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Adsorption Study of Carbofuran by Montmorillonite in Natural Water

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ABSTRACT

In agriculture, the use of pesticides is not only beneficial, but may also have negative consequences on the environment and human health. For this reason, understanding and studying the behavior of these products in different environmental compartments are of paramount importance to evaluate the impact of these pollutants on the environment. Adsorption remains the major phenomenon that controls the behavior of pesticides in soil. The goal of our study is to study the absorption of an extensively insecticide used in Morocco, carbofuran, in the presence of montmorillonite in natural water. The results show that the maximum adsorption of carbofuran is attained within 6 hours. Adapting data of adsorption to isotherms models of Freundlich and Langmuir allowed to deduce the values of the following adsorption parameters (n = 0.526; K_f =0.5) for Freundlich and (k_l=6.51; q_{max}=9.53) for Langmuir. Comparison of linear regression coefficients is in favor of the Freundlich model (r^2=0.9633>0.8639). Kinetically, adsorption of carbofuran on montmorillonite follows first- order model. The low retention of carbofuran by montmorillonite may be due to water competition that behaves as the solute to some adsorption sites and/or compensating cations Na^+, Ca^{2+} and Mg^{2+} present in our sample of natural water, which can saturate the surface sites of the montmorillonite.

Keywords: adsorption, clay, carbofuran, montmorillonite, natural water.

INTRODUCTION

The interaction of pesticides with the soil constituents regulates several agronomical and environmental phenomena. Adsorption remains the major phenomenon that controls their availability in soil, their mobility, and their efficiency with regard to their targets [1- 2].

The constituents involved often include clays, organic matter, minerals [3-6]. In water or soil, carbofuran degrades by hydrolysis, microbial decomposition and photolysis [7]. The maximum acceptable concentration for carbofuran in drinking water is 7µg/L [8]. Carbofuran degradation leads to several metabolites according to environmental conditions (pH, temperature, and ionic strength). The major metabolites included 3-hydroxycarbofuran, 3-cétocarbofurane, carbofuranephenol, 3-hydroxycarbofuranephénol and 3-cétocarbofuranephénol [1].

The evaluation of the retention is often made by means of adsorption isotherms adapted to models to deduce some useful environmental parameters for the assessment of the phenomenon [5-10]. In their study of the adsorption of carbofuran on the complex humic acid-montmorillonite, the adapted data to the Freundlich model has given values of K_f ranging from 0.30 to 157.6. The infrared analysis showed changes of the frequency bands C = O and C-N, indicating an interaction between the pesticide and the adsorbent. Furthermore, the adsorption studies are often done in distilled water under controlled conditions of temperature and pH. The adsorption in natural water can lead to different results because of the nature of water and its physicochemical composition. The goal of this study is to investigate the adsorption of carbofuran on montmorillonite in natural water.

MATERIALS AND METHODS

Sampling and physico-chemical analysis of surface water

The water-sampling site is located on the Sebou River in the Gharb region (Morocco), 45 km to the north of Rabat under the following GPS coordinates: 805-21-188E and 003-13-621N. 9. Samples are drawn and collected in clean glass bottles previously rinsed several times with distilled water, sealed and transported directly in a laboratory cooler for their analyses. The physicochemical analysis were made at the Institute of hygiene in Rabat. The pH and conductivity were measured using a pH meter and a conductivity meter model WTW 3110 SET1.

Chromatographical analysis

To ensure the absence of any trace of pesticide in the studied sample, an analysis was performed by gas chromatography coupled to mass spectrometry (QMS Polaris ion trap). The analysis conditions were the following: VB-5 column, at 220°C and 300°C for the injector and the oven respectively, in split less mode for one volume 1µLwith helium as a carrier gas at a flow rate of 1 mL/ min. The temperature of the ion source was 200°C. The conditions of programming of separation were shown in Table 1.

Table 1: The chromatographical conditions of separation

Ramp (°C/min)	Final Temperature(°C)	Time (min)
	100	4.00
10	150	0.00
5	240	1.50
15	280	6.00

During the study of the adsorption, carbofuran was analysed by AGILENT 1100 HPLC, equipped with a C18 column, the mobile phase is a mixture of methanol and distilled water (50% / 50%) with a flow rate of 1mL/ min. The UV detector was set at 285nm. The injection volume is 50µl.

