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Adsorption of Poly-phenolic Compounds of Optimized Extract of the Bark of Pittosporaceae by Pillared Clay in View of the Formulation of Powdered Insecticides

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Authors' contributions

This work was carried out in collaboration between all authors. Author MH designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors MJ and WB managed the analyses of the study. Authors CT, JKM and BBL managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The aim of this work is to formulate a powdery insecticide by adsorption of optimized poly-phenol extracts by aluminum pillared clay of Boboyo; in order to reduce the loss of post agricultural crops by preserving the environment. Different parameters (pH, initial concentration of adsorbate, temperature, and mass of adsorbent) those influence the formulation of the insecticide were optimized by adsorption of the gallic acid on the pillared clay. The study revealed that the maximum

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quantity of adsorption is reached after 10 minutes, it is believed that the quantities adsorbed with the increase in the concentration of the adsorbate and quantities adsorbed decreases with the increase of the mass of the clay, the pH and temperature. The kinetic model best suited for the adsorption of gallic acid is that of pseudo-second order. The adsorbed quantity from the monolayer coverage deduced from the Langmuir model is 11.82 mg/g. Thus, the formulation powdery snow of the insecticide is obtained by adsorption of an extract of poly- phenols on the clay materials while respecting the optimal condition provided by the gallic acid. The test insecticides of this formulation powder on the weevils of maize have shown that the lethal dose is 4%. This quantity induces a mortality rate of *Sitophilus zeamais* of 49±12.6% and an LD_{50} = 0.20% (R^2= 0.63) on 7 days compared to Malathion which is considered as the standard insecticide with a mortality rate of 100% on 7 days.

Keywords: Pillared clay; poly-phenolic compounds; gallic acid; insecticide.

1. INTRODUCTION

The world production of cereals has a capital importance to the economy of a country. In Africa, particular in Cameroon; that is, the Northern part, the culture of cereals plays an important role due to the high demand; that this either by local consumers or by the industries [1]. To increase the yields of cereals and compensate the loss of post-crops and better conserve cereals, agricultural producers should use more of fertilizers and insecticides [2]. The insecticides nevertheless remain an indispensable means of control for the infestation of foodstuffs during storage [3]. Some synthetic insecticides such as chlorinated derivatives have a negative impact on the environment and may induce a chronic intoxication of consumers, a resistance in pests [4]. In addition, these synthetic insecticides are not in the scope of all because of their cost which are extremely high. In the search for alternative methods to fight against these pests, according to Tapondjou et al. [5], the plant reign offers a lot of possibilities. However, the biopesticides of plant origin are frequently biodegradable and less toxic than the insecticides of synthesis. Previous work [1,3,6] carried out in this context, has shown the effectiveness of essential oils of plants against insect pests of cereals. Unfortunately, the volatility of these essential oils does not ensure a protection of cereals for a period of 7 to 8 months. However, the work of Souaibou (2010) carried out on *Pittosporum viridiflorum* shows that poly-phenolic compounds in the extract contained ethanol of this plant and have insecticidal properties. These poly-phenolic compounds have the advantage to be stable and available in the plants. As well, the extracts fixed on a solid support such as pillared clay is a feasible approach for the production of insecticide with a high duration in order to ensure protection of seeds stored. It is in this perspective that we are committed to the development of a formulation of insecticide on the basis of extracts of poly-phenolic and pillared clay. This approach aims at defining the interactions of clay/poly-phenolic compounds in order to optimize the effectiveness of the powdery formulation of insecticide. The objective of this work is to perform a powdery formulation of the insecticide by adsorption of the extract optimized in poly-phenols by the modified clay of Boboyo, as support of organic compounds. The work is to formulate the powdery insecticide by adsorption of an extract of poly-phenols on the pillared clay and to test the effectiveness of the insecticide powder formulated on the weevils of maize.

