



Natural Pyrethrum Extracts Photo-stabilized with Organo Clays

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Authors' contributions

This work was carried out in collaboration between all authors. Author HW did the field work analysis, Provision of finances for laboratory, co-ordination of laboratory and field work, Reading and final manuscript corrections. Author EM performed laboratory and field analysis, draft manuscripts write up. Author AG did Provision of finances for reagents purchase, Reading and final draft corrections, co-ordination of laboratory and field work. All authors read and approved the final manuscript.

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ABSTRACT

Botanical pesticide use in agricultural sector over synthetic pesticide would ensure less pest resistance and reduced environmental pollution. Natural Pyrethrum Extracts (NPE) are effective, environmental friendly pesticides, but are photo-labile, limiting their use in pest control. In the present study, naturally occurring montmorillonite (MMT) clay was purified following established procedures. Organo-clays were prepared by treating the purified clay with Hexadecyltrimethylammonium Bromide (HDTMA) and Trimethylphenylammonium Bromide (TMPA) organic cations. NPE molecules were loaded into these organo clays by simple immersion using NPEs solution to obtain NPE-organo clay composites. The samples were characterized using Fourier Transform Infrared (FT-IR) spectrophotometry and X-ray Diffractometry (XRD) techniques. *In situ* photo-stability tests conducted by exposing the NPEs-clay composites to sunlight for four hours revealed ~52% stabilization of NPEs by HDTMA modified clays. The findings demonstrated a great potential of clay to photo stabilize NPE and consequently improve the versatility of NPE-based pesticides. Bio-assay test on maize weevils revealed 100% mortality rate on NPE HDTMA-clay treatments at 120 hrs while the un-protected NPEs exhibited 18% mortality rate for the same

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duration of time. Clay synergizes NPE; acting as a carrier, photo- protector and desiccant to NPE pesticide in weevils' eradication. Embrace of this effective technology shall ensure enhanced food security and more income to the pyrethrum growing farmers.

Keywords: NPEs; Organo-clay; intercalation; photo-stabilization.

1. INTRODUCTION

Synthetic pesticides in the world agricultural sector have resulted to severe environmental pollution attributed to the pesticides loss processes such as degradation by photolysis, run offs, leaching and volatilization [1,2]. Thus, there is a growing demand for pesticide products with low health risk and those that may help conserve ecosystems and biological diversity [3,4]. Mann discussed the importance of use of natural chemicals for they are safer than conventional pesticides [5,6]. Among the botanical products being traded globally are the pyrethrum products from *Chrysanthemum cinerariaefolium*. Pyrethrum extracts are a combination of six natural esters of chrysanthemic acid; pyrethrins I & II, Jasmolin I & II and Cinerin I & II (Fig. 1) naturally extracted from pyrethrum flowers. The insecticidal esters are responsible for the quick knockdown properties of the pesticide and are safer to use [7]. According to Dickmann and Housset [8], the benefits associated with pyrethrum extracts pesticide development is difficult to estimate as it may be assessed in many different ways. Thousands of the houses have been protected

against termites, tens of thousands of restaurants, hospitals, ships and airplanes have been saved from pest attack. Millions of public saved from diseases such as malaria, allergies, and thus placing it in the led in achievements.

However, photo degradation of the NPEs is rapid in presence of UV light [9] that renders the botanical insecticide ineffective in such an environment. The drawback has necessitated development of photo-stable pyrethrins-based pesticide formulations. Previous research indicates that, pyrethrins formulations based on lignin-derivatives provided extended simulated sunlight protection [10]. David proposed introduction of biodegradable bioresmethrin on replacement of pyrethronyl alcohol portion of pyrethrins with 5-benzyl-3-furylmethyl moiety to enhance the stability [11], plant extracts have also been reported as potential photo-stabilizing agents of pesticides' active ingredients [12]. Wanyika et al. [13] observed that the natural pyrethrum extracts may be photo stabilized using fixed plant oils and tea extracts. The results indicated that the efficacy against the weevils eradication, increased when cotton seed oil was used [13].