Adsorption study

The calibration curve

A 100-ppm stock solution of carbofuran (purity 99.9%) was prepared and diluted to lead to concentration of test solutions ranging from 1 ppm to 20 ppm, which were used to plot the calibration curve.

Adsorption kinetics of carbofuran

The batch technique was used to study the process of adsorption of carbofuran. Test tubes contain 200mg of clay and 10ml of natural water, comprising carbofuran at a fixed concentration of 15 ppm. During experiment, an oscillating stirrer agitated them. The samples were taken at regular time intervals (T_0, T_{0+1}; T_{0+2},…….T_{0+7h}). The samples are centrifuged at 6000 rpm / min and a volume of 50 µL of the aqueous phase is injected into HPLC. Three replicates were performed for this test at an ambient temperature (22±2 °C).

Modeling the adsorption kinetics

The kinetic modeling of carbofuran retention by montmorillonite was conducted using the following two models:

✓The linear form of the kinetic model of the pseudo first order [11]:

$$\log(Q_i - Q_t) = \log(Q_i) - \left(\frac{k_1}{2.303}\right) \cdot t$$

With: - Qi: Quantity of initial adsorbate per gram of adsorbent ($mg.g^{-1}$)

- t: Contact time (hour);
- K_1: Constant adsorption rate for the first order ($time^{-1}$).

✓The linear form of the kinetic model of the pseudo second order: $\frac{t}{Q_t} = \frac{1}{k_2 \cdot Q^2} + \frac{t}{Q_t}$

With: -K_2: Constant adsorption rate for the pseudo-second order ($g.mg^{-1}.h^{-1}$).
- Qi: Quantity of initial adsorbate per gram of adsorbent ($mg.g^{-1}$).
-t : contact time in hours

The initial amount adsorbed Qi, constant pseudo-second order K_2 can be determined experimentally from the slope and intercept of $\frac{t}{Q_t}$ based on t.

Adsorption isotherms

Different Carbofuran concentrations (1, 2,5, 5, 10, 15,20 $mg.L^{-1}$) were prepared in natural water in the presence of 200mg of clay, the solutions obtained are stirred at ambient temperature for a fixed time duration equal to the predetermined equilibrium time during the kinetic study. Three replicates were performed for each concentration.

The amount of pesticide retained by the clay (Q_{ads}) is calculated by the difference between the initial concentration C_o introduced and the equilibrium concentration (C_e) according to the following relationship:

$$Q_{ads} = \frac{(C_o - C_e).v}{m}$$

Modeling the adsorption isotherms

Two models are frequently used in the literature to describe the adsorption of molecules in the solid- and solution interface: models of Langmuir and Freundlich.

The proposed equation to describe the Langmuir isotherm [12] is:

$$Q_{ads} = q_{max} \cdot \frac{(K_1 \cdot C_e)}{1 + K_1 \cdot C_e}$$

With: - C_e (mg/L): the concentration of adsorbatein solution at equilibrium,

- Q_{ads} (µmol/m²): the amount of adsorbent is fixed by the surface unit of adsorbent,
- q_{max} (mg/g) : the amount adsorbed at saturation is the maximum number of adsorption sites occupied per surface unit,
- - K_l (L/mg): constant affinity of the adsorbate for the surface of the adsorbent.

The Freundlichmodel is frequently used to describe the adsorption isotherms; it is defined by the following equation:

$\mathbf{Q_{ads} = K_f . Ce^n}$

With: - Q_{ads} ($mg.Kg^{-1}$): the amount of absorbed pesticide per mass unit adsorbent at equilibrium;
- C_e ($mg.L^{-1}$) : the pesticide solution concentration at equilibrium;
- K_f ($Ln.mg^{1-n}.Kg^{-1}$) and n: Freundlich constants.

For n equals to 1, the sorption isotherm is simplified through a linear relationship: $\mathbf{Q_{ads} = K_d . C_e}$

With K_d, the distribution coefficient (or partition coefficient) of the pesticide between the liquid phase and the solid phase.

