and CEC of natural clays

% Mass	Bentonite	Kaolin	Djabel Debbagh clay
SiO_2	65.97	50.82	46.29
Al_2O_3	16.20	37.50	43.73
Na_2O	2.86	0.17	0.23
CaO	4.53	3.01	3.33
K_2O	2.15	2.60	1.80
MgO	2.89	0.71	0.60
Fe_2O_3	3.39	3.16	2.02
SiO_2/Al_2O_3	4.07	1.35	1.05
Specific area (m^2/g)	23.76	22.71	49.69
CEC (meq/100 g)	80	5.2	13.8

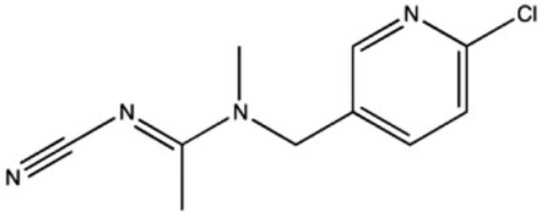

Fig. 1. (E)-N1-[(6-chloro-3-pyridyl-methyl]-N2-cyano-N1 methylacetamidine.

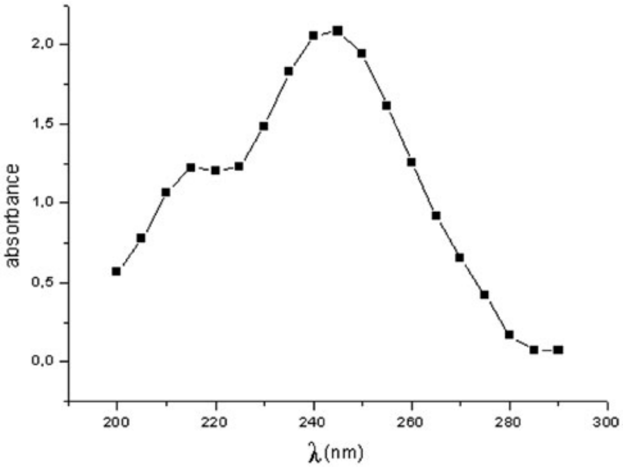

Fig. 2. Determination of the maximal wavelength of insecticide.

determined at given time intervals. After agitation, the suspensions were centrifuged at 2,500 rpm for 10 min, and the supernatant was kept and analyzed using a UV–visible spectrophotometer.

The UV–visible spectrophotometer gave the absorbance of each sample, from which the concentration could be deduced from the calibration curve which satisfied the Beer–Lambert law. Therefore, it became possible to determine the fixed quantity of insecticide q_t (mg/g) per gram of the adsorbent. This quantity was determined as follows (Eq. (1)):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \qquad (1)$$

where C_0 and C_t (mg/L) are the initial and time t insecticide concentrations, respectively, V (L) is the volume of insecticide solution and m (g) is the mass of adsorbent used.

4. Sorption isotherms

The sorption isotherms were established using clays suspensions in insecticide solutions, in a range from 20 to 300 mg/L. The experimental conditions were similar to those of the adsorption kinetics. The suspensions were stirred for 60 min, and then the supernatants were kept and analyzed using a UV–visible spectrophotometer.

5. Results and discussions

5.1. Characterization of adsorbents

5.1.1. Chemical composition

Table 1 presents the chemical composition of natural clays used as adsorbent in this study. These were found to contain a large percentage of SiO_2. The ratio SiO_2/Al_2O_3 for bentonite is in good agreement with that of montmorillonite, this ratio lies within the interval from 2 to 5.5 [21,22].

It was easy to notice that the chemical composition of the Algerian kaolinite is very close to that of the Indian kaolinite [23].

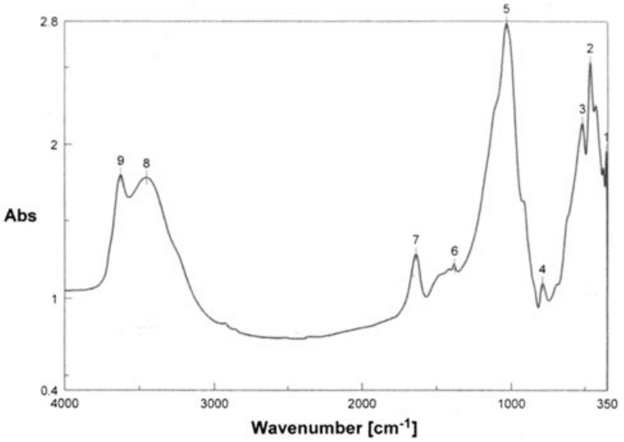

Fig. 3. Infrared spectra of bentonite.