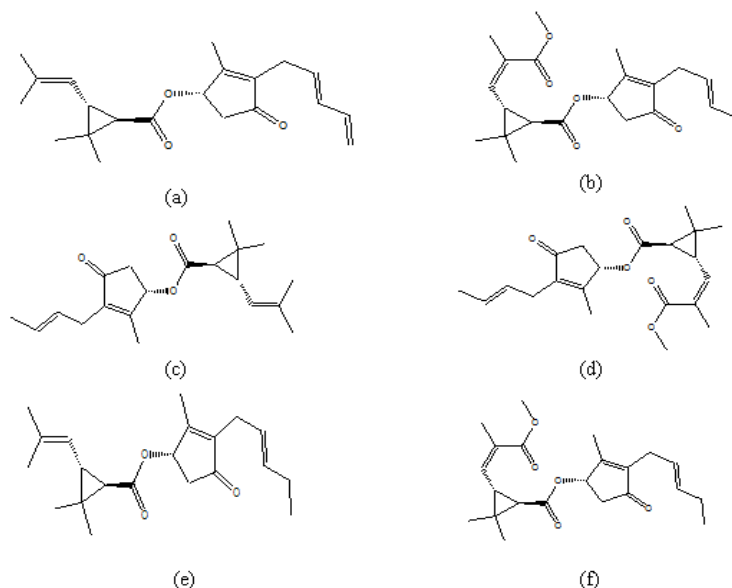


Fig. 1. Natural pyrethrum extract esters; (a) pyrethrins I, (b) pyrethrins II, (c) Cinerin I, (d) Cinerin II, (e) Jasmolin I and (f) Jasmolin II

Clay formulations have been suggested to be the best pesticide carriers due to their sustainability and economic viability [14]. The formulations reduce the photo degradation, leaching and volatilization thus solving environmental and economic problems [15]. Clay is a naturally occurring material composed of silicates, hydroxides, metal oxides and variable amounts of water trapped in the mineral structure by polar attraction. Montmorillonite (MMT) (Fig. 2) is a 2:1 phyllo-silicate clay comprised of two tetrahedral sheets sandwiching a one octahedral sheet.

Organo clay based materials have been proposed to prolong the efficacy and reduce the environmental impacts of pesticides in the soil. Clay minerals are negatively charged and hydrophilic thus cationic and highly polar neutral pesticides strongly adsorb on their surface. However, for hydrophobic pesticides adsorption, surface modification using organic cations such as quaternary ammonium salts is required. This increases clay efficiencies by replacing the existing exchangeable inorganic cations present in the clay gallery spaces with these organic cations to yield hydrophobic organo clays [17-19]. The selection of the cations may be based

on the natural origin and presence of diverse functional groups on the structure that is anticipated to influence the active ingredient sorption [20]. The length of the alkyl chain is responsible for arrangement of the intercalated organic cations in the clay interstitial space. Short alkyl organic cations chains forms monolayer while long alkyl organic cations chains forms bilayers, pseudotrimolecular arrangement or paraffin complexes [21].

Maize is a staple food in Africa that is usually stored to provide a major food security and planting seeds [22]. Maize farmers in Kenya face a major problem in controlling pests that attack their already harvested and stored maize grains. 44 Maize Weevils (*Sitophilus zeamais*) is the most predominant and destructive of them all [23]. Botanical products are readily used by farmers as they are less toxic, readily available and effective in these pests control [13].

In this study, the ability of MMT clay to photo-stabilize NPEs was demonstrated through modification of the clay using HDTMA and TMPA and the subsequent intercalation of the NPEs. Accelerated stability studies were conducted to confirm the enhanced photo-stabilization.

