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Research Article

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Removal of organophosphoriques pesticide from aqueous solution by dam silt

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ABSTRACT

This study was conducted to assess the removal efficiency of pesticide (organophosphorés) used, on a clay originated from barrage situated in a west of Algeria. The adsorption of pesticides from aqueous solution by local clay as a low-cost, natural and eco-friendly adsorbent was investigated. Different physicochemical parameters were analyzed: adsorbent mass, initial concentration of pollutant, and pH. The empirical results showed that all these parameters have an impact on the retention of pesticide on the clay. The equilibrium uptake was increased with an increase in the initial pesticide concentration in solution. The results of adsorption were fitted to the Langmuir and Freundlich isotherms. The Freundlich model represented the adsorption process better than Langmuir model, the exploitation of these isotherms follows the Freundlich model shows that the coefficient n obtained is within the range expected by Hassler 0.2-0.8, which is found that the mud is a good adsorbent for our pesticide.

Keywords: pesticides; Clay; Adsorption Isotherms; Water Treatment

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INTRODUCTION

Using pesticides has become a common practice in the agricultural sector. Though those products improve the percentage of yields, their use enhances more and more questions about their impact upon human health as well as environment. The potential risks of human health are noticeably seen through the detection of pesticides resi- dues in water, foodstuffs and even in breast milk [1,2].

The objective of applying pesticides is to protect plant against damage. However, crops can't absorb only a part of the pesticides quantity. The rest is exposed to evaporation volatilization and infiltration in order to create a contamination to groundwater.

Therefore, we are interested in to eliminate methylparathion by the adsorption process under static conditions that is a pesticides organophosphores, widely used in agriculture [3].

The adsorption remains a broadly used technique and easy to implement. The activated carbon is the most used adsorbent due to its extreme capacity of adsorption of organic materials [4]. However, this adsorbent has a high cost and remains difficult to regenerate for multiple uses. The search of another efficient and less expensive ad sorbent is an interesting task. In this context, the utilisation of the clay as an adsorbent has a great interest due to its efficiency and availability [5].

In this work, the adsorption capacity for methylparathion reactive was determined using local clay, which is a natural and available adsorbent . This adsorbent was used in its unprocessed state (size of particles < 2 µm). The parameters that influence adsorption such as pesticide initial concentration, contact time, adsorbent mass, solution pH. The description of the adsorption of the isotherm was done by applying linear transformations of two isotherms: Langmuir and Freundlich models.

EXPERIMENTAL SECTION

The silt used in this investigation was recovered from CHOURFA dam (western Algeria). The mass ratio SiO_2 / Al_20_3 is 3, 21. This may account with the high SiO_2 content. Some authors present this report as the index characteristic of montmorillonite when its value varies between 2 and 5.5. Mud was characterized by X-ray diffraction, using a Philips X-ray generator Type PW 1830 with a copper anticathode. The spectrum of X-ray diffraction shows that the mud is a mixture of montmorillonite, illite, kaolinite, the presence was noted: quartz as a major impurity in the mud and calcite. This composition is justified by the characteristic peaks (Fig I.) [1]. the specific surface area is calculated by the BET method [2, 3], using a machine such as achromatic Autosorb and is equal to 70.84 m2 / g. The clay is also characteerized by the utilization of dispersive energy of spectroscopy (EDS, type. The elements that constitute the clay are given in atomic and mass percentage in Table 1.

2.1. Activated materials

A-Sedimentation

An amount of 20 g of clay and 1 liter of distilled water are stirred mechanically for 2 hours to disperse the clay particles. This suspension is allowed to stand for 19 hours in 1 liter of test specimens. We siphon top part of the suspension to a height of 80 cm (corresponding to about 800 ml volume of the test). Then added with distilled water in the tubes, the suspension mixed thoroughly, is left settle and siphon again the upper part. This process is repeated until the fluid is clear to a height of 10cm. The recovered volume was centrifuged at 4500 tr / min for 15 min, after which the recovered amount of clay is dried in an oven at a temperature of 105 ^{0C}. The recovered powder is clay which the particle diameter is less than 2μ m, the performance of this operation is very low, it is of the order of 7 to 8%.

