Adsorption of Triterpene Extracts of *Momordica charantia* (Cucurbitaceae) Leaves by Local Kaolin from Boboyo, Far North Region (Cameroon)

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Abstract: Plant extracts are nowadays cited as suitable tools for better protection of stored grains insect pest attacks. These chemical insecticides are less attractive to producers because of their low persistence and difficulty to use as pure product. The present work aimed to study the formulation through adsorption of tetracyclic triterpene of the leaves of *Momordica charantia* (Cucurbitaceae) on kaolin. tetracyclic triterpene was obtained by macerated in methanol solvent. In this study, we tested the technical properties of kaolin physically and chemically, which include XRF, XRD, and FTIR. Based on the XRF test, the main composition of kaolin, SiO_2, Al_2O_3, and Fe_2O_3, CaO, MgO, K_2O, Na_2O, SO_3, P_2O_5 were 45.41, 20.54, 8.10, 0.13, 0.79, 01.10, 01.09, 0.04, and 0.03% respectively, while the rest were impurities. The FTIR spectra showed the functional groups of Al-OH, Al-O and Si-O. While the XRD diffractogram identified kaolinite as the main mineral phase in the presence of quartz, muscovite, and grossite tested in small quantities in the sample. The experimental parameters such as contact time, adsorbent dose, initial concentration of extract of triterpene and temperature were studied. The study revealed that the maximum 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 and temperature. The adsorbent showed good potential for adsorption with a maximum take up of 0.34 mg/g. The equilibrium data were well fitted by the Langmuir isotherm. Thermodynamic parameters suggested that the adsorption involved a chemical process, spontaneous, and endothermic in nature. The kinetic study showed that the second-order model gives a better description of the kinetics of the adsorption reaction. The study of the adsorption of triterpene extract by kaolinite can be used for a powdery formulation of insecticide.

Keywords: Isotherm Model, Kinetic Model, Tetracyclic Triterpene, Kaolinite, Thermodynamic Parameters

1. Introduction

Plant extracts are compounds concentrated in molecules derived from plant metabolism. The secondary metabolites originating from the latter have very important functions for the survival and proliferation of the plants such as chemical signals, defense producer against herbivores and pathogens as they participate in allelopathic responses (competition between plants for germination and growth) [1, 2]. Some provide protection against solar radiation and others facilitate the dispersal of pollen and seeds [3]. They are produced in very small quantities, of which more than 200,000 molecules have been identified such as phenolic compounds, alkaloids and terpenoids [2, 3]. The dynamics market of the constituents of these extracts is supported by an ever-increasing demand for natural ingredients. Thus, they are widely exploited by humans in the various fields, namely culinary as colors and flavors, medicinal as antibiotics,

antioxidant, drugs and agricultural as insecticides [4]. *Momordica charantia* is one of those popularly known plants for its numerous medicinal virtues. This plant belongs to the Cucurbitaceae family. It grows in tropical areas of the Amazon, Africa, Asia, India, South America, and the Caribbean and is used traditionally as both food and medicine [5, 6]. The plant is beneficial for its anti-tumorous, anti-fungal, anti-parasitic, anti-cancer, antiviral, anti-fertility, anti-bacterial and hypoglycaemic properties due to the presence of numerous phytochemicals [7]. In traditional medication, its fruits and leaves are used to cure several diseases like: gout, rheumatism, colic, worms, liver diseases and spleen [7]. These biological activities are attributed to their complex chemical composition; they are rich in proteins, triterpens, saponins, flavonoids, steroids, alkaloids, and acids [8]. The bioactive compounds are commonly obtained through conventional extraction techniques with many different types of organic solvents [5]. However, the work of Adesina et al. [9], Obembe et al. [10], Shibu et al. [11] and Zijun et al. [12] carried out on *Momordica charantia* shows that the methanol extract of leaves of this plant have insecticidal properties. Among the various constituents identified on the polar fraction of the methanol extract of leaves, we can highlight as characteristic of *M. charantia* the momordicines I and II [13]. The structures of the momordicines I and II were elucidated as 3β, 7β, 23] trihydroxycucurbita-5,24-dien-19-al and its 23-O-β-glucopyranoside, respectively [13]. Momordicines "cucurbitane-type triterpenoids" are the most important purified bioactive constituents isolated from the leaves of this plants which justify it insecticidal activitie [12, 14]. Thus, the industrial use of these compounds poses many problems because of the variability of their composition, their instability in storage and the allergenic potential of some of their constituents. Currently, it is recognized that temperature, light and oxygen availability have a major impact on the preservation of the integrity of the extract [15]. Faced with this handicap, fixing these extracts of triterpene to the surface of a solid support is one of the most used techniques. The clay, material power adsorbing, can be used as a support for organic compounds [16]. Thus, triterpenes compounds of optimized extracts from *M. charantia* fixed on clay constitutes a possible approach for producing a powdery insecticide formulation for industrial purposes. It is in this perspective that we are committed to promoting the development of a powdery insecticide formulation on the basis of triterpenes compounds of optimized extracts from the leaves of *M. charantia* and natural clay of Boboyo in view to reduce the extract concentration introduced without affecting the effectiveness of the finished product as well as modulating its release by prolonging its kinetic profile.

2. Material and Methods

2.1. Mineral Materials

The kaolin was collected from Boboyo locality (Far North Region of Cameroon) deposit. The samples taken were packaged in plastic paper packaging and transported to the laboratory. After collecting the raw clay lumps, stones and other heavy particles were removed from the samples mechanically. The samples taken were packaged in plastic paper packaging and transported to the laboratory. A 320 g of each sample was then dispersed in 16 L of distilled water for one week. The suspension was then used to obtain sample with size less than 2 μm by using sedimentation operation based on stocks law in an adapted disposal material as described by Nguemtchouin et al. [17].

The clay sample previously extracted (to obtain particles less than 2μm size particles) was then made homoionic sodium, focusing to remove all the undesired cation contained in the material clay used by replacing all the exchangeable cations of the natural clay by Na^+ ions. The method applied is the same used by Nguemtchouin *et al.* [17]. 50 g of clay sample are introduced into a beaker containing 2 L of a 1M NaCl (99.8% pure) solution. The mixture is stirred for 24 h with a magnetic stirrer. The sodium kaolin (Na^+Kaol) was separated using centrifugation and washed in distilled water until no residual halogen anions were detected by adding a 0.1 $mol·L^{-1}$ of silver nitrate ($AgNO_3$) solution to the filtrate. The suspension obtained was dried at 70°C for 24 h and the sodium clay obtained was sprayed into a porcelain mortar and sieved.

2.2. Plant Material and Maceration Procedure

The plant material consists of fresh leaves of *M. charantia* (Cucurbitaceae), locally called "Bitter melon". These leaves were harvested in Djarengol, in Maroua III Subdivision, Department of Diamaré, Far North Region (Cameroon) in November 2018 and identified by Dr Froumsia, Botanist at the University of Maroua. The plant material was then cut and dried in the laboratory for three weeks at 25°C. Finally, the dry leaves were pulverized in a grinder to obtain a fine powder. It was ground in a mortar and macerated for 72 hours in 3L of methanol (99.9% pure), then filtered on Whatman N°1 filter paper. The filtrate was concentrated in a BUCHI brand rotary evaporator at 75°C and dried in an oven at 50°C.