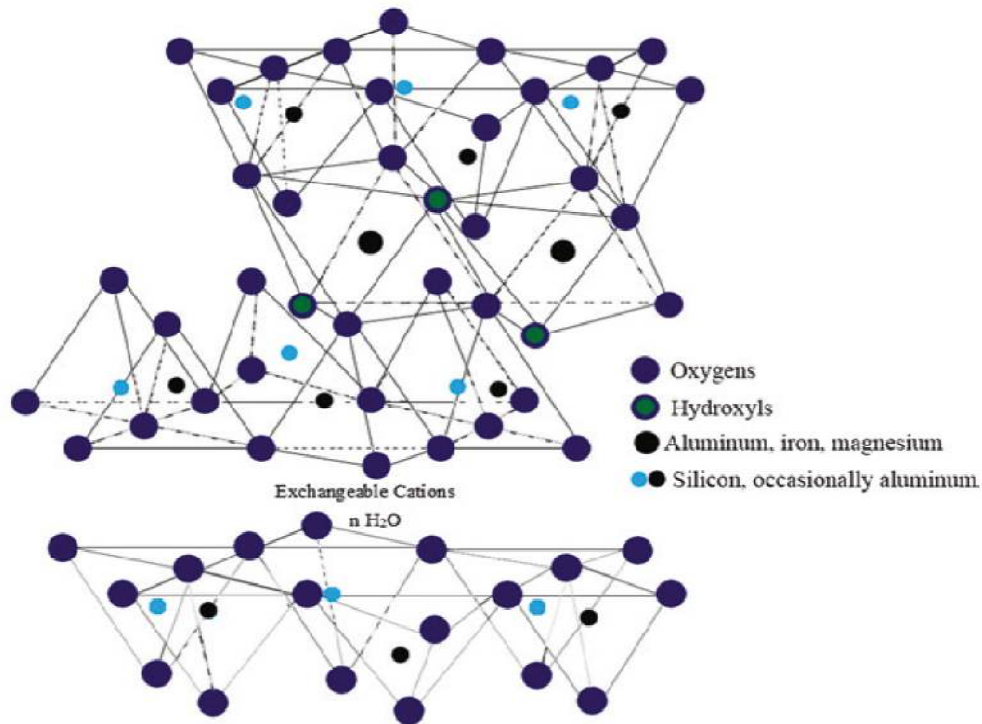


Fig. 2. The structure of montmorillonite clay [16]

2. MATERIALS AND METHODS

2.1 Solvents and Reagents

Solvents and reagents used throughout this research project were of high purity. Pyrethrum pale extract containing 50% NPEs was acquired from pyrethrum board of Kenya. HDTMA, TMPA, n-Hexane (analar), acetonitrile (HPLC) and absolute ethanol (analar) were purchased from Sigma-Aldrich, U.K.

2.2 Preparation of Organo Clay

Clay sample was acquired locally and purified according to the method described by James et al. [24]. The clay was modified with organic cations; Hexadecyltrimethylammonium bromide (HDTMA) and Trimethylphenylammonium Bromide (TMPA). Hexadecyltrimethylammonium bromide (2.00 g) was dissolved in 50 mL of a mixture of 1:1 v/v distilled water and ethanol [25]. Clay sample (2.00 g) was added to the solution and stirred using magnetic stirrer at 250 rpm for 12 hours to provide enough contact time between surfactant solution and the clay sample. The mixture was centrifuged at 6000 rpm for 20 minutes to remove the sediments. The clay solids were washed twice with; (a) 50 mL ethanol- distilled water in the ratio 1:1 and (b) in 97% ethanol. The washed out solids were separated by centrifugation at 6000 rpm for 20 minutes and sediments dried at 80°C in an oven to a constant mass. The sample was crushed to smaller particles using motor and pestle and allowed to pass through 200 µm mesh size. Trimethylphenylammonium bromide (2.00 g) was dissolved in 50 mL distilled water [26] and 2.00 g of clay added, and the solutions stirred using magnetic stirrer at 250 rpm for 12 hours. The mixture was centrifuged at 6000 rpm for 20 minutes. The sediment was washed twice with distilled water and the washed out solids separated by centrifugation at 6000 rpm for 20 minutes. The resultant solid was dried at 80°C in an oven and crushed to smaller particles.

The organo-clays (HDTMA-clay and TMPA-clay) were analyzed by FT-IR spectrophotometry and X-ray diffractometry.