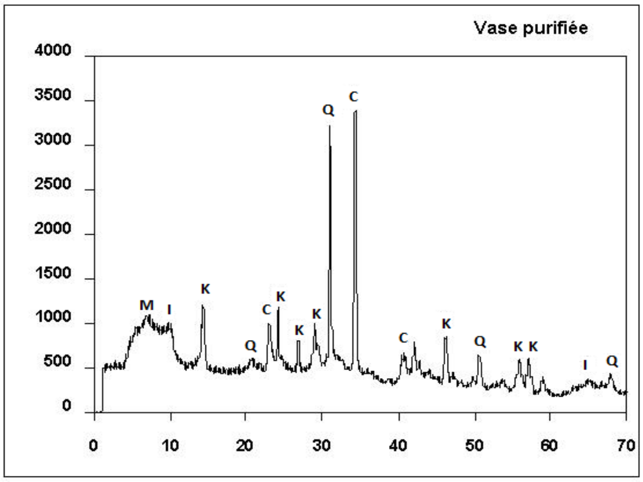

Figure 1: XRD patterns for raw silt. Montmorillonite (M), illite (I), kaolinite (K), quartz (Q), calcite (C)

Table 1. Mass percentage of the clay constituents

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	PAF*
	29.36	09.21	3.83	18.12	1.33	0.2	0.89	0.54	36.5

**PAF: perte au feu à 900 °C*

The methylparathion used in this study was purchased from Sigma-Aldrich and used without further purification. The chemical structure of the pesticide (λmax = 280 nm) is depicted in Figure 4. All methylparathion solutions used in this study were prepared by weighing and dissolving the reflasks where 100 ml of méthylparathion quired amounts methylparathion in distilled water.

Adsorption tests were performed in a set of erlenmeyer solutions with initial concentrations of 20 - 60 mg/l were placed in these flasks. Equal mass of 1 g/l of the clay was added to each flask. The pH of the solutions was original without any pH adjustment (6.7). The amount of adsorption at equilibrium, Qads (mg/g), was:

$$Q_{ads} = C_0 - C_e / R$$

Q_{ads}: Quantity of pesticide adsorbed per gram of ad- sorbent (mg/g).
C_0: Initial concentration (mg/1).

C_e: Equilibrium concentration (mg/l).
R: Mass of adsorbent per litre of aqueous solution (g/1).

RESULTS AND DISCUSSION

3.1. Adsorption Kinetics

The kinetic study of adsorption is an important step to evaluate the contact time necessary for reaching the equilibrium. The kinetics is achieved at initial pH of the solution for an initial concentration of 20 ppm, with a mass of clay of 1 g/1 and at T = 20˚C. The variation of the quantity adsorbed by the pollutant as function of time is illustrated in **Figure 2**.

It is clear from **Figure 2** that the amount of méthylparathion adsorbed, Q_{ads} increased with time. The equilibrium adsorption was achieved in 60 min for méthylparathion solution. According to this result, we can conclude that adsorption kinetic presents two distinctive steps. The first step corresponds to the transfer of external mass while the second is related to diffusion phenomena (transfer of internal mass).

The adsorption can be controlled by the step of the transfer of adsorbate through the external liquid film and/or that of diffusion of the solute inside the adsorbent particles [6,7].