2.3. Optimization of the Triterpene Extract

In order to optimize the extract of the triterpene compound, 20 g of the methanol extract (MeOH) were taken up in 200 mL of distilled water [18]. The aqueous solution thus obtained underwent a liquid-liquid extraction with hexane (Hex). To do this, the aqueous solution obtained was brought into contact with 200 mL of hexane and the whole underwent mechanical stirring for 30 minutes. After decantation, the two portions of each organic phase were combined and dried in an oven (50°C). At the end of this evaporation, the obtained hexanic extract was kept in the tightly closed bottle with aluminum foil under a lid.

2.4. Chemical Structure of the Bioactive Compounds in the Extract

Momordicin I and II were isolated and purified from M. charantia leaves using previously described methods by Popovich et al. [19]. Momordicin I and II purity was determined by high performance liquid chromatography (HPLC) and final purity was 97% for both compounds (Figure 1). Momordicin I and II were variably hydrophobic requiring dissolution in DMSO prior to dilution to final treatment concentrations. DMSO was used as a control vehicle in this experiment and adjusted to a final concentration of 0.5% in culture medium.
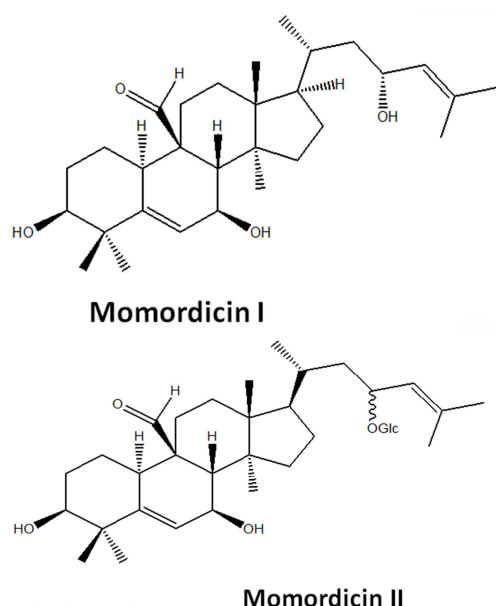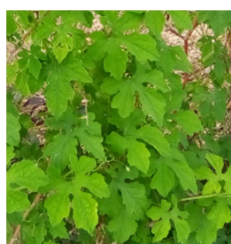

Momordicin I

Momordicin II

Figure 1. *Chemical structure of Momordicin I and II [12].*

2.5. Determination of Lupeol

The reference compound used in this work is lupeol, a pentacyclic triterpene isolated from the ethyl acetate extract of the leaves of *prosopis africana* in the ratio hexane/ethyl acetate (95: 5). The demonstration of this compound was carried out by the reagent of Liberman Buchard. Therefore, to 5 mL each of these dilute solutions, 5 mL of the acetic anhydrous / chloroform mixture (5/5: V/V) are added; then filter and treat the filtrate with a few drops of concentrated sulfuric acid until a green-purple color appears [20, 21]. Their absorbances are measured by UV-Visible spectrophotometry at 530 nm against the blank consisting of the supernatant obtained from a suspension of clay in methanol.

2.6. Adsorption of Triterpene Extracts by Clay

The adsorption experiments were carried out using the batch equilibration technique. The solutions of the triterpene extracts of 20, 40, 60, 80 and 100 mg/L concentrations are introduced in the flasks in pyrex of 100 mL. A mass determined of pillared clay is introduced in each solution. The suspensions were mixed on a rotary tumbler for 15 minutes. After phase separation by centrifugation the concentration of triterpene extracts. The filtrate (liquid phase) is then recovered and assayed by Liberman Buchard's reagent to be analyzed by UV-visible spectroscopy at wavelength of 530 nm and the solid phase, the clay complex-triterpene extracts which is most often an adsorption waste however constitutes the desired product. The samples were pipetted from the solution colored by the aid of a very thin point micropipette, which prevented the transition to the solution of the clays samples. The amount of dye adsorbed was calculated using the equation [22]:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

Where q_e is the equilibrium adsorption capacity per gram dry weight of the adsorbent (mg/g), C_0 is the initial concentration of triterpene extracts in the solution (mg/L), Ce is the final or equilibrium concentration of triterpene extracts in the solution (mg/L), V is the volume of the solution (L), and m the adsorbent mass (g).

Determination of specific surface area

Saers'method was used for the determination of the surface area [23, 24]. By agitating 1.5 g of the adsorbent sample for each in 100 ml of diluted hydrochloric acid of pH=3. Then 30 g of Sodium Chloride was added with stirring and the volume was made up of 150 ml with deionized water. The solution was titrated with 0.1M NaOH and the volume, v needed to raise the pH from 4–9 was then recorded. The surface area according to this method was calculated using the following equation.

$$S \ (m^2/g) = 32V - 25 \qquad (2)$$

3. Results and Discussion

3.1. Characteristics of Adsorbent

3.1.1. Fourier Transforms Infrared Analysis (FT-IR)

In the FTIR spectra of kaolinite, the wide absorption band at 3695 cm^{-1}, and 3622 cm^{-1} corresponds to the inner and outer structural hydroxyl Al-OH stretching with medium strength respectively. The peaks at 1634 cm^{-1}, were the H-O-H stretching and bending vibrations of the adsorbed water, respectively. In the region of low wavenumbers, there are characteristic bands of this clay at 991 cm^{-1} (Si-O stretching modes), 910 cm^{-1} (Al-Al-OH bonds) and 795 cm^{-1} (free silica and/or quartz admixtures, always present in natural samples). The peaks at 521 cm^{-1} and 454 cm^{-1} were assigned to the Si-O-Al and Si-O-Si bending vibration, respectively and 433

cm^{-1} (Si-O).

Table 1. Attribution of FT-IR spectrum bands of kaolinite.

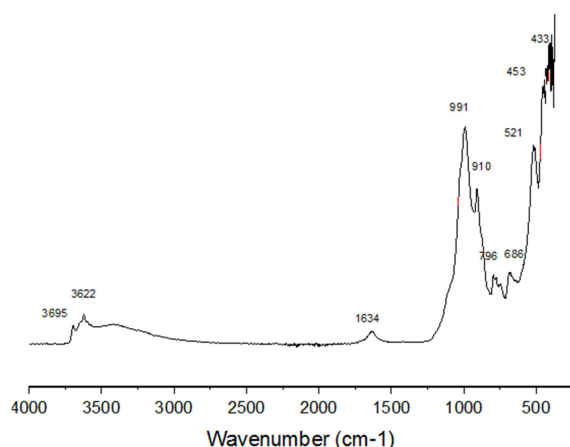| Wavenumber (cm^{-1})	Vibration type	References
3695	OH, mainly Al-OH-Al	[29, 30]
3622	OH of Al-Al-OH	[31]
1634	OH of water or Si-O, Si-O-Al	[32]
991	Si-O of orthosilicates	[33]
910	Al-Al-OH bonds	[25, 34]
796	Si-O stretching vibration of quartz	[22, 30]
686	Si-O- out-of-plane bending	[30]
521	Si-O-Al bending, Al octahedral	[30, 32]
454	Si-O-Si in-plane bending	[31]
433	Si-O	[22, 30]

Figure 2. FT-IR spectrum of Boboyo clay.