2.3 Sorption Kinetics of Natural Pyrethrum Extracts (NPE) into Clay Materials

The effect of various kinetic parameters on the intercalation of NPE into clay materials was

investigated. Stock solution of the NPE was made by dissolving 2.00 g NPE (50% active ingredient) in 1 L acetonitrile to make 1000 µg/mL. Using this as stock solution, five serial dilutions in the range of 0.5- 3.5 µg/mL were made in triplicates. The standards were run in SHIMADZU UV-Visible Spectrophotometer at 225 nm and a calibration curve was constructed [27]. The optimization experiments were carried out in triplicates.

The sorption efficiency was calculated using Equation (1):

$$\% \text{ sorption capacity} = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \% \quad (1)$$

Where C_i = initial NPE concentration (µg/mL); C_f = final concentration (µg/mL).

The adsorption capacity (Equation 2), q , was calculated based on the mass balance principle according to the following equation:

$$Q_e = \frac{C_i - C_e}{m} \times V \quad (2)$$

Q_e = Sorption capacity (amount of NPE ions adsorbed per unit mass of sorbent in mg/g); V = volume of the reaction mixture (mL); m = mass of adsorbent used (mg); C_i = initial concentration (µg/mL) and C_f = final concentration (µg/mL).

2.3.1 Effect of pH

NPE sorption was monitored for the pH range 3-7 using HCl regulate. All pH measurements were done using JENWAY model 210 pH meter. Each sample (unmodified, HDTMA and TMPA modified clay, 0.2 mg) was dispersed in 50 mL solution containing 3.5 µg/ mL NPE, stirred using rotary shaker at 100 rpm for 60 minutes. The solution was centrifuged at 6000 rpm for 20 minutes and analyzed using UV/Visible Spectrophotometry. The difference in initial and final concentrations in the supernatant was taken to be the amount adsorbed [27].

2.3.2 Effect of Temperature

Optimal pH of 3.5, 3 and 5 for the unmodified, TMPA and HDTMA modified clay materials respectively (0.2 mg adsorbate dose) was used to monitor the effect of temperature on sorption. Temperatures were varied from 25 -65°C using a thermometed rotary shaker at 100 rpm at NPE initial concentration of 3.5 µg/mL [28]. Solutions were withdrawn after 60 minutes, centrifuged at

6000 rpm for 20 minutes and the NPE concentration remaining in the supernatant measured using UV-Vis Spectrometer ($\lambda_{max} = 225 \text{ nm}$). The difference in initial and final concentrations in the supernatant was taken to be the amount adsorbed [29].

2.3.3 Effect of Initial Concentration and contact time

The experiment was carried out at optimum pH and temperature. Solution (50 mL) containing initial concentration of 0.5, 1, 1.5, 2.0, 2.5 and 3.5 $\mu\text{g}/\text{mL}$ NPE was added to 0.2 mg of each clay material and the solutions stirred using rotary shaker at 100 rpm. Solutions were withdrawn at various times (10, 30, 60, 90, 120 minutes), centrifuged at 6000 rpm for 20 minutes and the NPE concentration remaining in the supernatant was measured using UV-Vis Spectrometer. The difference in initial and final concentrations in the supernatant was taken to be the amount adsorbed.

2.3.4 Effect of sorbent dosage

Varying mass of clay, that is, 0.1, 0.2, 0.25, 0.5, 1.0 and 1.5 g were analyzed for NPE sorption at optimal initial concentration of 3.5 $\mu\text{g}/\text{mL}$, optimal pH, temperature and contact time and solution was stirred using rotary shaker at 100 rpm. Solutions were withdrawn, centrifuged at 6000 rpm for 20 minutes and analyzed using UV/Visible Spectroscopy. The difference in initial and final concentrations in the supernatant was taken to be the amount adsorbed.

2.3.5 Adsorption isotherms

The maximum adsorption capacities were determined by fitting the experimental data from section 2.5.4 in Langmuir and Freundlich isotherms [30].