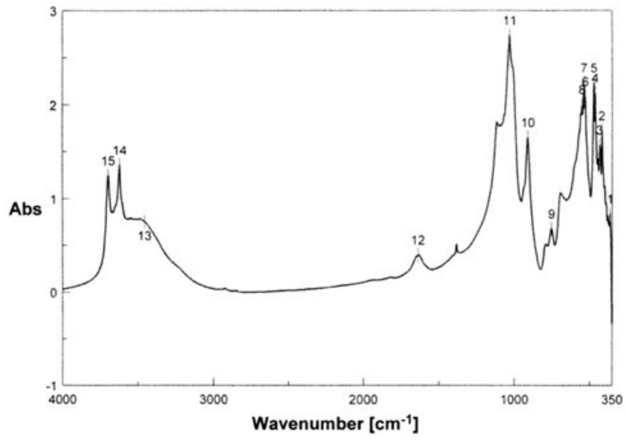

Fig. 4. Infrared spectra of Djebal Debbagh clay.

5.1.2. Specific area

The measured specific areas of three adsorbents are given in Table 1. The specific area of Djebel Debbagh clay is around 49.69 m^2/g. The bentonite and Kaolin have a specific area of 23.76 and 22.71 m^2/g, respectively.

5.1.3. CEC

Bentonite has a very large CEC compared to the kaolin and Djebel Debbagh clay. It is 5.2 meq/100 g for kaolin, 13.8 meq/100 g for Djebal Debbagh clay, and 80 meq/100 g for bentonite. The CEC of Djebal Debbagh clay lies within the same range as that of a clay of illite or chlorite type. The values found in the literature concerning CEC of bentonite and kaolin confirm the results obtained [21].

5.1.4. Infrared spectra analysis

The Infrared spectra of the clays are obtained, starting from the pastilles of KBr (0.1%) using a spectrophotometer. The infrared spectrums of the clays are given in Fig. 3, the band assignments for Bentonite, Djebal Debbagh clay, and Kaolin are shown in Table 2.

The FTIR spectra were recorded in the region of 400–4,000 cm^{-1}, the examination of these spectra reveals the principle absorption bands, and there is a very strong absorption of inner-OH at 3,623 and 3,695 cm^{-1} for bentonite, Kaolin, and Djebal Debbagh clay samples. Clay's samples showed a very strong but broad band of O–H–O at 3,452 and 3,455 cm^{-1} which indicates adsorption at the outer surface of the clay. However, the band between 1,300 and 1,700 cm^{-1} exhibits two peaks at 1,639 and 1,378 cm^{-1}, which correspond to the deformation of the OH bond, due to water molecules absorbed between the sheets (see Figs. 3–5). The broad bands around 1,033, 1,029, and 1,006 cm^{-1} correspond to Si–O-stretching. The 521, 548, 538, and 468, 472 cm^{-1} are related to the Al–O–Si and Si–O–Si deformations. For the clays, it appears that the Si–O and Al–O are the main sites of pesticide adsorption.

Table 2
Infrared data of Bentonite, Djebal Debbagh clay, and Kaolin

	Clays		
	IR frequencies (cm^{-1})		
Bands assignments	Bentonite	Kaolin	Djabal Debbagh Clay
ν_{OH} stretching vibration (H_2O)	3623, 3452	3695, 3622, 3439	3694, 3619, 3455, 3410
ν_{OH} deformation (H_2O)	1639, 1378	1639, 1385	1637, 1600
ν_{SiO} stretching vibration	1033	1006	1015, 1029
Quartz	790	913, 792, 694	911, 754, 805
$\Delta_{Si\text{-}O\text{-}M}{}^{VI}$ (M = Al, Mg, Fe)	521, 468, 360	548, 461, 418, 360	500, 538, 551, 529, 472, 462, 433, 417, 365