The FTIR spectrum of triterpene of momordica. C extract was analyzed and depicted in Figure 3.

A wide absorption band at 3369 cm^{-1} was seen. Those bands were appointed to the vibration of the hydroxyl groups. A similar observation was reported by Supraja et al. [35]. The absorption peaks at 2924, 2855 cm^{-1} (=C-H) and 1624 cm^{-1} (C=C) suggested that olefin was present in the compound and the band at 1708 cm^{-1} indicates the typical carbonyl group [35]. The FTIR spectrum region between 1200 and 1000 cm^{-1} was revealed that the OH side group's stretching vibration and the CO-C glycosidic vibrations dominate the spectrum by overlapping the ring vibration [36].

The chemical bonds identified in the FTIR analysis demonstrated that the triterpenoid compounds present in momordica. C leaf extract.

FTIR-ATR analysis on the adsorption of triterpene extracts on kaolinite.

FTIR spectrum of kaolinite before and after adsorption was observed and displayed in Figure 4. After the adsorption of triterpene extracts, there was a substantial reduction in the intensity of the absorption peak in the range between 1200-500 cm^{-1}.
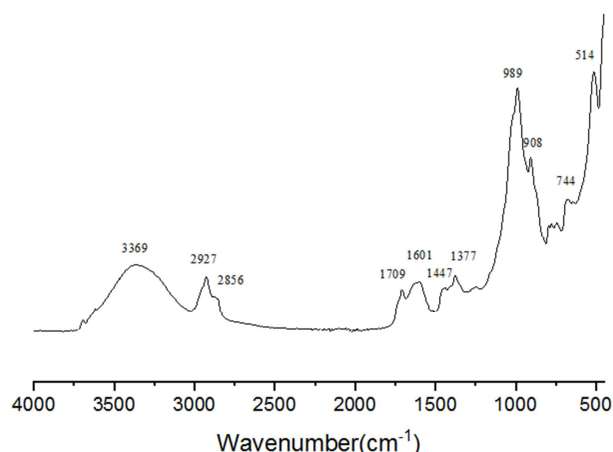

Figure 3. FT-IR spectrum of triterpene extracts from Momordica charantia leaves.

The intensity of the absorption band ranged between 1200-500 cm^{-1}, which comprises of Si-O and Si-O-Si groups, inner surface Al-OH groups, inner Al-OH groups, and Si-O-Al and OH groups, was reduced, because of the interactions between those functional groups with triterpene extract. Similar results were obtained by [37].
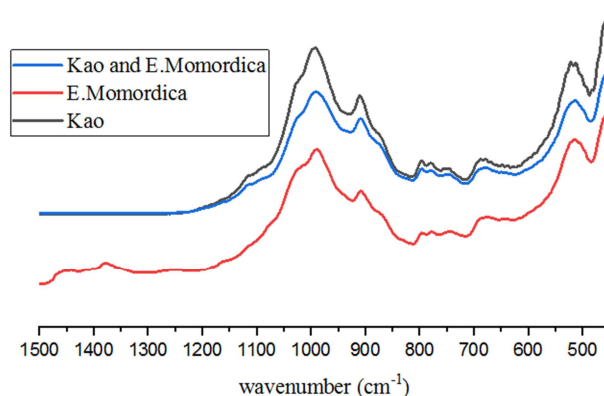

Figure 4. FT-IR analysis on the adsorption of triterpene extract on kaolinite.

3.1.2. Elemental Composition of Adsorbent

X-ray fluorescence (XRF) method has been used to identify the major minerals and chemical compounds present in the clays. The main oxides are SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO. The kaolin was rich in SiO_2 (45.41%), in Fe_2O_3 (8.10%); and in Al_2O_3 (20.54%) and contained only small amounts of CaO, MgO, K_2O, Na_2O, SO_3 and P_2O_5 (Table 2). Loss on ignition (LOI) was 15.26%. The chemical composition indicated the presence of considerable amounts of silica-and iron-bearing impurities. According to reports by Shibu et al. [11], the kaolin has high amount of silica 69.30% and lower alumina 24.30%. Other researchers achieved silica content of 47.81% and alumina 22.01%; which is related to this report [38]. The specific surface area of the clay was determined using Saers' method, and the value obtained was 7.65 m² g^{-1}.

***Table 2.** Elemental composition of Boboyo clay.*

Compound	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	Na₂O	SO₃	P₂O₅	LOI
Wt (%)	45.41	20.54	08.10	00.13	00.79	01.10	01.09	00.04	00.03	15.26

3.1.3. X- ray Diffraction
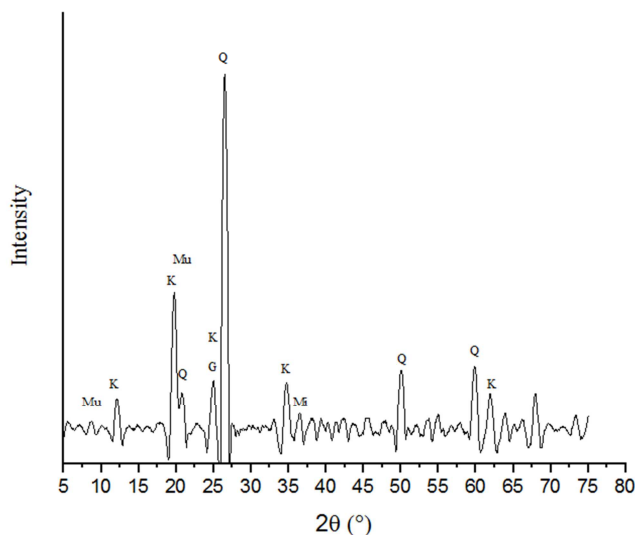
K: Kaolin; Q: Quartz; Mu: Muscovite; Mi: Microline; G: Grossite.

***Figure 5.** X-ray diffractogram of Boboyo clay.*

The identification of the kaolin mineral component is done by comparing the peak intensity position (2θ) in the sample X-ray diffraction-gram with the peak position value of the diffraction intensity (2θ) standards contained in the Joint Committee for Powder Diffraction Standards (JCPDS). The price of the peak intensity of the technical kaolin is shown in Figure 5. The absorption peaks appear at 2θ=12.26°; 20.77°; 20.97°; 25.19°; 26.53°; 34.9°; 35.8° and others. These findings are consistent with other previously reported works [22]. The absorption peaks found at 2θ=12.26°; 20.77°; 20.97°; 25.19°; 26.53°; 34.9°; 35.8°. The peak at 2θ=12.26° is the distinctive XRD form of kaolin (K). Some impurities like quartz (Q) (peaks around 20.97°; 26.53°), muscovite (Mu) (8.15°; 20.77°), microline (Mi) (32.25°) and grossite (G) (29.19°) are also present. The kaolin sample showed predominant phases as kaolin and quartz, which are commonly found in kaolin as one of the major compositions.