2. MATERIALS AND METHODS

2.1 Physico-chemical of Clay

The pillared clay used for the realization of this work is the one prepared by Harouna et al. [7]. The characteristics of the natural clay of Boboyo that they have used to the jumper wire by the aluminum are presented in Tables 1, 2 and 3.

Table 1. Some characteristics of the natural clay of Boboyo [7]

Parameters	Moisture index (%)	pH	Rising content (%)	Densty
Values	22.39	8.53	95.98	1.39

Table 2. Granulometric analysis of the Boboyo clay [7]

Fraction	$< 2\,\mu m$	$2-20\,\mu m$	$20-50\,\mu m$	$50-200\,\mu m$	$200-2000\,\mu m$
% composition	13.4	38.95	20.25	15.11	5.5

Table 3. Characteristics of quality and performance of the pillared clay Boboyo [7]

Index of iodine (mg/g)	Specific surface mesoporeuse (m^2/g)
190.35	55.8

2.2 Method of Adsorption of Gallic Acid by the Pillared Clay

The adsorption experiments were carried out using the batch equilibration technique. The solutions of the gallic acid of 20, 40, 60 and 80 mg/L concentrations are introduced in the flasks in pyrex of 100 mL. The solutions are maintained at 30, 40, 50, and 60°C and agitated with the help of a thermostated bath at a constant speed of 120 rpm. A mass determined of pillared clay is introduced in each solution. The pH values of heavy metal solutions were in the range of 6.4 and 7.0 without further adjustment in order to simulate the natural water system. The suspensions were mixed on a rotary tumbler for 15 minutes. After phase separation by centrifugation the concentration of gallic acid in the supernatant was determined by measuring the absorbance using a UV-visible spectrometer (Pharo-100) at wavelength of 750 nm and the solid phase obtained is the insecticide sought.

2.3 Procedure of the Formulation of Insecticide

The powdery formulation of insecticide has been carried out taking into account the optimization of the parameters during the adsorption of gallic acid which is taken as a compound poly-phenolic reference. To have a powdery formulation of 0.2 g, a mixture with a solution of extract for poly-phenols contains 80 mg/L and 0.2 g of pillared clay is introduced in a beaker of 100 mL. The mixture is homogenized by a magnetic stirrer for approximately 10 minutes and placed in the oven at 30°C to complete the evaporation of the solvent. The flavored powder of the poly-phenol compound obtained is kept in vials hermetically sealed in order to exclude the moisture and prevent the photo-degradation.

2.4 Study of the Insecticidal Activity

Here we want to assess the duration of the activity of the formulation of powder snow in function of dose in active principle. Thus, with the type of modified clay put in contact with extracts of poly-phenol, the doses of the powdery formulation were varied to 1%, 2% and 4% expressed in gram of powdery formulation per gram of seed maize (Fig. 1).

Fig. 1. Boxes containing the maize treated with powders of insecticide and containing 10 insects

Each box containing powders of insecticide receives a quantity of 20 g of maize grain and 10 insects' hungry beforehand for 48 hours and then stored at room temperature. The number of dead insects will be counted after 24, 48, 72, 96 and 168 hours of observation [6]. The negative control is the natural clay and pillared only, the positive witness that we have used is the Malathion which is an insecticide generally used by the riparian populations to protect the maize from insects. The repetition is performed 3 times for each concentration and the mortalities observed are expressed after correction by the mathematical expression of Abbott (1925):

$$M_C = \frac{M_0 - M_t}{100 - M_t} \times 100 \qquad (1)$$

Where M_C is corrected mortality in %; M_T is mortality observed in the Witness and M_O is mortality observed in the test.

The lethal dose for 50% of the population of insects LD_{50} is calculated by the method of probit, for the comparison of the toxicity of the poly-phenolic compounds tested. The percentages of mortality are transformed into probit, the regression of the logarithm of the dose in function of the probit fatalities on the software MINITAB (version 12) has helped to determine the LD_{50} for the compound concerning each bruche studied.