Langmuir isotherm equation (equation 3) is linearly represented as follows:

$$\frac{C_e}{Q_e} = \frac{1}{b} Q_0 + \frac{C_e}{Q_0} \quad (3)$$

Where Q_e is the total NPE uptake (mg/g), C_e is the NPE equilibrium concentration while only Q_0 and b are Langmuir constants. Langmuir plots of C_e/Q_e versus C_e determined Q_0 and b from slope and intercept respectively.

Freundlich equation (Equation 4) is linearly represented as follows:

$$\text{Log}Q_e = \text{Log}K_f + \frac{1}{n} \text{Log}C_e \quad (4)$$

Where Q_e and C_e have the same meaning as in Langmuir equation while K_f and $1/n$ are Freundlich constants. Freundlich plots of $\text{Log} Q_e$ versus $\text{Log} C_e$ determined Q_0 and b from slope and intercept respectively.

2.3.6 Kinetic models of sorption

Data from section 2.5.3 was fitted in pseudo-first order and pseudo-second order kinetic models as described by Marija et al. [31]. The linearized pseudo first-order kinetic model (Equation 5) is represented as follows:

$$\text{Log} (Q_e - Q_t) = \text{Log} Q_e - \frac{K_1}{2.303} t \quad (5)$$

Where Q_e and Q_t are the amount of NPE adsorbed on the different clay materials ($\mu\text{g}/\text{mL}$) at saturation and at time t ($\mu\text{g}/\text{g}$) only [32] while K_1 is the pseudo-first order kinetics rate constant. Straight lines of $\log (Q_e - Q_t)$ versus t were used to determine the rate constant, K_1 and correlation coefficient. Pseudo second order kinetics model (Equation 6) linearized form equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{K_2 (q_e)^2} + \frac{1}{q_e} \cdot t \quad (6)$$

Where Q_e and Q_t are as described above while K_2 is the pseudo-second order kinetics [30]. Straight lines of t/Q_t versus t were used to determine the rate constant, K_2 .

2.4 Loading of NPE into Clay Materials

NPEs (3.5 $\mu\text{g}/\text{mL}$) dissolved in 50 mL acetonitrile was added to each clay sample (1.00 g). The solution was stirred using thermomated rotary shaker for 120 minutes at 45°C and pH 3 for both the Un-modified and TMPA modified clay; pH 5 for HDTMA modified clay D at 100 rpm to provide enough contact [29]. The mixture was centrifuged at 6000 rpm for 20 minutes to remove the sediment. The clay solids were then washed twice with acetonitrile to remove the adsorbed NPEs on clay surface. The washed out solids were separated by centrifugation at 6000 rpm for 20 minutes and resultant solid was dried at 80°C in an oven to a constant mass. The resultant clay sample was crushed to smaller particles using motor and pestle. The sample was allowed to pass through 200 μm mesh size.

The NPE-clay composites were characterized by FT-IR spectrophotometry and X-ray Diffractometry.

2.5 Accelerated Photo Stability Test

Optimal quantification of the NPE was achieved by HPLC on 250 mm x 4 mm C 18 column with acetonitrile (85%) and water (15%) as the mobile phase [33]. The flow rate was 1 mL/ min with an injection volume of 10 µl where the NPE were detected at UV absorption of 225 nm. Standard pyrethrum extract containing 1000 µg/ mL NPEs was prepared from the 50% NPEs pale extract by dissolving 2.00 g of the extract in 1 L of the mobile phase. Calibration standards containing 10 – 180 µg/ mL NPEs were prepared by serial dilution of the stock solution using the mobile phase. A calibration graph was obtained by plotting the sum of peak areas of the six pyrethrum esters against the concentration of the standards. The concentration of NPEs in the samples was obtained by interpolation of the best line of fit.

The protective effect of the clays and modified clays on the NPE was confirmed by illuminating NPE samples with UV light from a UV lamp at 254 nm and 366 nm, and natural sunlight for 4hrs. NPE (0.00848 mg), (0.0136 mg) and (0.0106 mg) were used as control for Un-modified, HDTMA-clay and TMPA-clay respectively. The irradiations were performed in quartz cuvettes (1x1 cm; total volume 3 mL) with Philips PL-S 9W/12 lamps. The distance between the lamps and the cuvettes was 5 cm and temperature was maintained at 25°C. The NPE initial and final concentration was determined using HPLC.