3.2. Adsorption Studies

3.2.1. Effect of Contact Time

The study of the influence of time was carried out in order to determine the equilibrium time when the quantity of the triterpene extract fixed is maximum. The quantity adsorbed per gram of clay as a function of time is illustrated in Figure 6. The results presented have shown that the adsorbed amount of triterpene extract increases rapidly in the first 5 minutes to reach an optimum of 0.23 mg/g and remains approximately constant after 10 minutes, indicating a state of balanced. This shows that the balance of extract adsorption by the adsorbent used is very fast. The rapidity of the

reaction is explained by the availability of the high number of vacant adsorption sites on the clay surface at the initial stage of adsorption. Then, adsorption gradually slows down as the remaining unoccupied outdoor sites are difficult to occupy. In addition, the extract molecules are medium in size and can be easily diffused into the internal pores until they are saturated, which will reduce mass transfer between the liquid phase and the solid phase over time. These lead to a decrease in the adsorption rate and we observe a plateau which corresponds to the state of equilibrium after 10 minutes. Consequently, maximum adsorption (0.23 mg/g) of triterpene extract is obtained after 10 minutes during our work. In the rest of this work, a contact time of 10 min seems largely sufficient to reach equilibrium.
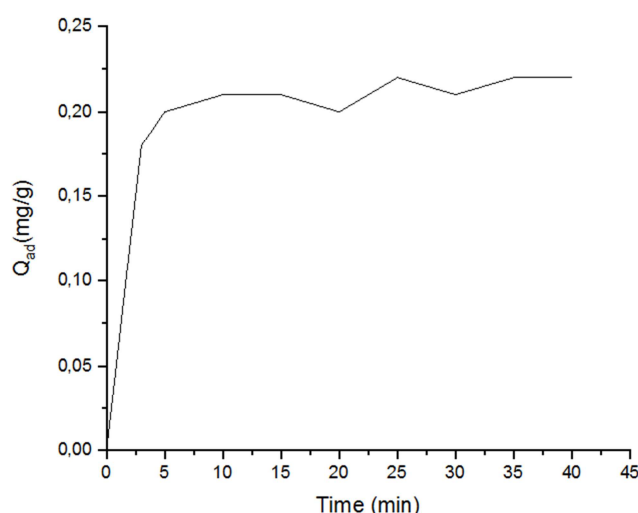
***Figure 6.** Effect contact time on adsorption of triterpene extract (C₀=20mg/L; m=0.02g; V=20mL, T=25°C).*

3.2.2. Effect of Solvent

The study of influence of solvent on adsorption capacity of triterpene extract led us to vary methanol, hexane and ethyl acetate solvents while retaining the initial concentration of the substrate in solution and the initial mass of the adsorbent. Figure 7 gives us the variation of adsorbed quantities of these compounds according to the different solvents. Knowledge of the type of solvent used is an essential parameter for determining the maximum adsorption capacity in solution [39]. The results presented have shown that the variability of the organic solvent used has a remarkable influence on the adsorbed quantity of triterpene extracts. The amount of triterpene extract absorbed by the clay increases from ethyl acetate to methanol. Methanol was found to be the most suitable solvent for this adsorption study. This suggests that methanol has made it possible to make a strong interaction between the molecules of the extract and the different functional groups (Figure 3) present in the interfoliar spaces of the clay, implying the use of Van der Waals type bonds,

hydrogen bonds and even can be chemical bonds [40]. Furthermore, the adsorbate used in our work was obtained by optimizing the methanol extract to triterpene using hexane as a solvent having a high affinity for this family of compound. However, the high adsorbed quantity observed in methanol compared to the other solvents could be explained by a greater solubility of the extract known as "optimized in triterpene" by the extraction solvent implying a strong interaction between clay and extract of triterpene [4, 41]. In contrast, the hexane extract believed to be the most concentrated in triterpene [18] was moderately fixed by clay. This could be explained by the process of polarization of the molecules of triterpene extract to the solvent used. Similarly, it has been reported by Sana et al. [4] and Jian et al. [42] that the solubilization of an organic compound does not necessarily depend on the type of solvent from which it was isolated but rather on the affinity of the compound to the solvent.
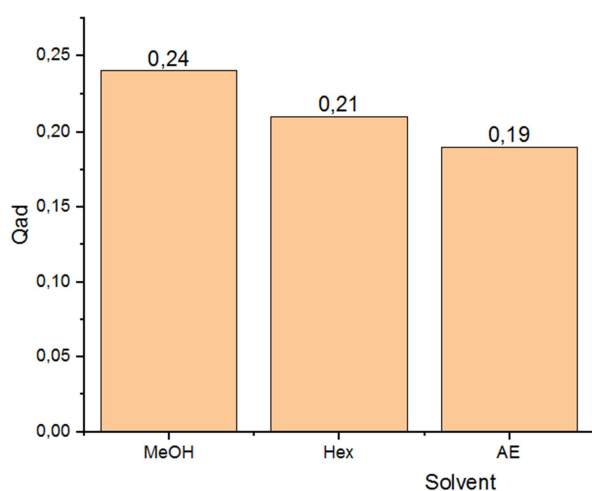

Figure 7. *Effect of solvent on adsorption of triterpene extract (solvent: AE, Hex, MeOH; C_0=20mg/L; m=0.02g; V=20mL, t=30min and T=25°C).*
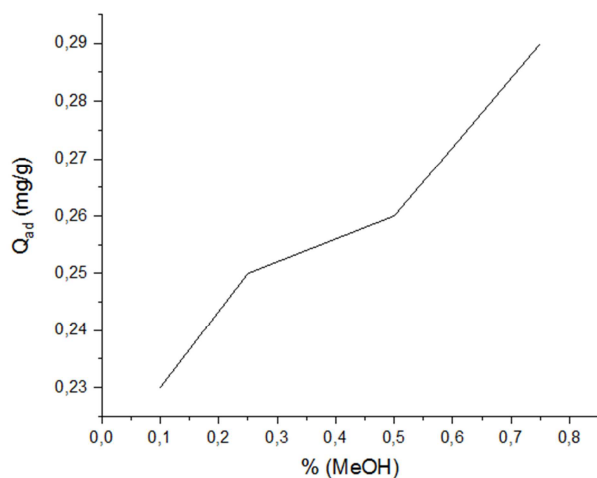
3.2.3. Effect of Dilution of Solvent

Figure 8. *Effect of methanol dilution on adsorption of triterpene extract (MeOH10%; MeOH25%; MeOH50%; MeOH75%; C_0=20mg/L; m=0.02g; V=20mL and T=25°C).*

The study of influence of dilution of solvent on adsorption capacity of triterpene extract has led us to vary the concentration of the methanol solvent from 10 to 75% while retaining the initial concentration of the substrate in solution. Figure 8 gives us the variation of the adsorbed quantity of this compound studied as a function of the concentration of the solvent.