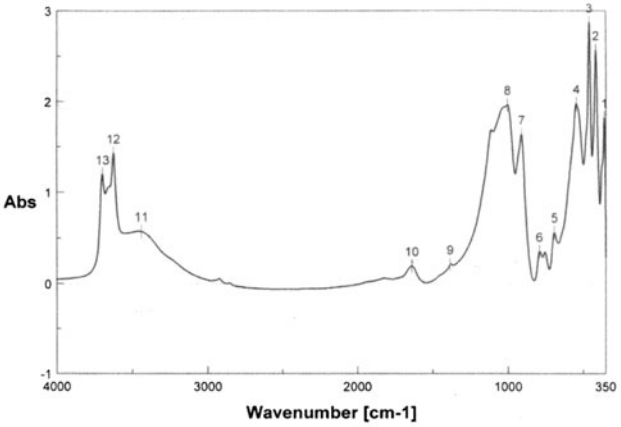

Fig. 5. Infrared spectra of Kaolin.

5.2. Application

5.2.1. Kinetics study

According to the results, kinetic adsorption of insecticide on clays turn out to be similar from the first minutes of contact, followed by an increase up to a state of equilibrium (Fig. 6).

The time of equilibrium was 30 min; the insecticide was adsorbed on different matrices with nearly the same kinetics, but a different adsorption capacity. This could be explained by the difference between the tested clays from their specific area point of view. On the other hand, the value of q_t for the bentonite as adsorbent was high compared to the two other clays.

At the equilibrium, the bentonite fixed more insecticide than the kaolin and Djebal Debbagh clay. The results obtained are summarized in Table 3.

Table 3
Results obtained at equilibrium

Clays	The mass fixed at equilibrium (mg/g)
Bentonite	7.49
Djebal Debbagh clay	6.67
Kaolin	6.56

The evolution of the initial pH of the solutions was investigated during the kinetic study; the data are represented in Fig. 7. For the kinetics of insecticide adsorption on clays, we noticed an increase in the initial pH value. To better understand this phenomenon, we studied the evolution of the pH of distilled water, free of any insecticide, in contact with the bentonite, Djebel Debbagh clay, and the kaolin under the same operating conditions as previously.

Fig. 8 shows a fast and important increase in the initial pH of distilled water, in the case of bentonite. As for the clay from Djebel Debbagh and the kaolin, this increase was low which means that the bentonite adsorbs more acid species than the Djebel Debbagh clay and the kaolin.

In order to optimize the conception of an adsorption system to remove the insecticide, it was important to establish the most appropriate correlation for the kinetic data for each system. Several kinetic models could be used to express the adsorption rate constants of solutions on solids. The adsorption kinetics was tested using the following well-known models:

The pseudo-first-order kinetics model which uses the Lagergren equation [24,25]:

$$\log \frac{(q_e - q_t)}{q_e} = -\frac{K_v t}{2.3} \tag{2}$$

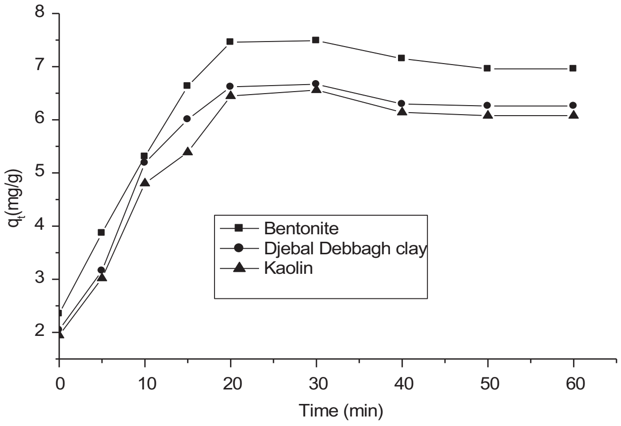

Fig. 6. Adsorption kinetic of insecticide on clays.

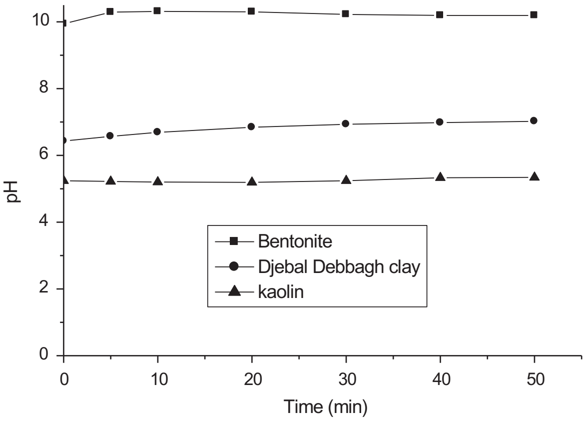

Fig. 7. Evolution of pH of insecticide in the presence of clays.