Analysis of clay

Clay sample used is a montmorillonite, origin of Almeria, Spain. It was analysed by X-rays powder diffraction in order to identify its chemical structure. The apparatus used was X'PERT MPD PRO, configuration PW 3064/xx Spinner – PANALYTICAL.

The analysis conditions were: Start angle (2θi): 3°, final Angle (2θf): 90°, Step size= 0.06. Counting time: 120s.

RESULTS AND DISCUSSION

The physico-chemical characteristic of natural water

The physicochemical properties of the water used are presented in Table 2. According to the Moroccan standards [13], our sample is rated between excellent and good and as little to medium hard (limestone).

Table 2: physicochemical characteristics of natural water

parameters	values
pH	7.49
Conductivity	560µs/cm
Ca^{2+}	54.51 $mg.L^{-1}$
Mg^{2+}	20.91 $mg.L^{-1}$
Na^{+}	56.8 $mg.L^{-1}$
NO_3^{-}	5.14 $mg.L^{-1}$
Cl^{-}	110.05 $mg.L^{-1}$
SO_4^{2-}	55.05 $mg.L^{-1}$
HCO_3^{-}	176.9 $mg.L^{-1}$
Organic material	1.34 $mg.L^{-1}$
TH (Hydrotimetric index)	23.2

The obtained results by gas chromatography affirm that no trace of pesticide was detected in natural water solution.

X-ray diffraction analysis of montmorillonite

After phase identification (figure 1), the chemical structure of the clay is the following, a montmorillonite15A: $NaO._3$ (Al, Mg)2 Si4 O_{10} (O H)$_2$ -4 H_2 O.

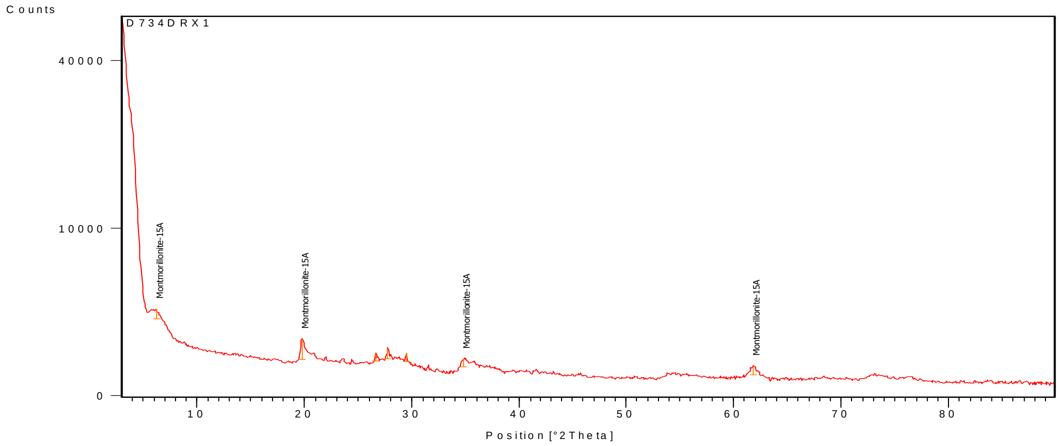

Figure 1: X-ray diffraction of montmorillonite used

Variation of carbofuran concentration in natural water in presence of clay

The variation of the carbofuran concentration over time in the presence of clay is illustrated in Figure 2.