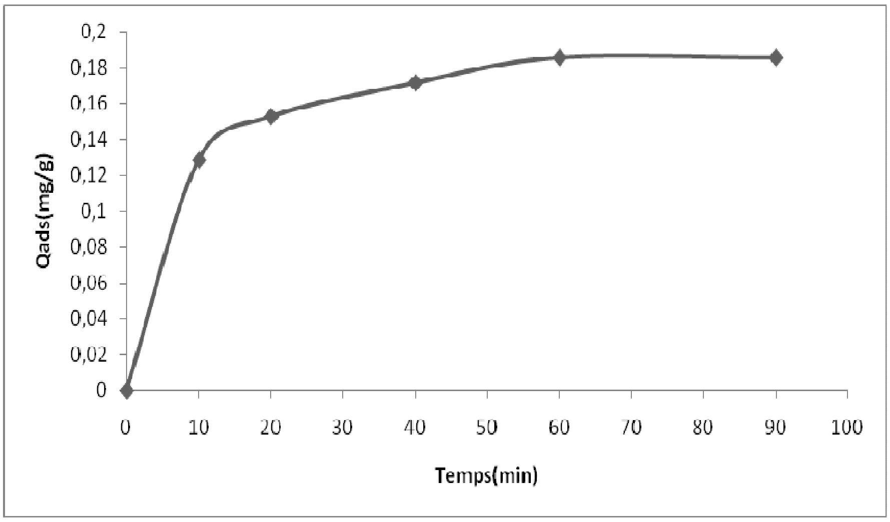

Figure 2. Adsorption kinetic of méthyl parathion (C_0 = 20ppm) on the clay

3.2. Effect of Solution pH on méthylparathion Adsorption

Since hydrogen ions affect the surface charge of the adsorbents and the adsorbate species [8-10], the sorption is greatly affected by the variation of solution pH In order to investigate the effect of pH on adsorption of méthylparathion onto clay, experiments were performed with 20 ppm initial concentration between pH 2 and 8 at 20˚C and R = 1 g/1 of clay. As it seen from **Figure3** adsorption decreased with increasing pH. It was observed that the adsorption is highly dependent on pH since it has strong influence on the surface charge of the adsorbent. Attraction forces between more positively charged surface and méthylparathion are responsible for increasing adsorption with decreasing pH. According to surface chemistry theory, clay particles and pesticide molecules are both surrounded by an electric double layer due to electrostatic interactions. The isoelectric point (PZC) of the natural adsorbent was found to be at pH of 5.7. For values of pH < PZC, the clay surface has been positively charged. In one hand, it favors the adsorption of méthylparathion that is characterized with a high electronic density caused by Kekule forms of two nucleuses. In the other hand, by electrons functional groups which performs Mesomeric effect (+M) due to nitrogen and oxygen atom hybridized sp^3, and Inductive effect (+I) caused by methyl group. Additionally All this has proven affinity between positive surface of the clay.

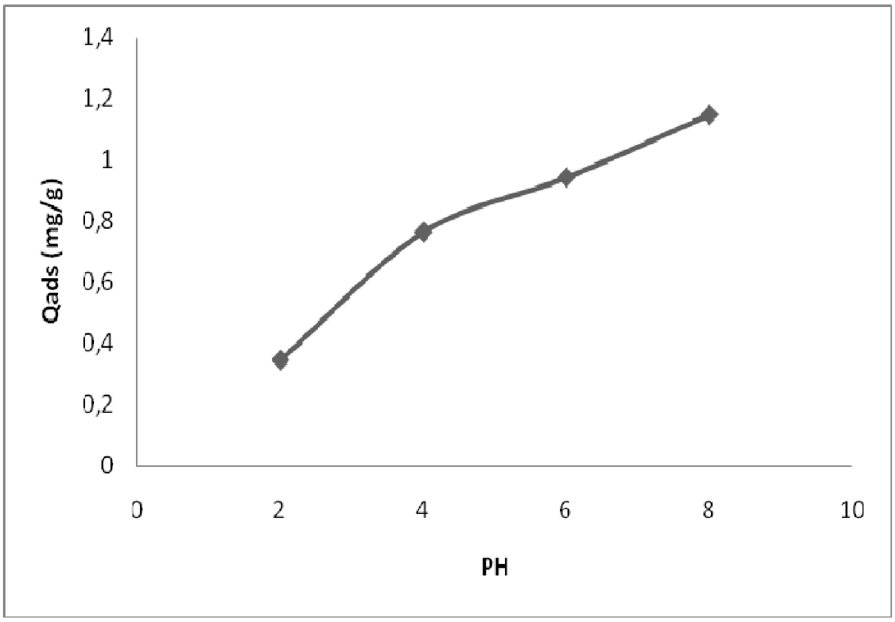

Figure 3:pH effect on Carbaryl adsorption (C_0 = 10 mg/l)