The dilution of solvent is an important factor which can affect the adsorption process [43]. It appears from Figure 8 that, the increase in the amount of methanol in the medium results in an increase in the amount of triterpene extract adsorbed. The amounts adsorbed vary from 0.23 to 0.29 mg/g. Indeed, the dilution of methanol caused the change from the most concentrated to the least concentrated medium tending towards the aqueous medium. Thus, the decrease in the adsorbed quantity observed could be influenced by the partial solubility of the adsorbate following the addition of a large amount of water in methanol. Consequently, a low dispersion of the molecules of the extract in the medium causes a decrease in the amount adsorbed. However, the increase in the adsorbed amount of triterpene extract in methanol could be justified easily by the phenomenon of the great solubilization of the extract by the solvent. Thus, the more the molecules are dispersed in the medium, the more they easily diffuse towards the adsorption sites.

3.2.4. Effect of pH

The initial pH of dye solution is an important parameter which controls the adsorption capacity. This pH can be influenced by the surface charge of adsorbent, the degree of ionization of adsorbate molecule, and extent of dissociation of functional groups on the active sites of the adsorbent [44]. Hence, the adsorption of triterpene extract on the clay was examined from solution at different pH values covering a range of 3 to 11. The highest adsorption capacity was obtained at pH=5 while the maximum adsorption was 0.25 mg/g. The removal is affected by the change in the pH value of the solution. In acidic medium, the surface of the kaolinite is surrounded by H^+ ions, which decrease the interaction of the solute ions with the sites of the kaolinite material. On the contrary, in the basic medium, the concentration of H^+ ions decreases and generates a good interaction between the triterpene extract ions and the sites of the surface. The carbonyl and hydroxyl groups that present in the triterpene extract (momordicine) which contain electronegative oxygen were the groups that responsible for the electrostatic interactions between triterpene extract and the kaolinite. Similar adsorption behaviors of phenol were reported by several investigations [45]. In order to confirm this result, it was necessary to determine the pH_{pzc} of the adsorbent. Therefore, the point of zero charge (pHpzc) of the adsorbent is the main parameter influencing the adsorption phenomenon. Generally, the zero point of charge of kaolinite is in order to pH=4.0 [5]. When the solution has pH>pH_{pzc} the surface of the clay is negatively charged which promotes the adsorption of molecule cationic. For pH < pH_{pzc} the surface of the clay is

charged positively, and thus likely to be repulsive to the molecule cations. The removal increase can be explained by electrostatic attraction between the particles of the material, which is positively charged, and the anionic molecule, which is negatively charged. Therefore, with increasing pH above $pH_{pzc}=4$, the removal of cationic molecule by the kaolinite increased slightly.

3.2.5. Effect of Adsorbent

The study of influence of mass of adsorbent applied on adsorption capacity of triterpene extract led us to vary the amount of the adsorbent from 0.02 to 0.1g while retaining the initial concentration of the substrate in solution. It appears from Figure 10 that, the increase in the amount of adsorbent results in a decrease in the amount of triterpene extract adsorbed per unit of mass. The amounts adsorbed decrease from 0.22 to 0.04 mg/g with the increase in the mass of adsorbent. This can be explained by the fact that since the mass of adsorbent increases, there is a decrease in the number of active adsorption sites due to the superposition of the particles of adsorbent on the surface of the solid and inversely the adsorbed amount of the triterpene extract causes the increase in the mass of adsorbent. This result could also be justified by the phenomenon of normalization of the quantities adsorbed. Indeed, the increase in the amount of adsorbent leads to an increase in its total available surface area without any influence on the content of triterpene extract in the medium. This may be due to the creation of an aggregation of particles and a slowdown in the diffusion of molecules in the pores of the material [47]. Thus, the less saturated the medium, the more easily the molecules diffuse towards the adsorption sites. This evolution is in accordance with the kinetic stages of liquid phase adsorption which are external diffusion (transfer of the solute to the surface of the solid of the adsorbent), diffusion on the surface of the solid, intraparticle diffusion (diffusion in the pore) and the adsorbent-adsorbate interaction. Thus, in the rest of our work, an amount of 0.02 g of clay will be necessary to fix the maximum amount of triterpene extract.
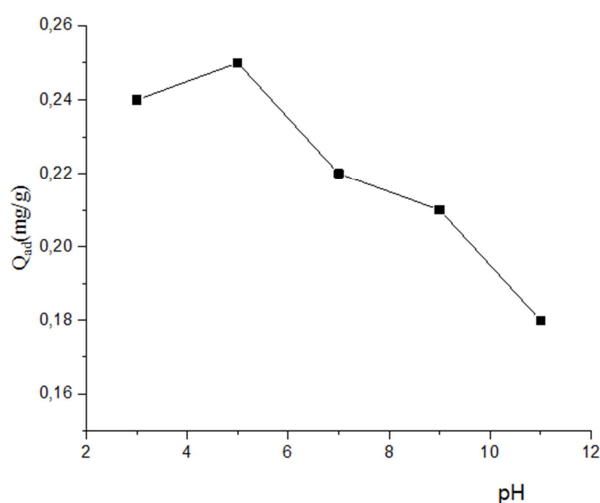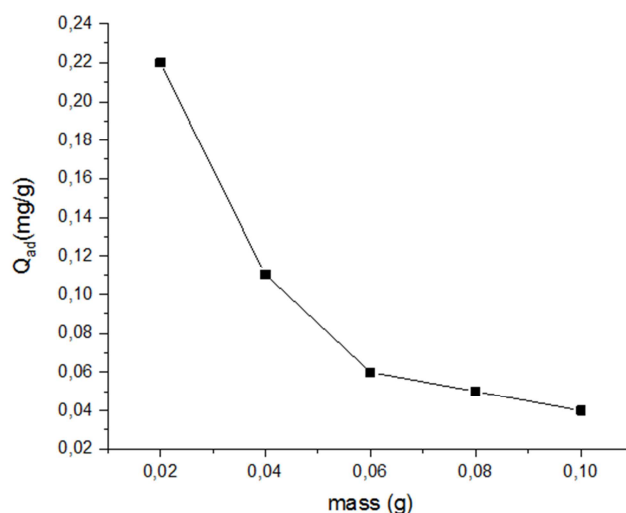

Figure 10. *Effect of adsorbent dosage on adsorption of triterpene extract (MeOH75%; $C_0=20$ mg/L; m=0.02 g; m=0.04 g; m=0.06 g; m=0.08 g; m=0.1 g; T=25°C).*

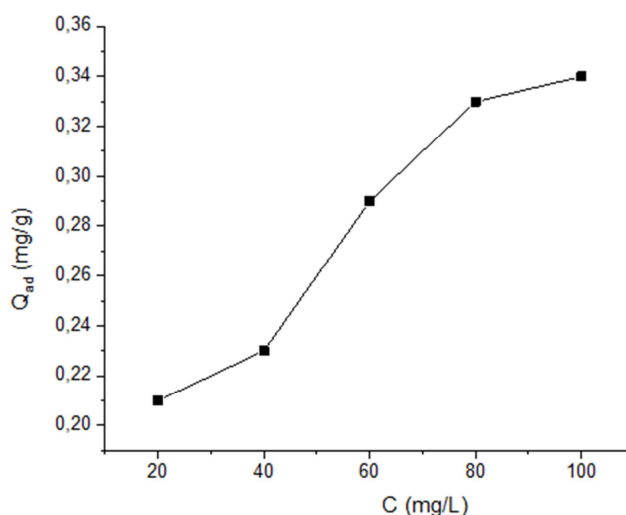**Figure 11.** *Effect of concentration on adsorption of triterpene extract (solvent: MeOH75%; C=20 mg/L; C=40 mg/L; C=60 mg/L; C=80 mg/L; C=100 mg/L; m=0.02 g; V=20 mL, T=25°C).*