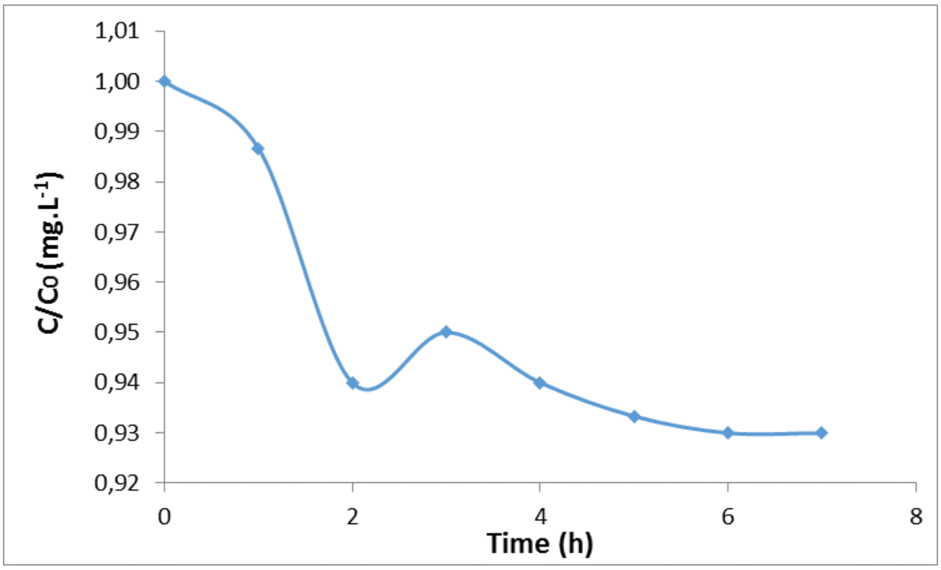

Figure 2: Variation of the carbofuran concentration over time

The variation of the carbofuran concentration over time shows a rapid decrease after 2 hours, followed by a slow achievement of equilibrium between the solution and the adsorbed quantity. The rapid decrease in the carbofuran concentration in the solution can be essentially assigned to its adsorption on clay.The phenomenon of hydrolysis could be rejected since the carbofuran does not hydrolyze, before 240 hours at neutral pH, which pH is close to that of our study (pH = 7.49) [14].

Kinetics of carbofuran adsorption

The layout of pesticide amounts retained on the clay over time of clay-pesticide contact is presented in figure 3.

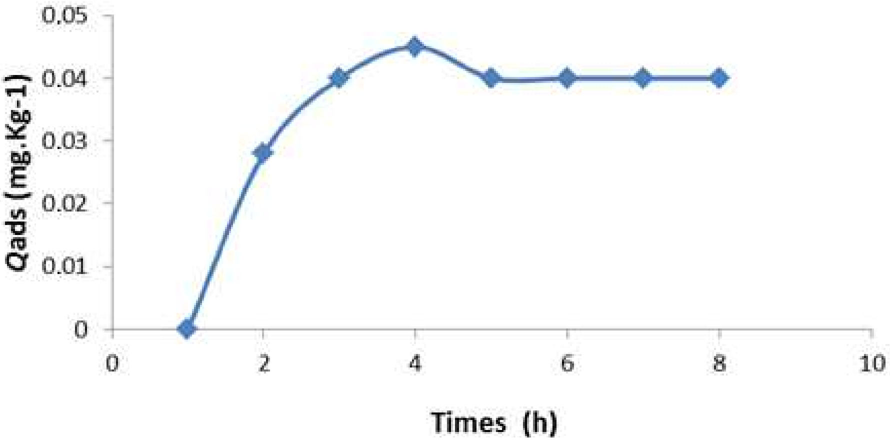

Figure 3: Kinetics of adsorption of carbofuran at 22±2 °C

The shape of the curve indicates adsorption kinetics composed of two parts. Part I is relatively rapid within 4 hours followed by an equilibrium phase such phenomenon reported by other authors [15-17].

During the rapid phase, a high proportion of carbofuran was adsorbed in less than 6 hours. This step would correspond to the adsorption of the pesticide on the most accessible sites probably located on the outer surfaces of the soil particles [18-20]. Similar results were reported on the active carbon [21]. In the second phase, the adsorption of carbofuran continues, but more slowly. This limitation of the adsorption rate can be due to the saturation of the sites or to the competition with water, which acts as a solute for some adsorption sites [22]. In addition, many compounds dissolved in the natural surface water can affect the adsorption process by competing with the pesticide molecules for adsorption sites [23].

In fact, the predominant cations in our natural surface water (Ca^{++}, Mg^{++}, Na^{+}) may be involved in the mechanisms of adsorption, particularly by formation of cationic bridges and saturation of the clay. These results are in agreement with those found by Pitsch et al. [24], who showed that different adsorption sites present on the clay surface are gradually saturated by compensating cations introduced into the environment, along the way as the pH increases.Other authors reported the difference in behavior of these cations in contact with the clay surface as [25-5-26].