3.3. Pesticide Initial Concentration Effects

It is clear from **Figure 4** that the amount of méthylparathion adsorbed, Q_{ads} increased with time. The equilibrium adsorption was achieved in 60 min for méthylparathion solution with initial concentrations of 20 - 60 ppm (R = 1 g/1). The fact that the diffusion of the pesticide molecules of the solution at the surface of the adsorbent is accelerated by the increase of the concentration in pesticides. This observation could be explained by the theory that in the process of méthylparathion adsorption, initially the pesticide molecules have to first encounter the boundary layer effect and then diffuse from the boundary layer film onto adsorbent surface and then finally, they have to diffuse into the porous structure of the adsorbent [11-13].

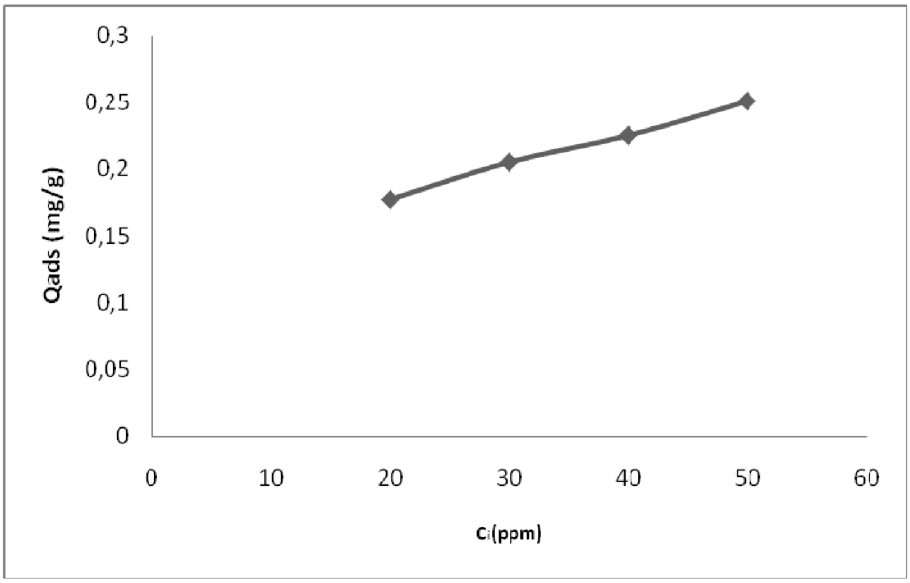

Figure 4: The effect of the initial concentration of méthylparathion

Therefore, méthylparathion solutions of higher initial concentrations will take relatively longer contact time to attain equilibrium due to higher amount of méthylparathion molecules. The amount of méthylparathion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. In this study, the adsorption capacity at equilibrium (Q_{ads}) in- creased with an increase in the initial pesticide concentrations from. When the initial concentration increased, the mass transfer driving force would become larger, hence resulting in higher adsorption of méthylparathion.

3.7. Adsorption Isotherm

The adsorption isotherm was obtained by utilizing the same previous conditions. The concentration range of initial concentration used is 5 to 15 mg/1. The experiences were performed taking into consideration the equi- librium time that is 60 min.

The adsorption capacity of clay for méthylparathion was studies for different initiale pesticides concentrations as shown in fig 4 the result indicat that the adsorption capacity increases with increasing the initial pesticide concentration. The increase in adsorption capacity with concentration is probably due to a high driving force for mass transfer. In fact, high concentration in solution implicates high molecules of pesticide fixed at the surface of the adsorbent. Several theories of adsorption equilibrium were applied for the analysis of equilibrium sorption data obtained.

3.7.1 Langmuir Model

The Langmuir adsorption model [14] is established on the following hypotheses:
1) uniformly energetic adsorption sites,
2) monolayer coverage, and
3) No lateral interaction between adsorbed molecules. Graphically, a plateau characterizes the Langmuir isotherm.

Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once a pesticide molecule occupies a site, no further adsorption can take place at that site. A mathematical expression of the Langmuir isotherm is given by Equation (2):

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

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

Where Q_{ads} (mg/g) is the adsorbed amount at equilibrium,
C_e is the equilibrium pesticide concentration (mg/l), K_L is Langmuir equilibrium constant (l/mg) and Q_{max} the maximum adsorption capacity (mg/g).

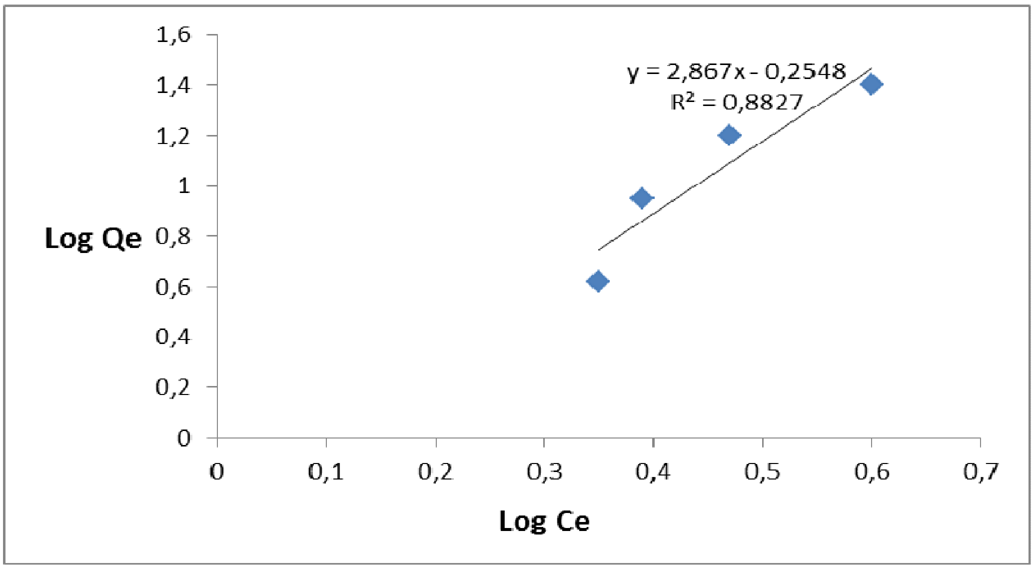

Figure 5: the Langmuir isotherm model

3.7.2.Freundlich Model

The Freundlich isotherm endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption. The energy of adsorption varies as a function of surface coverage [15]. This equation is also applicable to multilayer adsorption and is expressed by the following equation:

$q_e = k\, c_e^{1/n}$

Where K_F is the Freundlich constant and n is the heterogeneity factor. The K_F value is related to the adsorption capacity; while 1/n value is related to the adsorption intensity.