3.2.6. Effect of Initial Concentration of Triterpene Extract

The influence of initial concentration of triterpene extract on the adsorption capacity of the clay was carried out with a mass of the material of 0.02 g, a contact time of 10 min and at a temperature of 25°C. The results obtained are shown in Figure 11. It can be seen from Figure 11 that the adsorbed amount of triterpene extract increases considerably with the increase in the concentration of adsorbate. The increase in the concentration causes the increase in the training force of the concentration gradient therefore the increase in the molecular diffusion of triterpene in solution on the surface of the adsorbent. The percentage of the maximum amount adsorbed for an initial concentration of 100 mg/L is around 1.75%. The result seems to indicate that if the concentration of the molecules is high in the solution, there will therefore be more molecules which will diffuse towards the surface of the sites of the particles of the support and consequently the retention

Figure 9. *Effect of pH on adsorption of triterpene extract (solvent: 10%MeOH; $C_0=20$ mg/L; m=0.02 g; V=20 mL, t=10 min and T=25°C).*

becomes more important. Thus, the higher the concentration of the solution, the more numerous the molecules of extract in the solution and the more they are in contact with the adsorbent then the percentage of adsorption increases [48, 49]. Similarly, the increase in the initial concentration of triterpene extract would result in an increase in the number of molecules present in the medium and therefore in the number of molecules adsorbed per unit mass of clay. This phenomenon was also observed in 2016 by [28]. who, working on the adsorption of gallic acid and the optimized extract of the bark of the pittosporum viridiflorum (*pittosporaceae*) trunk by Boboyo clay, found a maximum percentage of elimination of 11.82 mg/g with a concentration compared to the results of the present work.
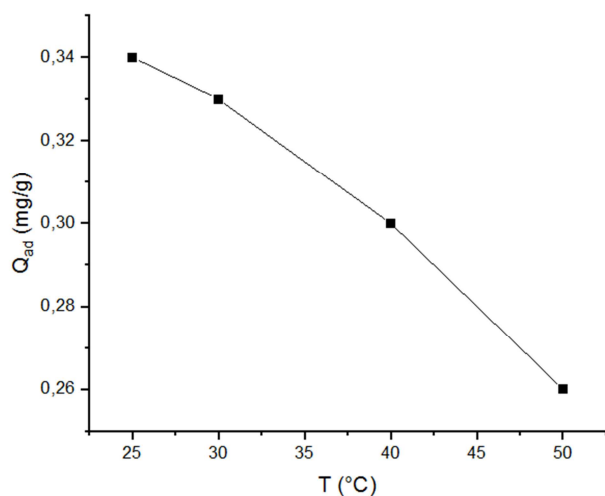

Figure 12. *Effect of temperature on adsorption of triterpene extract (T=25°C, T=30°C; T=40°C; T=50°C; Co=100 mg/L; m=0.02 g; V=20 mL).*

3.2.7. Effect of Temperature

Temperature is a major variable in the adsorption process. It is found that the quantity adsorbed decreases when the temperature increases. Figure 12 shows the variation in the amount of triterpene extract adsorbed as a function of temperature. Temperature is an important factor that can affect the adsorption process. From this result, there is a gradual decrease in the amount of triterpene extract adsorbed per gram of clay from 0.34 to 0.26 mg/g when the temperature increases from 25 to 50°C. Indeed, the decrease in the adsorption capacity with the increase in temperature would be due on the one hand to the degradation of triterpene extract previously fixed to the surface of the clay material [42] and on the other hand by the destruction of the functional groups present on the surface of the adsorbent as shown in Figure 2 above. Similarly, this decrease would also be due to the weakening of the adsorptive forces between the active sites on the adsorbent and the molecules of triterpene extract following the increase in temperature [28]. Similarly, the decrease in the efficiency of adsorption at high temperatures has also been explained by the fact that several particles of clay adsorbents are destroyed at temperatures above 25°C and the suspension (Clay+solution) becomes homogeneous at elevated temperatures [28]. These results are contrary to

those obtained by Aksas [49] and Domga [50]. Overheating adversely affects the course of the adsorption phenomenon and can lead to an increase in the desorption kinetics. Thus, the decrease in the adsorption capacity with temperature indicates that the process is exothermic and would lead under these conditions to physical adsorption. So the best results are obtained in the area of ambient temperature.

A study of the temperature dependence of the adsorption process gives valuable information about thermodynamic aspect of the adsorption. The thermodynamic parameters for the present study including Gibbs free energy of adsorption $\Delta G°$, changes in enthalpy of adsorption ($\Delta H°$) and changes in entropy of adsorption ($\Delta S°$), were determined using the following equations [51]:

$$\Delta G = -RTlnKc \qquad (3)$$

$$lnKc = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (4)$$

$$\Delta G° = \Delta H° - T\Delta S° \qquad (5)$$

Where R is the universal gas constant (8.314J/mol.K) and T is the solution temperature in K.

The equilibrium constant (Kc) can be calculated using the equation below:

$$Kc = \frac{Qe}{Ce} \qquad (6)$$

Equilibrium constant (Kc) for the adsorption process was determined by plotting ln q_e/Ce vs q_e and extrapolating to zero q_e. The values of $\Delta H°$ and $\Delta S°$ were obtained from the slope and the intersection with the intercept at the origin of ln (Kc) versus 1/T (Figure 10).

Table 3. *Thermodynamic parameters relative of adsorption of triterpene extracts on clay mineral at different temperatures.*

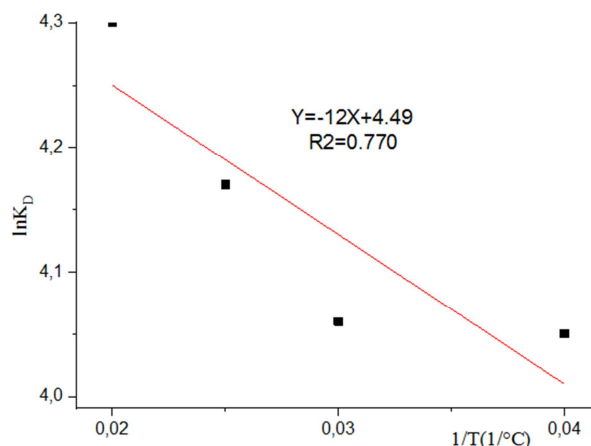| T (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (J/mol)	R²
298	-11.121			
303	-11.208	99	37.32	0.770
313	-11.581			
323	-11.954			

Figure 13. *Plot of ln (K_D) versus temperature (1/T) for the adsorption of triterpene extracts on the clay.*