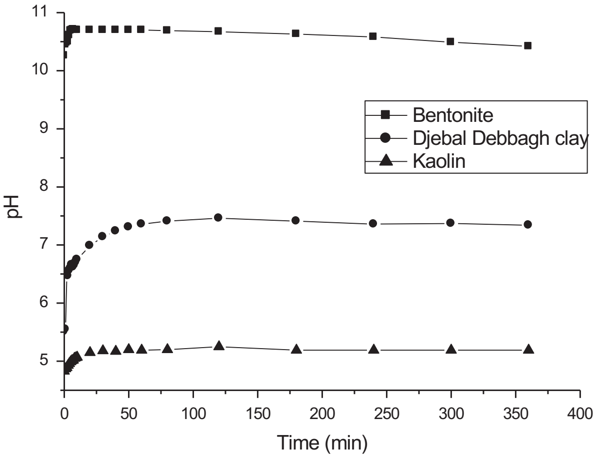

Fig. 8. Evolution of the pH of distilled water free from insecticide, in presence of clays.

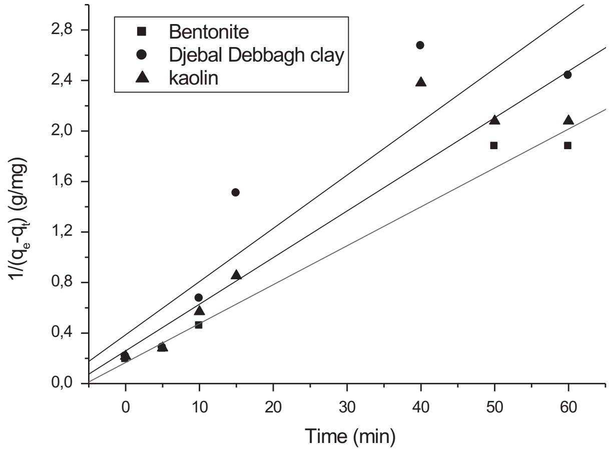

Fig. 9. Determination of rate constants for the second-order-model of insecticide adsorption on clays.

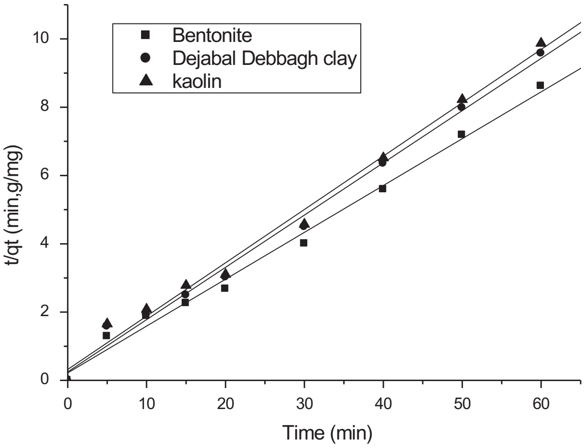

Fig. 10. Linearization of adsorption kinetics of insecticide on clays for the pseudo-second-order model.

For the second-order model, the adsorption rate constant k is given by the following relation [26]:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{3}$$

where, q_e and q_t are the amounts adsorbed per unit mass of adsorbent, at equilibrium and at any time t, respectively, and kv is the pseudo-first-order adsorption rate constant.

Pseudo-second-order kinetics [27,28]: The pseudo-first-order kinetics does not properly represent the kinetics of the adsorption process, and the pseudo-second-order kinetics may be applied using the linear equation,

$$\frac{t}{q_t} = \frac{1}{K_2' q_e} + \frac{t}{q_e} \tag{4}$$

where $k´$ is the pseudo-second-order adsorption rate constant. The kinetic models are shown in Figs. 9–11.

The validity of the studied models was further verified using the sum of errors (SE%) given by the following equation:

$$\text{SE} = \frac{100}{n-1} \sum \frac{|Qe, \exp - Qe, cal|}{Qe, \exp} \tag{5}$$

where n is the number of data points, reports that the fit is better when SE values are below 5. [29].