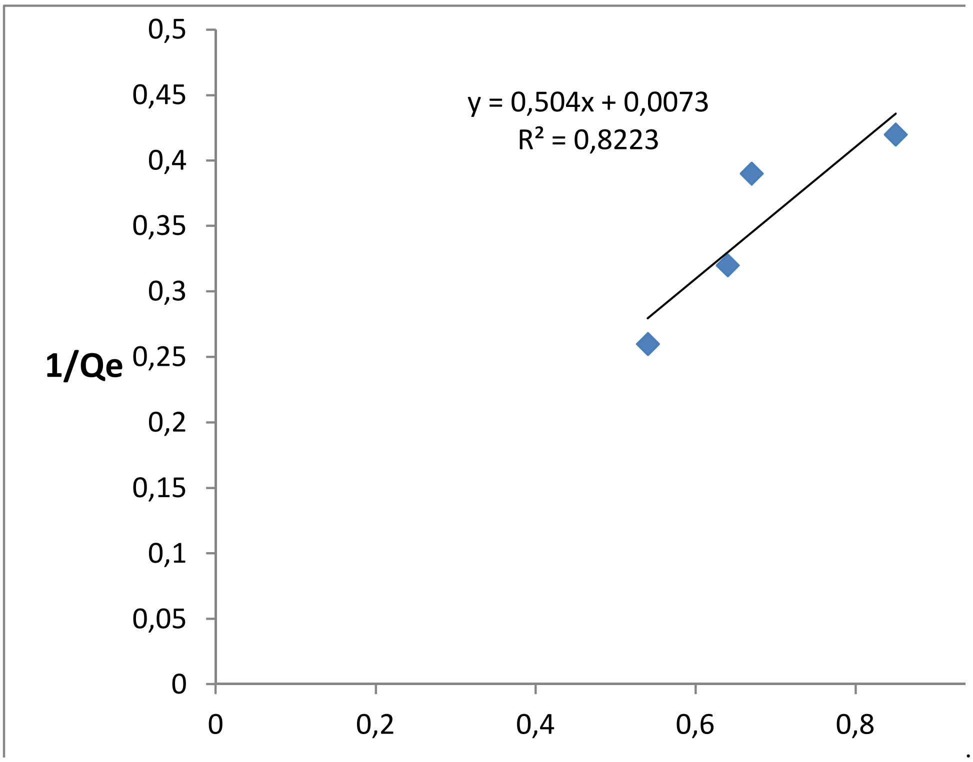

Figure 6: the Freundlich isotherm model

3.7.3. Analysis of Adsorption Isotherms

The amounts of adsorbed quantities of méthylparathion at the equilibrium (Q_{ads}), versus equilibrium pesticide concentration were drawn in **Figure 4**. The isotherm form was type L in Giles classification [16]. The experimental ad- sorption isotherm obtained was compared with the adsorption isotherm models and the constants appearing in each equation of those models were determined by nonlinear regression analysis[16]. The results of these analy- ses are tabulated in **Table 2**. The correlation coefficients (R^2) are also shown in this table. The table indicates that all the isotherms give reasonable fit to experimental data. Based on the correlation coefficient, R^2 liste in table 2, it can be concluded that the adsorption of méthylparathion on our clay at 20˚C was demonstrated well by both of Langmuir and Freundlich isotherm models. The correlation coefficient, R^2 for both models was $0.8223 \leq R^2 \leq 0.8827$. The adsorption process was favorable as Langmuir separation factor, R_L was $0 < R_L < 1$ and supported by n values of Freundlich which were less than one.

Freundlich's isotherm model, is represented by an equation with two parameters (K_F and n), which consist of exponential distribution of energies of some adsorption sites on the surface of the support, which is characterized by an adsorption in located sites. Furthermore, this is applicable in the case of dilute solutions. The value 1/n gives an indication on the validity of the adsorption of adsorbent-adsorbate system.

The values of the Freundlich coefficient n, obtained with our pesticide are in the range expected by Hassler 0.2-0.8 [17]. If we refer to the mathematical considerations Treybal, mud is good adsorbent for this pesticides.

Table 2. Adsorption isotherm constants for adsorption of méthylparathion by silt

silt	*Freundlich*			*Langmuir*		
	n	**k**	**R^2**	**q_m (mg/g)**	**b (l/mg)**	**R^2**
Methyle parathion	0.3425	0.5567	0.8827	136,9821	0.01448	0.8223

CONCLUSION

In this study, the removal of méthylparathion from aqueous solution by this clay, as a natural available adsorbent, was investigated. Adsorption capacity of adsorbent increased with increasing initial concentration of méthylparathion and. The equilibrium up- take was increased with the increasing of the initial concentration of pesticide in solution. The increase in mass adsorbent leads to increase in pesticide adsorption due to increase in number of adsorption sites. The pH experiments showed that the significant adsorption takes place in acid range. The Langmuir and Freundlich adsorption models were used to describe the equilibrium between adsorbed méthylparathion on the adsorbent (Q_{ads}) and méthylparathion in solution (C_e) at different concentrations. The equilibrium data were best described by the Freundlich isotherm model. The results show that the natural clay is an excellent adsorbent for the used pesticide. Finally, this local clay can be used as an effective natural adsorbent for the economic treatment of water.

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