3. RESULTS AND DISCUSSION

3.1 Kinetics Studies

In order to determine the kinetics of gallic acid by modified clay, 200 mg of pillared clay was mixed with 20 mg/L of gallic acid solution in tubes. The dispersions were shaked for time varying from 2 to 40 minutes in a shaker.

Fig. 2 shows how the results of the kinetics studies of gallic acid is obtained by pillared clay of Boboyo at 50 mg/L gallic acid initial concentration. As shown in Fig. 2, the amount of gallic acid adsorption increases rapidly during the first minutes and stabilizes at the end of 10 minutes for a maximum adsorption of 2.94 mg/g. These phenomena can be interpreted by the fact that at the beginning of adsorption, the number of active sites available at the surface of the adsorbent is much more important than that of the remaining sites after a certain time. As well beyond the time of contact, the molecules of gallic acid need time to disseminate to the inside of the pores of the adsorbent. The formation of a level of saturation can be explained by a balance of adsorption where all the sites on the surface of adsorbent are occupied. The fast fixation is explained by the high affinity of the support to the retention of gallic acid [8].

To predict and better explain the mechanism of adsorption of the gallic acid on the pillared clay, the experimental results of the kinetics of adsorption have been compared with the theoretical models of diffusion particulate intra, pseudo-first order and pseudo-second order.

The correlation coefficients R^2, the quantities of ions adsorbed to the balance and rate constants of different kinetic models that have been tested are represented in the Table 4.

It is therefore clear from Table 4 that, the models of pseudo-first order and the dissemination intra-particular are not applicable for the explanation of the adsorption of gallic acid on the modified clay in the light of low values of the coefficients R^2 for these models. However, the value of the coefficient R^2 is greater than 0.90 of the model of pseudo-second order and shows that the latter is applicable to the experimental data [9]. This indicates that the adsorption is done in two steps:

- The first step is the dissemination of the molecules of gallic acid toward the surface of pillared clay;
- The second step is the interaction of molecules of gallic acid at the surface of clay bypassed.

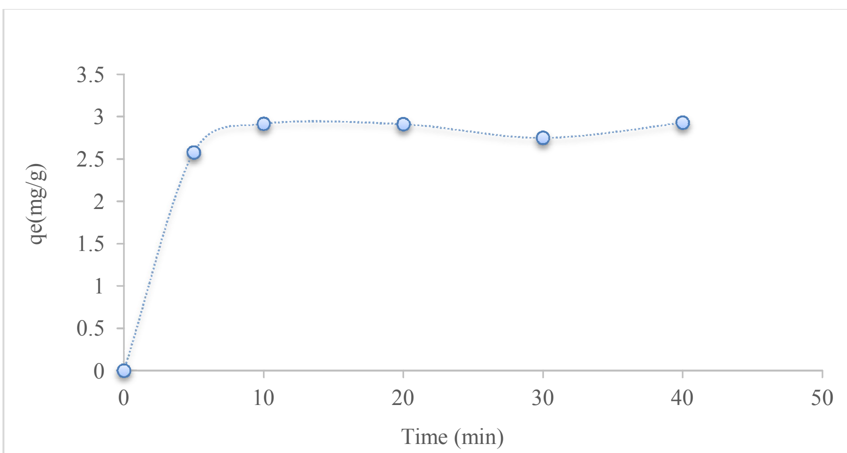


Fig. 2. Kinetics study for gallic acid uptake by pillared clay from Boboyo

Table 4. Summary table of constants of the different kinetic models and their correlation coefficients R^2

Model of pseudo-first order			Model of pseudo-second order			Dissemination model intra particulate		
Qe (cal) ($mg.g^{-1}$)	K_1 (min^{-1})	R^2	Qe (cal) (mg/g)	K_2 ($mg/g^1/min^1$)	R^2	Kint (mg/g $min^{-1/2}$)	C ($m^2.s^{-1}$)	R^2
1.44	0.37	0.79	16.10	0.05	0.95	2.18	2.68	0.77

3.2 Influence of the Mass of Pillared Clay of Boboyo to the Adsorption of the Gallic Acid

The study of the influence for the mass adsorbent is applied on the adsorption capacity of the gallic acid, which has led us to vary the amount of adsorbent 0.2 to 1.4 g while maintaining the initial concentration of the substrate in solution at 20 mg/L. Fig. 3 gives us the variation of the amount adsorbed of the compound studied as a function for mass of the pillared clay.