The thermodynamic parameters, the standard Gibbs energy ($\Delta G°$), standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) for triterpene extracts at various temperatures obtained are given in Table 3. It can be seen from this table that all the ($\Delta G°$) values are negative, which indicates that the adsorption is spontaneous and thermodynamically favorable. However, the negative value DG decreased with an increase in temperature, indicating spontaneity of the adsorption process of the clay which was more favorable at higher temperatures. Similar observation is made in the adsorption of oxytetracycline on kaolinite [51]. Furthermore, the positive sign of $\Delta H°$ confirmed the endothermic nature of adsorption process. The value of 99 kJ/mol for $\Delta H°$ higher than 40 kJ/mol is indicative of chemical adsorption process occurring on the surface of clay material [52]. Besides, the positive values of the $\Delta S°$ show the increased randomness at the solid/liquid interface, with some structural changes in the adsorbate and adsorbent. Similar observation is made in the adsorption of oxytetracycline on kaolinite [52]. Increase in entropy for adsorption in the liquid phase has been reported by Adarsh et al. [53]. Normally, adsorption of gases leads to a decrease in entropy due to the orderly arrangement of the gas molecules on a solid surface. However, adsorption of solute from the solution on a solid surface is a complex phenomenon and the entropy of the system is determined by degree of freedom of adsorbate (solute) and solvent molecules. The positive value of entropy could be due to the affinity of the clay and desorption of solvent molecules from the surface of adsorbents.

3.3. Isotherm Studies

Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, describe how the adsorbate interacts with adsorbents, and comprehensive understanding of the nature of interaction. Isotherms help to provide information about the optimum use of adsorbents [22, 44]. When optimizing the design of an adsorption system, it is essential to establish the most appropriate correlation for the equilibrium curve. Several isotherm equations are available for analysis of experimental sorption equilibrium parameters. However, Langmuir and Freundlich models are the most widely used type of isotherm. These models were used to explain the interaction between triterpene extracts and kaolinite in this study. They are the best models for explaining adsorption trends and are based on the rationale that the adsorbents become saturated with adsorbate after sufficiently long contact times [22].

3.3.1. Langmuir Isotherm

The Langmuir model is suited to describe the adsorption of monolayer onto homogeneous surfaces. The adsorption can be represented by the following equation:

$$\frac{Ce}{qe} = \frac{1}{KLqmax} + \frac{Ce}{qmax} \qquad (7)$$

Where qe (mg/g) is the amount of dye adsorbed at equilibrium, Ce (mg/l) is the equilibrium concentration, KL (l/g) is the Langmuir constant and q_{max} is the monolayer adsorption capacity. In addition, one can use the Langmuir isotherm to extract a dimensionless term RL called the separation factor. The value of RL indicates the type of the isotherm (i) unfavorable (RL>1), (ii) linear (RL=1), (iii) favorable (0<RL<1), or (iv) irreversible (RL=0). It is defined as [44]:

$$RL = \frac{1}{1+KLCo} \qquad (8)$$

Where KL is the Langmuir constant and C_0 is the initial concentration of adsorbate in solution.

3.3.2. Freundlich Isotherm

The Freundlich model is based on the fact that the adsorption takes place on heterogeneous surfaces and assumes that the absorption occurs on sites with different adsorption energies. The model gives a representation of the equilibrium between the amount of adsorbate in solution and that on the surface of the adsorbent. This equation is also applicable to multilayer adsorption and is expressed by the following equation:

$$Logqe = LogKF + \frac{1}{n}logCe \qquad (9)$$

Where qe is the amount of solute adsorbed per unit mass of adsorbent (mg/g), Ce is the equilibrium concentration, KF is the Freundlich constant and n is the heterogeneity factor. The value KF is related to the adsorption capacity, while the value of (1/n) is related to the adsorption intensity. When n=1, the adsorption is linear, meaning that sites are homogeneous and there is no interaction between the adsorbed species; when 1∕n < 1, adsorption is favorable and the adsorption capacity increases while new adsorption sites appear. When 1∕n > 1 adsorption is not favorable, adsorption bonds become weak and the adsorption capacity decreases.
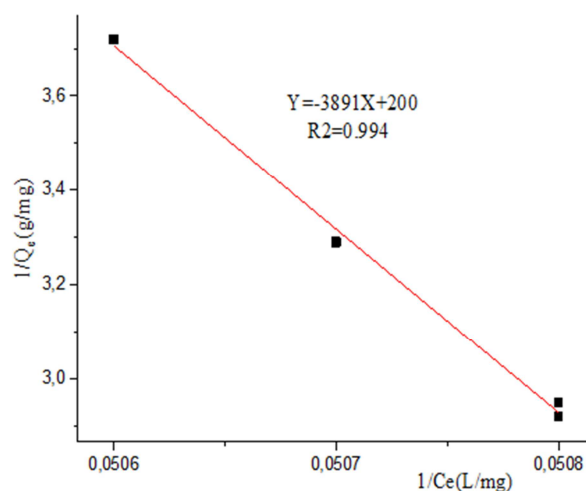

Figure 14. Linear plot of the model of Langmuir.

Table 4. Langmuir and Freundlich isotherms constants.

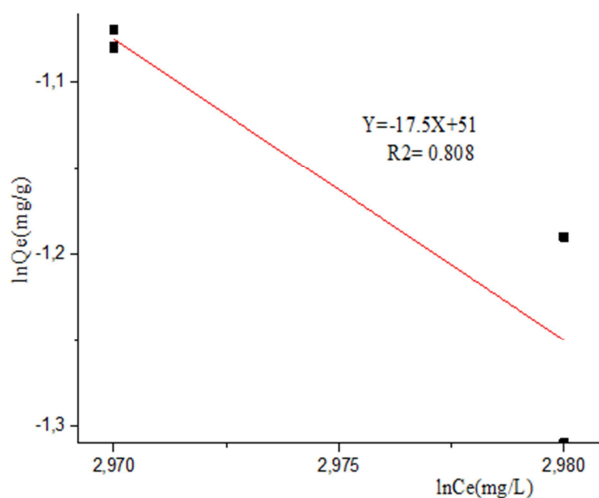| Langmuir				Freundlich		
Q_{max} (mg/g)	K_L (L/mg)	RL	R^2	K_F (mg/g)	$1/n_F$	R^2
0.0002	19.45	0.002	0.994	138.63	0.05	0.808

Figure 15. Linear plot of the Freundlich model.

The variation in the amount of triterpene extract adsorbed per gram of clay as a function of the concentration at equilibrium (Ce) was determined and the results modeled. The adsorption parameters according to the Freundlich and Langmuir equations are summarized in Tables 4 below. As observed, the value of R² obtained from the Langmuir isotherm equation (0.994) was higher than that from the Freundlich (0.808) isotherm equations. These results showed that the adsorption experiments data could be well described by the Langmuir model. The adsorption occurred on the homogeneous surface as a monolayer, and the maximum monolayer adsorption capacity (q_{max}) was found to be 0.002 mg/g. Similar observation is made in the adsorption of methylene blue onto modified Tamazert kaolin [45]. The RL

value was obtained within the range 0<RL<1, indicating that the adsorption of triterpene extract on the clay material is favorable.