2.6 NPE Loaded Clay Material Bio assay Tests on Maize Weevils

Adult maize weevils (*Sitophilus zeamais* Motschulsky) were collected from naturally infested maize grains from a local market in Thika town. The insects were then reared on clean and un-infested maize grains under laboratory conditions of 27±2°C [34]. Fine fabric was used to cover the glass jars to prevent weevils' escape and also to allow for air circulation [35]. According to Masiwa, [36], weevils have a minimum life cycle of 28 days at temperature of 27°C in an incubator, and after four weeks the insects were thoroughly sieved. The infested and oviposited grain was returned in the incubator at temperatures of 27°C, and after

one week, 20 vigorous, healthy insects were used for the bio assay analysis.

Each sample was first exposed to sunlight for a period of 4 hrs before the experiment kicked off. Bio assay analysis was carried out by treating clean undamaged maize with NPEs loaded clay materials having 75% active ingredient granular formulation; NPE-Clay, NPE-TMPA clay, NPE-HDTMA clay and Clay, TMPA-Clay, HDTMA-Clay, degraded NPE in comparison to both the un-degraded NPE and untreated maize (control) using 20 maize weevils, at two concentrations of 0.1 g and 0.5 g, a method described by Wanyika et al. [13,37] with slight modifications. A completely randomized design was used to arrange the 27 jars used in the experiment, with each treatment being done in triplicates and the insects examined daily [38]. Clean maize grains were first sieved through 2.00 mm mesh size to remove any foreign and fluffy materials. Each sample (0.50 g and 1.00 g) corresponding to 2.5% and 5.0% w/w concentrations were added to 30 g of the clean maize grain, the mixture was shaken for 30 minutes and put in 250 mL glass jars. Adult maize weevils (20) of mixed sex were introduced and mortality rate observed at 24, 48, 72, 96 and 120 hrs in each experiment. The grains were sieved using 2.00 mm mesh size and the numbers of live and dead pests were counted where they were considered dead when there was no response on gentle touch using faint brush. The % mortality rate was calculated using equation 7. Dead insects were discarded. Data obtained was subjected to Analysis of Variance (ANOVA) and significantly different means separation obtained using the Least Significantly Difference (LSD) at 5% level of probability [39,40].

Percentage weevil mortality =

$$\frac{\text{Number of dead weevils}}{\text{Total number of pests}} \times 100 \quad (7)$$

3. RESULTS AND DISCUSSION

3.1 HDTMA and TMPA Modified Clays

3.1.1 FT-IR spectra

The FTIR spectra (Fig. 3) after modification of clay, indicated presence of intercalated HDTMA⁺ as extra intense peaks at the range of 2800 cm⁻¹ to 2900 cm⁻¹ attributed to the CH₂ anti-symmetrical stretching vibrations and CH₂ symmetrical vibrations respectively that had been

observed in the pure HDTMA-Br. This confirmed presence of intercalated HDTMA⁺ in the montmorillonite clay [25,41].

On modification of clays with TMPA (Fig. 3), peaks at the range of 1410 cm⁻¹-1470 cm⁻¹ were observed. They were ascribed to the phenyl ring of the TMPA cation and confirmed intercalation of the surfactant in the clay. The new bands in the range of 2960 cm⁻¹- 3035 cm⁻¹ were attributed to symmetrical stretching vibration of C-CH₂ of alkyl chain while the band around 1487-1490 cm⁻¹ was assigned to the trimethylammonium quaternary group vibration; C-N(CH₃)₃⁺ [25,41].