It is clear from Fig. 3 that, the increase in the quantity of adsorbent leads to a decrease in the quantity of gallic acid adsorbed by the unit of mass. The quantities adsorbed decrease from 2.94 to 0.41 mg/g with the increase of the mass of adsorbent. This result is justified by the phenomenon of standardization of quantities adsorbed. Infact, the increase in the quantity of adsorbent leads to an increase in its total surface area available without any influence on the content of gallic acid in the medium. This may be due to a creation of an agglomeration of the particles and a slowdown of the dissemination of the molecules of gallic acid in the pores of the material [10]. Thus less mid saturated, more molecules broadcast and more easily to the sites of the adsorbent. This result is similar to that obtained by Kanouri, Labide (2013) which, in working on the adsorption of phenol on the bentonite of Maghnia, has found out that an increase of the mass of the adsorbent 0.1 to 0.5 g, allow you to reduce the amount of phenol adsorbed of 2.78 to 0.83 mg/g. These results are still justified by the work done by Harouna et al. [7] on the adsorption of Mn^{2+} and Zn^{2+} ions in aqueous solution by the pillared clays of Boboyo and Djongmaila (2014) on the adsorption of Cu^{2+}, PO_4^{3-} and the Mn^{2+} ions by the bridged clay of Karewa. Indeed, it finds out that, the adsorbed quantities are maximum for a mass of 0.2 g of the modified clay. These results are in agreement with those of Beigang et al. *(*2012) and Djakba (2013).

3.3 Effect of Solution Concentration on Gallic Acid Adsorption

The influence of the initial concentration in phenolic compound on adsorption capacity of pillared clay was conducted in a mass material of 0.2 g, pH=6, time contact 10 minutes, temperature 25°C. The result is presented in Fig. 4.

It is clear from Fig. 4 that the quantity of gallic acid adsorbed per gram of the pillared clay increases with the increase in the initial concentration. The increase in the quantity adsorbed of the gallic acid is linked to the emergence of new sites of adsorption and to a transfer of matter more important due to a stronger dissemination. The maximum quantity adsorbed of gallic acid is obtained for an initial concentration of 80 mg/L. This result is explained by the fact that the higher the concentration of the solution, the greater the molecules of gallic acid are numerous in the solution and the more they are in contact with the adsorbent then the percentage of adsorption increases [11]. The work of Djongmaila is in agreement with the results reported in the present work. This lead us to say that the phenolic compound of reference has a good compatibility against the pillared clay of Boboyo.