The effect of pH on the adsorption of carbofuranhas also been studied [27-28], who reported that the adsorption of carbofuran increases as the pH decreases. At high pH, adsorption decreases, this may be due to masking carbofuran's functional groups, and the repulsion by the clay surface negatively charged.

It has been observed that a change in pH of the solution may alter the properties of pesticides' molecules as well as the clay surface properties and, consequently, its adsorption, [29]. Salmanet et al. also reported the possibility of modifying the surface's properties of activated carbon according to the pH of solution [28].

Modeling the adsorption kinetics

The treatment of the kinetics' data based on the two tested models yields the kinetic parameters presented in table 3. The corresponding linear curves of regression are presented in figures 4 and 5.

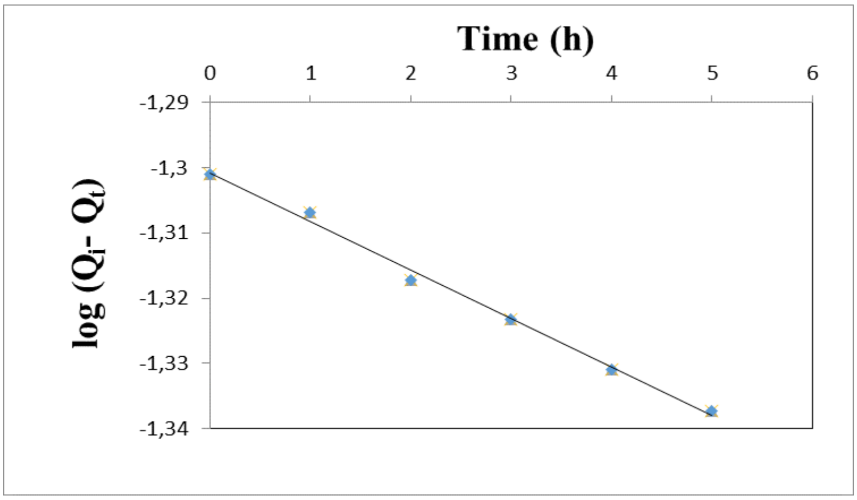

Figure 4: Linear regression curve, according to pseudo-first order kinetic mode

Table 3: The constants of the kinetics

pseudo-first order			pseudo-second order		
K_1 (h^{-1})	R^2	Q_e ($mg.g^{-1}$)	K_2 ($g.mol^{-1}.h^{-1}$)	R^2	Q_e($mg.g^{-1}$)
0.0074	0.9946	1.3	0.3519	0.9468	20.065

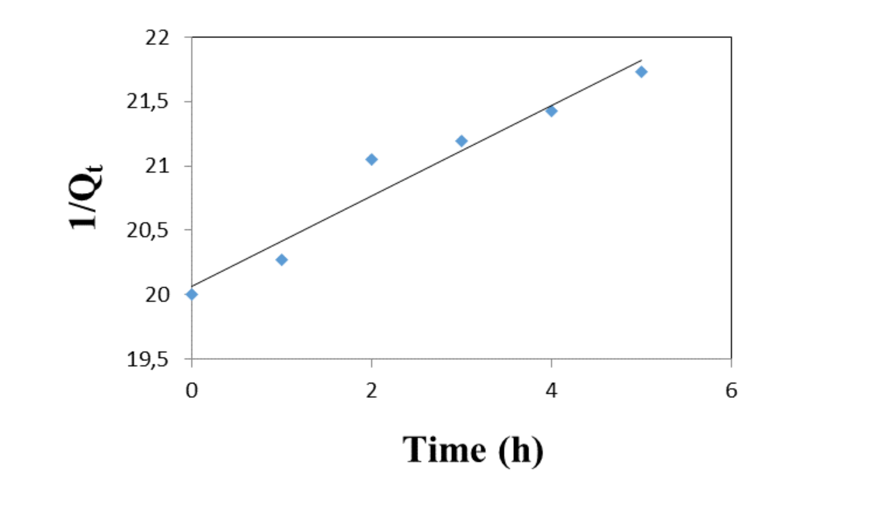

Figure 5: Linear regression curve, according to pseudo-second order kinetic model

The isotherm of carbofuran adsorption

The isotherm of carbofuran adsorption is obtained for concentrations varying from 1 to 20 mg.L^{-1}. The six-hour-contact time was predetermined during the kinetic study (fig. 6). The variation of the adsorbed quantity increases regularly depending on the equilibrium concentration and reaches equilibrium in the range of 10 and 15 mg.L^{-1}.