Experimental results (Tables 4–6) show low SE% values for three kinetic models. The pseudo-second-order kinetic model gives a good description of the adsorption of insecticide; this model is derived from adsorption processes where the rate-controlling step is an exchange reaction.

Only the pseudo-second-order model adequately described the kinetics of insecticide adsorption with a high correlation coefficient. The constants obtained from the slopes and intercepts are summarized in Tables 4–6.

Although the Lagergren plot was linear, it did not fulfill the essential condition of yielding the same q_e values as given by experiments. The pseudo-second-order kinetic plot of t/q_t vs. t was of better linearity ($R^2 = 0.994$), considering all the above results, the kinetics of insecticide adsorption on clays satisfies the pseudo-second-order equation.

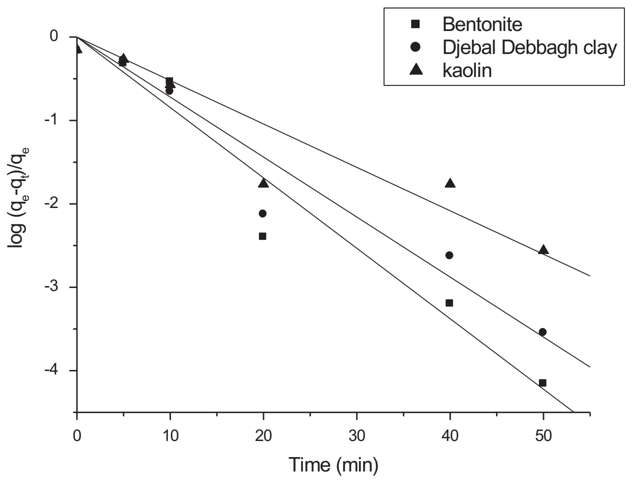

Fig. 11. Linearization of adsorption kinetics of insecticide on clays for the first-order rate.

Table 4
First-order rate constants

Parameters of first-order	kv(min^{-1})	R^2	SE(%)
Bentonite	0.193	0.953	0.320
Djebal Debbagh clay	0.165	0.944	0.209
Kaolin	0.131	0.918	0.09

5.2.2. Effects of pH

The pH of the solution may affect the adsorption process [21–23,27,28]. Studies on the influence of the pH of pesticide solution on the adsorption efficiency of clays were carried out in the pH range between 2 and 12.

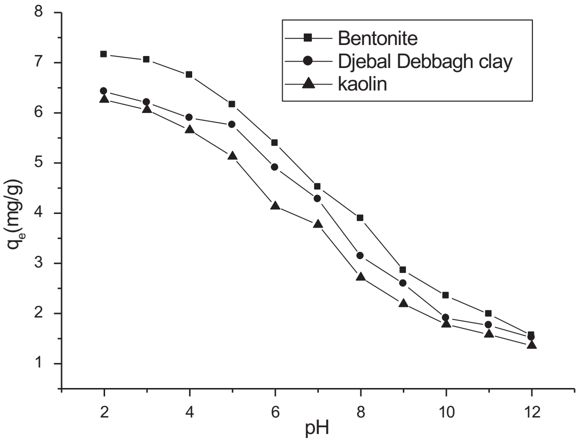

Fig. 12. Influence of the pH on adsorption kinetics of insecticide on clays.

Fig. 12 shows that the quantity adsorbed by clay decreases with increasing pH. The highest adsorption efficiency was obtained at pH 2, which is in good agreement with the results of other studies on pesticide adsorption [16,30,31]. The pH affected the properties of the sorbent surface. At very low pH, the surface of the sorbent would be surrounded by hydronium ions, and this could enhance the sorbate interaction with the binding sites of the sorbent because of the greater attractive forces, and consequently increase its uptake on polar adsorbents [32].