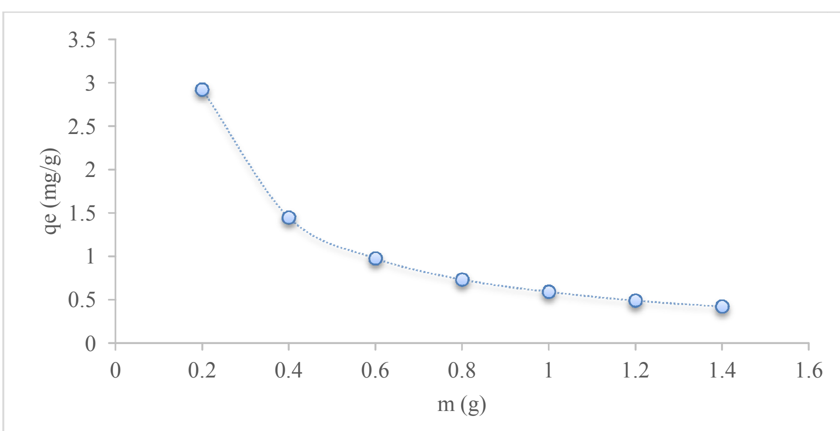


Fig. 3. Effect of mass on adsorption of gallic acid on pillared clay

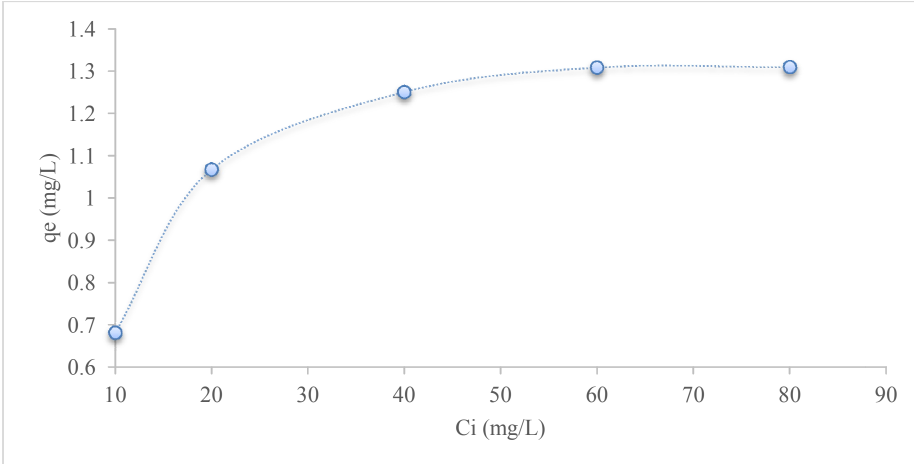


Fig. 4. Effect of gallic acid concentration on adsorption on pillared clay

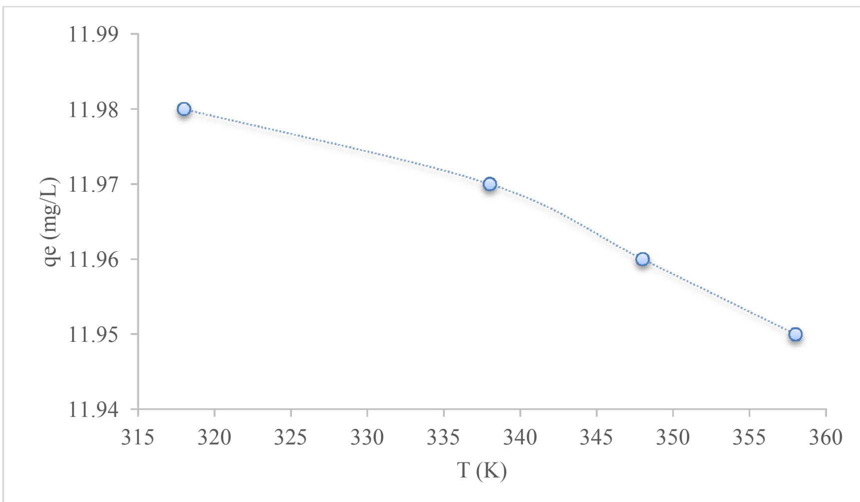


Fig. 5. Effect of temperature on adsorption of gallic acid on pillared clay

3.4 Effect of Temperature

Evolution of the fixation of gallic acid has been studied for an initial tenor which is static for each (20 mg/L) and at different temperatures (between 25°C and 65°C). The measurement of the residual tenor in gallic acid for each case study has been realized after 10 minutes of contact time with modified clay [12,13].

Fig. 5 shows the adsorption of gallic acid with the pillared clay. The results in Fig. 5 shows that temperature does not seem to have any significant influence on the adsorption of this acid. The absorbed quantity is 11.98 mg/g. These values decrease very little with increasing temperature, indicating the exothermic character of the adsorption process. A decrease in the absorbed quantity with temperature implies physisorption [7].