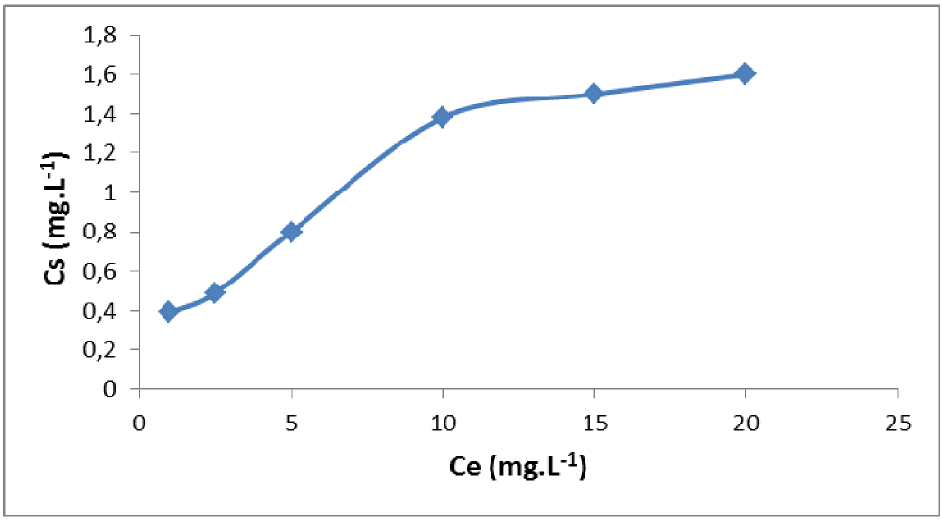

Figure 6: isotherm of carbofuran adsorption

The isotherms of this class present, at a weak concentration, a concavity facing upwards. In such case, the adsorbed molecules favor the further adsorption of other molecules. This is due to molecules that get attracted by forces of Van Der Waals and group together [30].

Modeling the isotherms of carbofuran's adsorption

Models of Langmuir and Freundlich

The treatment of data, according to models of Freunlich, and Langmuir, has enabled to determine the adsorption parameters relative to the two models (table 4).

The comparison between regression coefficients (r^2) shows that the carbofuran's adsorption isotherm is better described by the Freundlich model, rather than by the Langmuir one (r^2 Freunlich > r^2 Langmuir). This model is generally obtained in the case of micro porous adsorbents, with a progressive saturation of the adsorption sites that are roughly equivalent. Similar results were pointed out by others authors [21].

The adsorption of molecules to the solid-solution interface, according to the Freundlich model, is made in heterogeneous surfaces, comprising different types of adsorption sites, whereas the Langmuir model describes an adsorption at the level of homogeneous sites [31-32].

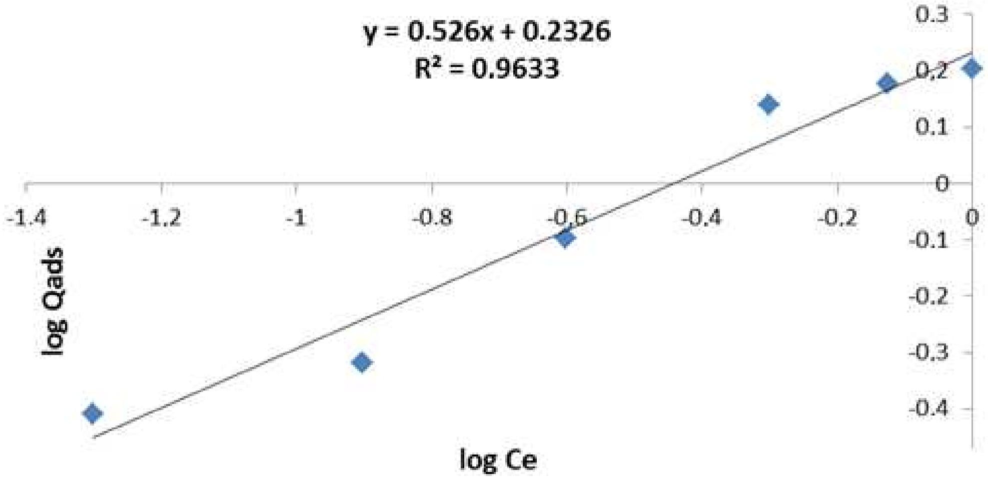

Figure 5: Linearization of the carbofuran's adsorption isotherms, by the Freundlich model