3.4. Kinetics Studies

Adsorption kinetics is a very useful tool which gives a better comprehension of adsorption processes and mechanism. It also helps to examine the adsorbent's performance. The kinetics of triterpene extract adsorption on Boboyo clay was analyzed using first order, second order and intra-particle diffusion Lagergren models. The pseudo-first-order kinetic model was suggested by Lagergren to describe the adsorption in solid/liquid systems based on adsorption capacity. The pseudo-second-order model can be applicable to the process involving chemisorption. The intra-particle diffusion model is another commonly used model, which is capable of identifying the reaction pathways and adsorption mechanisms and predicting the rate-limiting step [52]. The respective linearised equation of pseudo-first order, pseudo-second order models and intraparticle diffusion models are:

$$Ln(qe - qt) = -k_1 t + Lnqe \qquad (10)$$

$$t/q = 1/K_2 q_e^2 + t/q_e \qquad (11)$$

$$q_t = kint\sqrt{t} + C \qquad (12)$$

where k_1, k_2 and k_{int} are the respective pseudo-first, pseudo-second order and intraparticle diffusion, kinetic constant, q_e and q_t are the respective amount of adsorbent at equilibrium and at time t, C is an indication of boundary layer effect of the adsorbent particles.

Table 5. Pseudo first order, pseudo second order and intraparticle diffusion parameters.

Pseudo first order			Pseudo second order			Intraparticle diffusion		
K_1 (L/min)	Q_1 (mg/g)	R^2	K_2 (g/mg.min)	Q_2 (mg/g)	R^2	K_{int} (mg/g.min$^{1/2}$)	C_1 (m²/s)	R^2
0.057	8.33	0.9207	3.988	0.23	0.9974	0.0092	0.1746	0.7726

The kinetics of triterpene extract adsorption on Boboyo clay was analyzed using first order, second order and intra-particle diffusion Lagergren models in Table 5. The conformity between the experimental data and the predicted model is based on the values of the correlation coefficients (R^2), and the kinetics parameters with each regression coefficient are summarized in Table 5. The better fitting results along with the higher regression coefficients for the adsorbent can be gained when using the pseudo-second-order model (R^2=0.994) rather than pseudo-first-order model (R^2=0.920), indicating the chemisorption role is prevalent for of triterpene extracts removal in material. In addition, the

calculated value of adsorption capacity, q_e (0.23 mg/g) is matched well with the experimental ones. These results implied that the adsorption was better described by the pseudo-second order kinetic, indicating that the adsorption mechanisms of triterpene extract depended on the adsorbate and adsorbent. The values of the calculated theoretical adsorbed quantities (0.23 mg/g) of the model of pseudo-second order are very close to adsorbed quantities obtained experimentally (0.34 mg/g). This model reflects the existence of strong interactions between the clay surface and the molecules of the adsorbates.
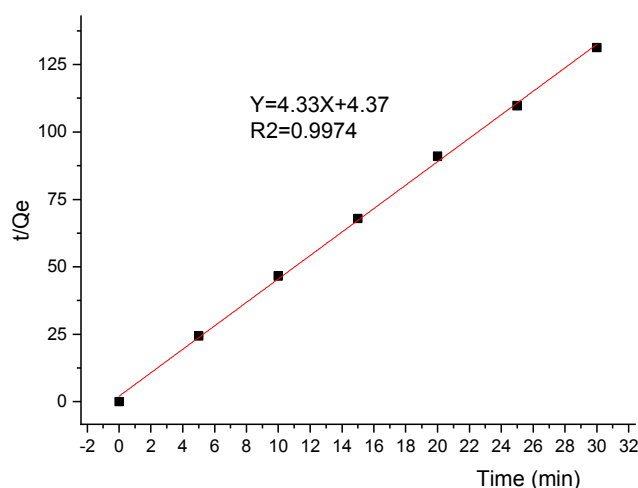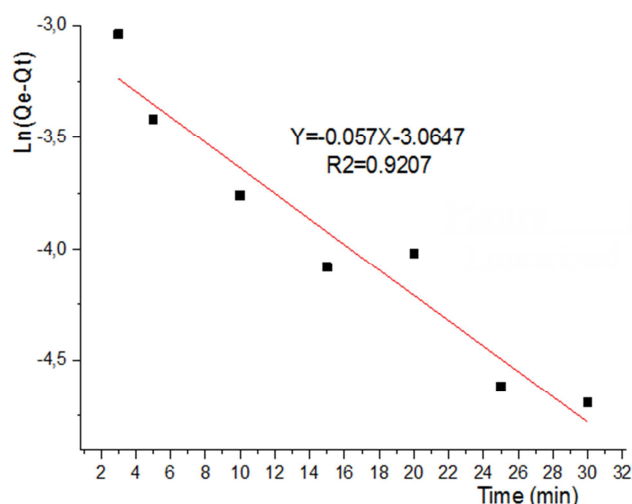
Figure 16. Linearized pseudo-first order plots.

Figure 17. Linearized pseudo-second order plots.

adsorption process even at lower temperature. The positive value of $\Delta H°$ showed the endothermic nature of the adsorption. The study of the adsorption of triterpene extract by Boboyo clay can be used for a powdery formulation of insecticide.
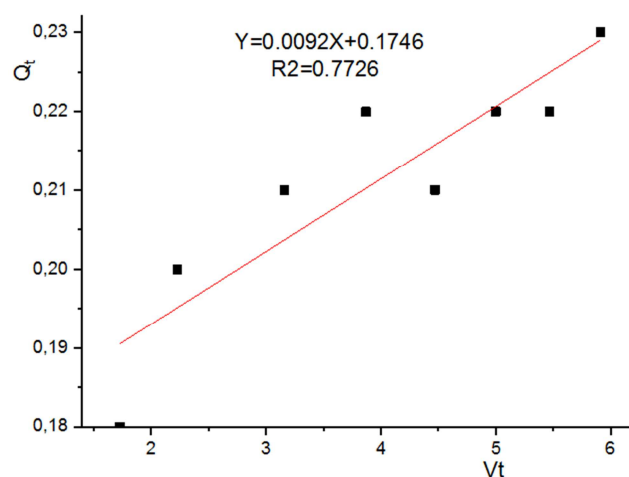

Figure 18. Linearized intraparticle diffusion plots.

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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time due legal or ethical reasons.

Compliance with Ethical Standards

Conflict of interest All authors declare that they have no competing interest.

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4. Conclusion

The purpose of this present study is to enhance the extract from the leaves of *Momordica charantia* and Boboyo clay, using this natural clay as a support for organic compounds, in order to promote a powdery formulation of insecticide. The study of certain parameters which influence the adsorption in batch mode is done. The adsorption of triterpene extract is very rapid, and equilibrium is reached in less than 10 minutes. The kinetic model of pseudo-second order is applicable to the adsorption of triterpene extract. The amounts adsorbed decrease with increasing mass of adsorbent and temperature. However, they increase with the increase in the initial concentration of triterpene extract. Adsorptions of triterpene extract onto the clays are more described by the Langmuir model with a maximum adsorption capacity of triterpene extract of 0.34 mg/g, at 25°C and 100 mg/L initial concentration of triterpene extract. A pseudo second order kinetic model explained the rate of adsorption of triterpene extract on the adsorbents. The thermodynamic parameters $\Delta G°$, $\Delta H°$ and $\Delta S°$ indicated the spontaneity of the

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