3.5 Adsorption Isotherms

3.5.1 Langmuir isotherm

The Langmuir isotherm is based on the assumptions that adsorption takes place at specific homogeneous sites within the adsorbent, there is no significant interaction among adsorbed species, and the adsorbent is saturated after the formation of one layer of adsorbate on the surface of adsorbent [7]. The Langmuir isotherm equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (2)$$

Where, C_e is the equilibrium concentration of the remaining solute in the solution (mg/L), q_e is the amount of the solute adsorbed per mass unit of adsorbent at equilibrium (mg/g), q_{max} is the amount of adsorbate per mass unit of adsorbent at complete monolayer coverage (mg/g), and b (L/mg) is a Langmuir constant. The q_{max} and b values were calculated from the slopes $(1/q_{max})$ and intercepts $(1/bq_{max})$ of linear plots of C_e/q_e versus C_e Fig. 6. The deducted parameters of adsorption of Langmuir isotherm are summarized in Table 3. The plot is found to be linear with good correlation coefficients ranging from 0.94 to 0.99. This indicates the applicability of Langmuir model in the present study.

3.5.2 Freundlich isotherm

The Freundlich isotherm model can be used to describe the non-ideal adsorption of a heterogeneous system and reversible adsorption [9]. The isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

This expression can be linearized to give the following equation:

$$log q_e = log K_F + \frac{1}{n} log C_e \quad (4)$$

Where, K_F (mg/g) and n are Freundlich adsorption isotherm constants. The values of K_F and $1/n$ are determined from the intercept and slope of the linear regressions. A value of n above one indicates a normal Freundlich isotherm while n values less than one are indicative of cooperative adsorption [7]. A plot of $\log(q_e)$ versus $log(C_e)$ for the studied sample is shown in Fig. 7. The deducted parameters of adsorption of Freundlich isotherm are summarized in Table 5. The plots were found to be linear with good correlation coefficients ranging from 0.97 to 0.99. This indicates the applicability of Freundlich model in the present study. The n values for the studied samples are more united and therefore, adsorption is favorable.

3.6 Thermodynamic Parameters

Thermodynamic parameters have been determined to the qualification of adsorption phenomenon of the gallic acid on pillared clay of Boboyo. The deducted estimates of ∆H° and ∆S° of the experimental data is found in Table 6.

As illustrated from the results in Table 6, the negative value of ∆S° indicates the positive nature of the present adsorption phenomenon. Also, the negative value of ∆H° proves the exothermic and physical nature of this retained phenomenon of gallic acid [9]. These results are in agreement with the above studied model.

Table 5. Values of the various parameters of the isotherms models studied

Langmuir	**R_2**	0.99
	K_L (mg/L)	0.06
	Q_m (mg/g)	11.82
Freundlich	**R_2**	0.96
	K_F (g/L)	1.08
	n_F	0.22

3.7 Insecticide Tests

The results of the insecticides tests of our powdery formulations are presented in Fig. 8 below. The results show that the rate of mortality of insects caused by the two formulations increase as a function of the concentrations and the duration of exposure, but remain lower than those of the poudrox. The differences in mortality between the concentrations are more significant from the fourth day. They also illustrate that the percentage of mortality of the large concentration (4%) in the seventh day is: 96% for the natural clay, 98% for the pillared clay. This shows that the powder formulated by the pillared clay is the more insecticide. In addition, we find that the poudrox used here as a positive control kills (80.00±2.50)% the first day and 100% of mortalities is reached in the second day. However the powder made reached on average 80% of the insects in the seventh day at a concentration of 4%. This allow us to demonstrate that with the concentration of 4% of our extracts behave exactly as the poudrox. An increase in time of exposure would potentiate more of our powders. Thus we can say that instead of using the poudrox which is very toxic to protect stored commodities [14], the powdery insecticides of *Pittosporum viridiflorum* can be used to protect our food stored with a good performance. Table 7 presents the lethal doses required to kill 50% (DL_{50}) and 90% of the insects (DL_{90}). These results have been obtained by doing a logarithmic regression whose equations are as follows:

$$y = 4{,}977\ln(x) + 63{,}18\ pour l'argile naturelle \quad (6)$$

$$y = 30{,}03\ln(x) + 220{,}8\ pour l'argile pontée \quad (7)$$

These lethal doses, although higher than those of the essential oils of the same plant [15], reflect the possibility to use our extracts to combat *Sitophilus zeamais.* Yet the lower volatility of our extracts will make them more malleable by the peasants.

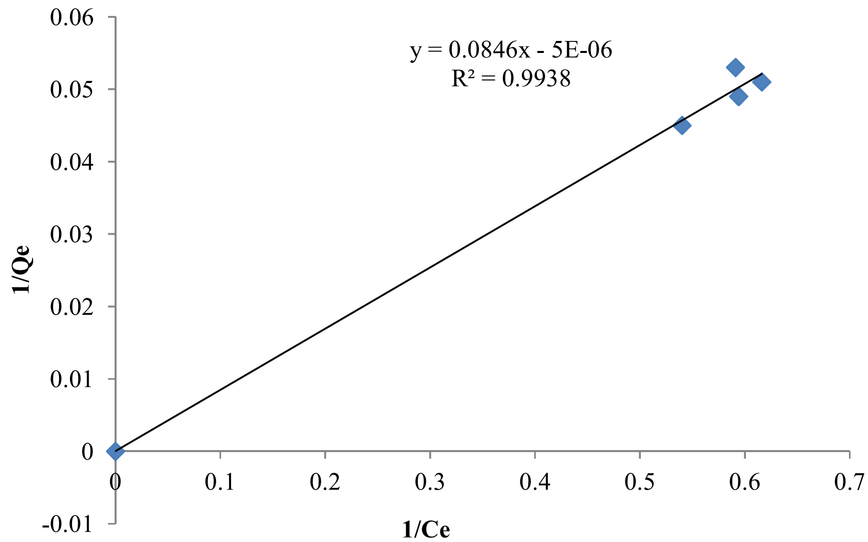


Fig. 6. Langmuir plot for the gallic acid uptake by pillared clay mineral from Boboyo

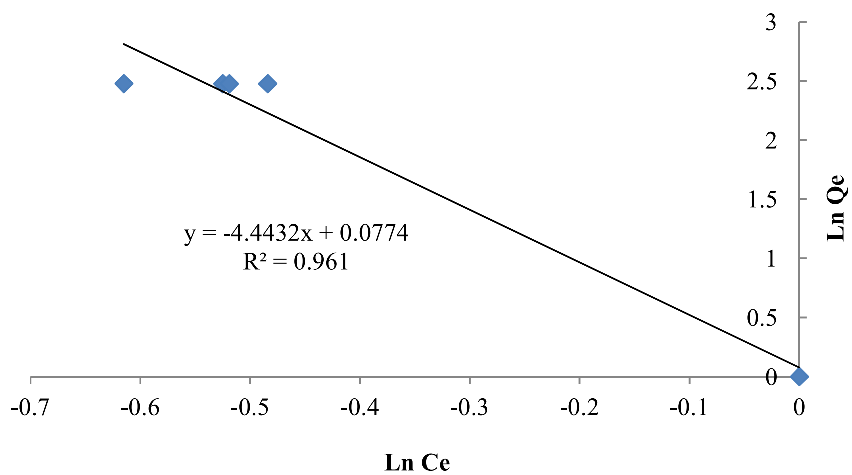
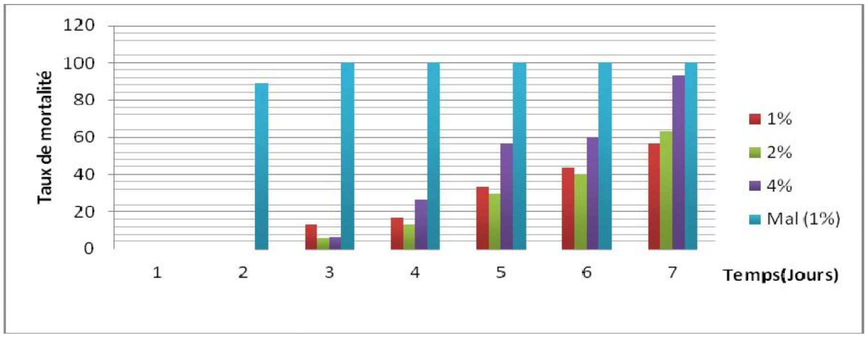