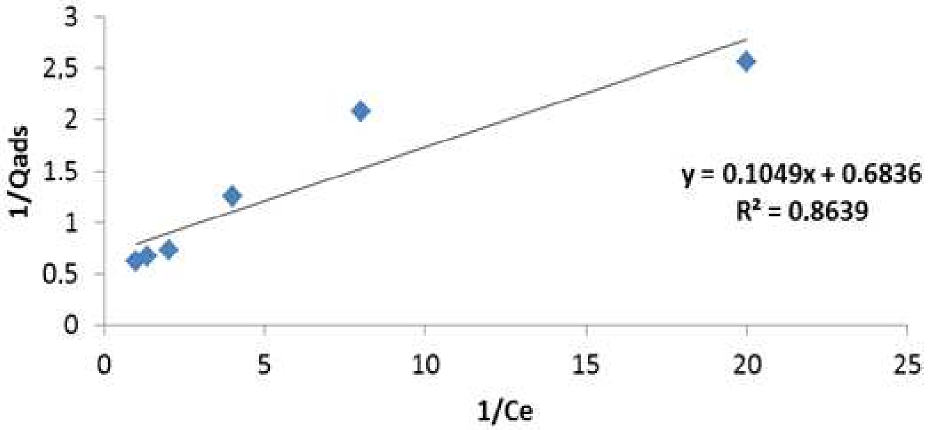

Figure 6: Linearization of the carbofuran's adsorption isotherms, by the Langmuir model

Table 4: The parameters and correlation coefficients, Langmuir and Freundlich for the carbofuran adsorption on the montmorillonite at 22± 2°C

Isotherms Model	Parameters		
Langmuir	q_{max} (mg. Kg^{-1})	K_l (L/mg)	R^2
	9.53	6.51	0.8639
Freundlich	K_f(Ln.mg^{1-n}.Kg^{-1})	n	R^2
	0.5	0.526	0.9633

The carbofuran adsorption is not linear (n<1). This signifies a decrease of the available adsorption sites when the concentration of the solution increases. The solid is saturated during the filling of the monolayer. There will, be thus, weak interactions at the surface of these supports, as was stipulated by Avom et al. [33] with other organic components.

Furthermore, the constant of Freunlich K_f attests the capacity of adsorption of a pollutant considered by the solid [34]. The more the K_f value is high, the more the retained quantity is substantial. In our case, the obtained result of K_f is 0.5, reflecting a moderate adsorption of carbofuran on the montmorillonite in the presence of natural water.

The analysis of data regarding the quick adsorption part shows linearity between the adsorbed quantity and the Ce. This attests a perfect proportion between these two quantities and enables to estimate the partition coefficient $K_{d.}$

The calculation is made using the relation $K_d=\frac{C_s}{C_e}$, assuming linearity in the rapid phase. So, $K_d = 2.8mL.g^{-1}$.

To conclude, the adsorbed quantity of carbofuran via the montmorillonite is weak. This type of clay presents a very weak affinity to the carbofuran, in the presence of natural water.

CONCLUSION

The retention of carbofuran by the montmorillonite is moderate in the presence of natural water. The compensating cations can play an important role in the saturation of sites on the surface of the montmorillonite, which triggers a competition between the pesticide molecule and the cations.

The kinetic study has revealed that the adsorption is quick during the first contact hours to attain the equilibrium within 6 hours. The kinetic data shows the kinetic model of the first-order.

The Freunlich model describes better the carbofuran's adsorption isotherm, than the Langmuir model. The Freundlich model $K_f(Ln.mg^{1-n}.Kg^{-1})$ and the distribution coefficient K_d are of the order of 0.569 and 2.8 $ml.g^{-1}$, respectively.

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