3.1.2 XRD Analysis

The raw clay sample had several peaks; d₍₀₀₁₎ centered at 9.6849 Å, d₍₀₀₂₎ centered at 4.8424 Å, a sharp peak d₍₁₁₂₎ centered at 3.2283 Å and d₍₁₁₃₎ peaks centered at 3.1393 Å. Upon HDTMA intercalation, the peaks shifted to d₍₀₀₁₎ 12.1904 Å; d₍₀₀₂₎ at 5.5056 Å; d₍₁₁₂₎ at 3.2879 Å and d₍₁₁₃₎ at 3.2283 Å that signified increment of the basal spacing as an evidence of successful intercalation (Fig. 4). Basal spacing increased on TMPA intercalation to 12.1665 Å, 6.0832 Å, 3.2361 Å and 3.0416 Å at d₍₀₀₁₎, d₍₀₀₂₎, d₍₁₁₂₎ and d₍₁₁₃₎ miller indices respectively. Similar observations were made by Zusana et al. [41]. The observed basal spacing difference on HDTMA and TMPA modification may be explained by the fact that TMPA and HDTMA are short chain and long chain alkyl ammonium cations respectively, both may have formed mono-layer coverage. According to Zhu et al. [42], the organic cation arrangement into the clay gallery spaces may be lateral monolayer (1.45-1.47 nm), lateral bi-layer (1.75-1.85 nm) and tri-layer (1.91-2.0 nm). However, of the two cations, HDTMA modification of the original clay greatly increased the clay gallery spaces.

3.2 NPE Sorption Kinetics

3.2.1 pH influence

The sorption of NPE pesticide in clay was significantly influenced by low pH of 3.0. It decreased on increase to pH 7 in the solution after 60 minutes contact time (Fig. 5). At pH 3-5, more protons were available increasing electrostatic attraction between the negatively charged NPE molecules and positively charged clay surfaces enhancing sorption. At higher pH of 7, the number of positively charged sites

decreases, increasing number of negatively charged sites. This resulted to increased repulsive forces between NPE molecules and clay sites hence reduced sorption. This observation was in accordance with reported pesticides sorption mechanisms [43-47].

3.2.2 Effect of temperature

Temperature is an important factor that affects the sorption of pesticide molecules into clay materials [48]. Fig. 6 shows increase in NPE molecules sorption with increased temperature from 25°C- 65°C. With temperature increase up to 45°C, the kinetic energy of the NPE molecules increase resulting to increased sorption [49]. NPE sorption into un-modified clay may have been attributed to electrostatic interactions between the NPE molecules and cations present in the clay gallery space, while in the modified clays, it may have been due to the electrostatic interactions between the negatively charged NPE molecules and the positively charged clay gallery space [50].

3.2.3 Effect of initial concentration and contact time

Observations made from Fig. 7 are that the amounts of NPE sorbed increased with time until point of saturation at 120 minutes. The initial curved portion in all the samples was attributed to a rapid diffusion of NPE pesticide molecules into the available sorption sites on the clay adsorbent [51] that was followed by linear portion that signified a gradual sorption attributed to low concentration of NPE molecules in the solution as well as fewer available sorption sites [52]. This sorption process may thus be concluded to have occurred in two distinctive steps including; transfer of adsorbate through external liquid film and also diffusion of solute inside the adsorbent particles [48]. Of the three samples, HDTMA modified clay was the best in the adsorption of NPE pesticide molecules.

3.2.4 Effect of Adsorbent dose

Sorption efficiency increased with increase in adsorbate dose (Fig. 8) attributed to the increased number of available sorption sites on clay surfaces to a point of saturation at 1.0 g [53]. HDTMA modified clay had the highest sorption efficiency that may have resulted from the modification of the clay surfaces that led to increased sorption of NPE molecules.