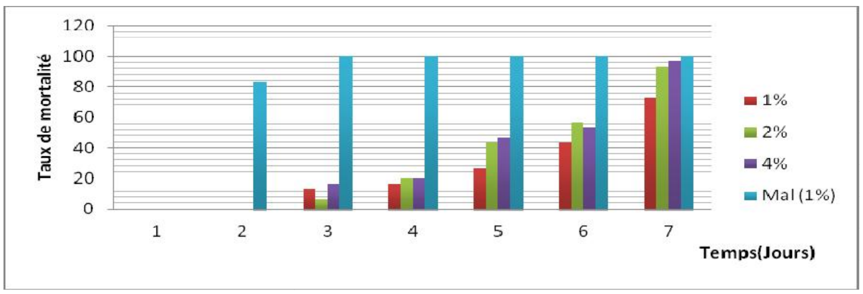
Fig. 7. Freundlich plot for the gallic acid uptake by pillared clay mineral from Boboyo

Table 6. Thermodynamic parameters of adsorption of gallic acid on pillared clay mineral from Boboyo at different temperatures

ΔG° kJ/mol				$(\Delta H°).10^{-4}$ kJ/mol	$(\Delta S°).10^{-2}$ kJ/mol.K
327°K	337°K	347°K	357°K		
-4.6	-4.49	-4.62	-4.76	-1.66	1.33



(a) Formulation with natural clay



(b) Formulation with clay by passed

Fig. 8. Mortality rate of *Sitophilus zeamais* as a function of the concentrations and the time with which our powdery is formulated

Table 7. Lethal doses killing 50% (DL50) and 90% of the insects (DL90) of different extracts

	Pillared clay	Natural clay
DL50%	385.634	3,864
DL90%	8.074×10^{13}	1.057×10^{3}

4. CONCLUSION

This study of the adsorption of the extract of poly-phenols by the pillared clay is a contribution to a powdery formulation of insecticide. This study had the aim to make our contribution to the enhancement of poly-phenolic compounds and pillared clay of Boboyo as a support of organic compounds, with a view to obtain a powdery formulation of the insecticide by adsorption of poly-phenolic compounds by the clay. The study of the influence of some parameters on the retention of these adsorbates has engaged our attention. The bulk of work can be summarized in the following points:

The adsorption of extract of poly-phenols is very fast and the balance is reached in less than 10 minutes.

The kinetic model of pseudo-second order is applicable to the adsorption of the gallic acid, this implies the assumption that the adsorption is happening in two phases: The dissemination of the adsorbate to the surface of the adsorbent, followed by the interaction adsorbent-adsorbate.

The quantities adsorbed decrease with the increase of the mass of adsorbent and the increase of the temperature. They grow with the increase of the initial concentration of extract of poly-phenols. The amount adsorbed increases in acid medium (pH<7), decreases in basic medium (pH>7).

The process of adsorption is spontaneous, the reactions of adsorption of poly-phenols is exothermic and the type physical.

The experimental results on the adsorption of the compound have been confronted with the theoretical models of Langmuir, Freundlich with correlation coefficients greater than 0.90.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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