5.2.3. Effect of temperature and thermodynamic parameters

The effect of temperature on the adsorption of pesticides using different clays was studied in the

Table 5
Pseudo-second-order rate constants

Parameters of pseudo-second-order	q_e (mg/g)	K' (min^{-1} g/mg)	R^2	SE(%)
Bentonite	7.37	0.034	0.994	0.20
Djebal Debbagh clay	6.60	0.039	0.987	0.13
Kaolin	6.53	0.032	0.985	0.057

Table 6
Second-order rate constants

Parameters of second-order	q_e (mg/g)	K (min^{-1} g/mg)	R^2	SE(%)
Bentonite	5.98	0.059	0.962	4.03
Djebal Debbagh clay	6.02	0.064	0.951	1.624
Kaolin	5.84	0.044	0.931	1.829

temperature range from 15 to 55°C. For this purpose, 1 g of each adsorbent was added to 300 mL of the pesticide solution (100 mg/L). This study showed a slight decrease in the removal efficiency of pesticide when the temperature increases (Fig. 13).

The results show that the temperature has a significant effect on the adsorption. They indicate that pesticide adsorption on natural clays takes place with low energy attraction, hence the predominance of physical adsorption. [30–32]. The temperature increase made the pesticide to lower its affinity for the adsorbent surface, which is in agreement with other studies on pesticide adsorption onto various materials [30,32].

The determination of the thermodynamic parameters of insecticide adsorption by clays is a phenomenon accompanied by a thermal process [33] which could be exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$). Measuring the adsorption heat was the main criterion which allowed differentiating chimisorption from physisorption.

$$\Delta G = -RT \text{ Ln } K_c \tag{6}$$

The adsorption heat ΔH is given by the relation of Gibbs–Helmholtz [34–38]:

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

$$\text{Ln}K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{8}$$

$$K_c = \frac{(C_0 - C_e)}{C_e} \tag{9}$$

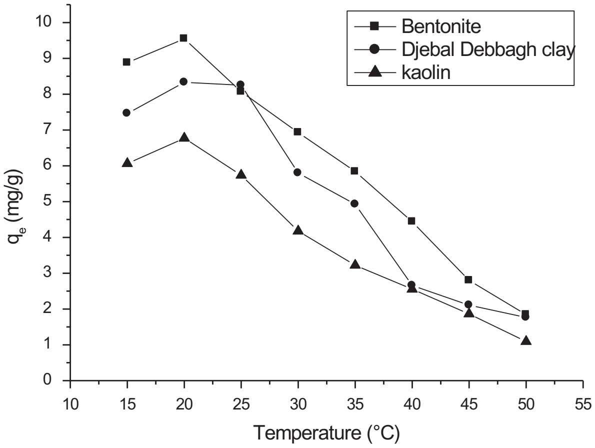

Fig. 13. Influence of temperature on adsorption kinetics of insecticide on clays.

where R is the ideal gas constant, T is the temperature (K), K_c is the distribution coefficient (amount of insecticide removed per gram of clay divided by its concentration in the liquid phase).

The thermodynamic parameters calculated from the slopes and the intercepts are shown in Fig. 14 and reported in Tables 7 and 8.

Insecticide-clay interactions took place through sufficiently strong exothermic interactions accompanied by thermodynamically favorable entropy and Gibbs energy changes. The influence of temperature (from 288 to 323 K) on the adsorption of insecticide on clays was investigated. The values of thermodynamic parameters showed that the adsorption process of insecticide on clays is exothermic. A positive ΔG value indicates that the removal process is non spontaneous with clays.

5.2.4. Sorption isotherms

The plot of the amounts sorbed as a function of the equilibrium concentrations C_e (Fig. 15) shows the insecticide sorption isotherms by clays. The adsorption capacity q_e is always increasing with C_e.

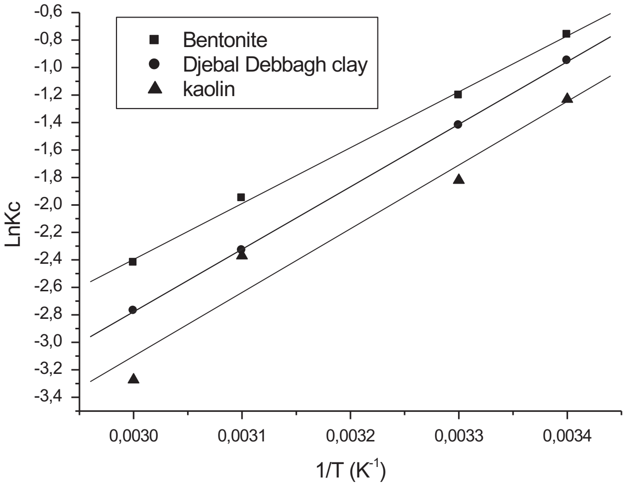

Fig. 14. Plot of ln Kc vs. $1/T$ for insecticide removal by clays.

Table 7
Values of thermodynamic parameters for insecticide removal by clays

	ΔH (kJ/mole)	ΔS (J/mole K)	R^2
Bentonite	−33.82	−121.38	0.998
Djebal Debbagh clay	−37.82	−136.51	0.999
Kaolin	−38.54	−141.33	0.949

Table 8
Values of thermodynamic parameters, for insecticide removal by clays, at various temperatures

	ΔG (kJ/mole)			
	288 K	293 K	303 K	323 K
Bentonite	1.137	1.74	2.95	5.38
Djebal Debbagh clay	1.49	2.177	3.54	6.272
Kaolin	2.16	2.86	4.28	7.109

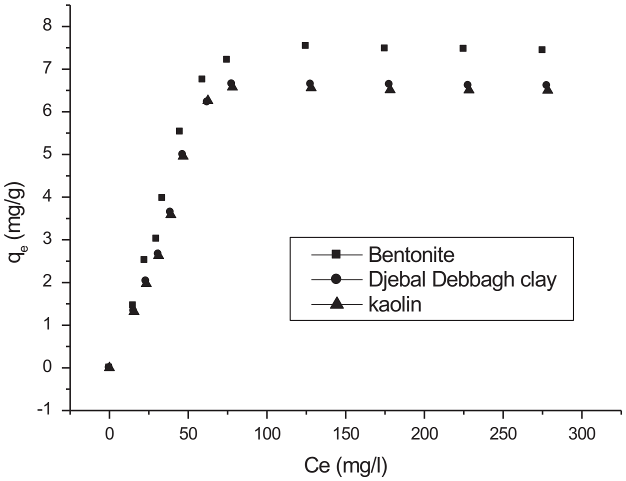

Fig. 15. Adsorption isotherm of acetamiprid removal by clays at 25°C.

The isotherms are in agreement with the Langmuir model or type I isotherm. At the highest concentrations in this range, the adsorption is weakly observed. Thus, the removal capacity is in the decreasing order: Bentonite > Djebal Debbagh clay > Kaolin.

5.2.5. Adsorption isotherms modeling

The adsorption equilibrium is usually described by an isotherm equation, whose parameters express the surface properties and affinity of the adsorbent. Adsorption isotherms can be generated based on theoretical models, where Langmuir and Freundlich models are the most commonly used ones [39]. The Langmuir model assumed that uptake of adsorbate ions occurred on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation may be written as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{10}$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium insecticide concentration (mg/L), q_m and b are Langmuir constants.

The Freundlich isotherm is suitable for a highly heterogenous surface. The empirical Freundlich [40] equation based on adsorption onto a heterogeneous surface is given:

$$q_e = KC_e^n \tag{11}$$

where K and n are the Freundlich constants for the system. The test results of adsorption isotherms modeling by Langmuir and Freundlich models are represented in Figs. 16 and 17 and reported in Tables 9 and 10.

The Langmuir model is also fitted for describing the sorption behavior of insecticide. However, the plot of C_e/Qe as a function of the equilibrium concentrations C_e shows the linearization of the isotherms adsorption. The values of q_m obtained confirm the tendency observed previously.

Table 9 shows that the Langmuir equation gave a fairly good fit to the sorption isotherm. The main characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which was defined as:

$$R_L = \frac{1}{((b \times C_0) + 1)} \tag{12}$$

where C_0 is the initial insecticide concentration. The R_L value indicates the shape of the isotherm as follows: favorable adsorption is indicated by $0 < R_L < 1$

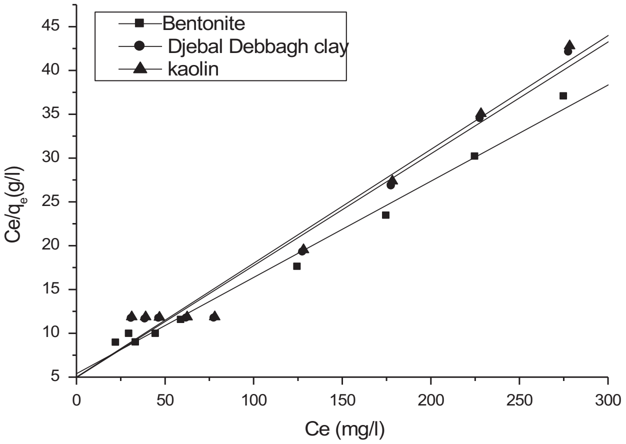

Fig. 16. Langmuir plot for the acetamiprid removal by clays.

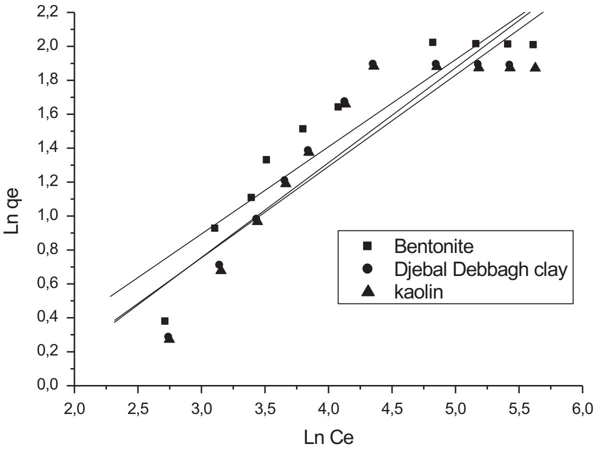

Fig. 17. Freundlich plot for the acetamiprid removal by clays.

Table 9
Parameters of the Langmuir model

Clays (mg/g)	q_m (mg/g)	B (l/g)	R^2
Bentonite	9.17	0.02	0.994
Djebal Debbagh clay	7.85	0.025	0.986
Kaolin	7.75	0.021	0.985

Table 10
Parameters of Freundlich model

	k	n	R^2
Bentonite	0.523	0.513	0.936
Djebal Debbagh clay	0.398	0.558	0.918
Kaolin	0.422	0.538	0.907

while $R_L > 1$, $R_L = 1$ and $R_L = 0$, describe, respectively, unfavorable, linear, and irreversible adsorption [41]. The R_L values calculated for the initial insecticide concentration (100 mg/L) are 0.333, 0.285, and 0.322 at 25°C, respectively. Hence, the adsorption of insecticide is favorable.

Table 10 summarizes the parameters of the Freundlich model. According to the correlation coefficients R^2 is obtained, we deduce that the Freundlich model is not adequate for the adsorption isotherms modeling of insecticide by clays.

6. Conclusions

Three Algerian clay samples: bentonite, kaolin, and Djebal Debbagh clay were used for the removal of insecticide from aqueous solutions. Good adsorption results were obtained with the bentonite under operating conditions of 30 min shaking time, natural pH of insecticide solution (pH = 7.03), 100 mg/L initial insecticide concentration, and 1 g/300 mL clay dose. The adsorption kinetics showed better agreement with the pseudo-second-order model. The adsorption kinetics of pesticide on clays allowed us to choose the bentonite as the best adsorbing clay. So the increase in the pH and temperature had a negative influence on the adsorption. The optimal operating parameters, pH of the solution and the temperature were selected as pH 2 and 20°C. A positive Δ*G* value indicates that the removal process is non spontaneous with clays. These results also showed that insecticide sorption on clays is an exothermic process. The insecticide sorption follows the Langmuir model with determination coefficients higher than 0.90 for the three materials. The adsorption is supported by Langmuir and Freundlich isotherms and the adsorption coefficients indicated favorable adsorption. This work has really enlightened the path to an interesting perspective in the field of pesticide removal with low-cost sorbents.

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List of symbols

CEC — cation exchange capacity
C_0 — the initial insecticide concentration (mg/l)
C_t — the insecticide concentration at time t (mg/l)
V — the volume of insecticide solution (l)
m — the mass of adsorbent used (g)
q_e — the amount adsorbed per unit mass of adsorbent at equilibrium
q_t — the amount adsorbed per unit mass of adsorbent at any time t
kv — is the pseudo-first order adsorption rate constant
k' — is the pseudo-second order adsorption rate constant
R — is ideal gas constant
T — is temperature (K)
K_c — is distribution coefficient (amount of removed insecticide per gram of clay divided by its concentration in the liquid phase)
ΔG — change in Gibbs free energy
ΔH — change in enthalpy
ΔS — change in entropy

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