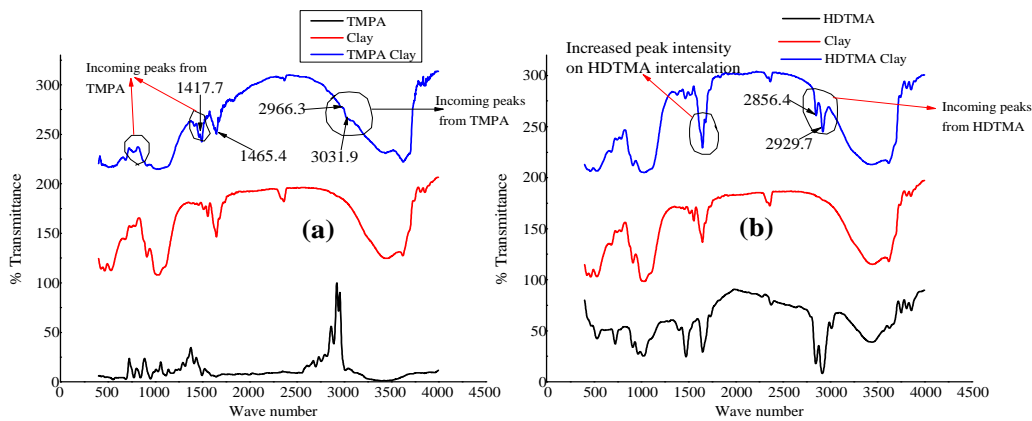
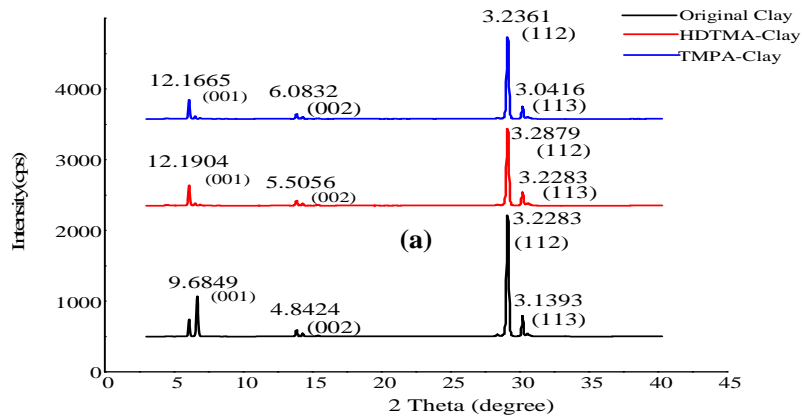


Fig. 3. FT-IR spectra for clay (a) modified with TMPA and (b) modified with HDTMA



Raw Sample (Å)	HDTMA Modified (Å)	TMPA Modified (Å)	Basal Spacing Increment on HDTMA Intercalation (Å)	Basal Spacing Increment on TMPA Intercalation (Å)
9.6849 ₍₀₀₁₎	12.1904 ₍₀₀₁₎	12.1665 ₍₀₀₁₎	2.5055	2.4814
4.8424 ₍₀₀₂₎	5.5056 ₍₀₀₂₎	6.0832 ₍₀₀₂₎	0.6632	1.2408
3.2283 ₍₁₁₂₎	3.2879 ₍₁₁₂₎	3.2361 ₍₁₁₂₎	0.0596	0.0078
3.1393 ₍₁₁₃₎	3.2283 ₍₁₁₃₎	3.0416 ₍₁₁₃₎	0.089	-0.0977

Fig. 4. (a) XRD patterns for different clay materials and (b) inset table for basal spacing increment

3.2.5 Sorption isotherms

In the sorption of NPE into Un-modified clay, the data fitted best in Langmuir adsorption model as shown in Fig. 9. This was concluded from high product moment correlation coefficient R^2 of 0.998. Similar results were observed by Djebbar et al. [54]. It was thus assumed that sorption of NPE on the Un-Modified clay took place on a homogeneous site, and once NPE molecules occupied a site, no further adsorption took place

[49]. Low Q_{max} and b values suggested low affinity of the pesticide molecules on the adsorbent. Q_{max} is related to maximum absorption capacity while b is related to sorption energy [30]. The Q_{max} values were 0.02837 ± 0.0001 mg/g, 0.05214 ± 0.0013 mg/g and 0.04309 ± 0.0003 mg/g for Unmodified, HDTMA and TMPA modified clays respectively indicating that HDTMA modified clay had the highest adsorption capacity. Separation factors (b) > 1 signifies un-favorable sorption, $b < 1$

signifies favorable sorption, $b = 1$ signifies sorption process is linear while $b = 0$ signifies that the sorption process is irreversible [30,54]. With this in mind, therefore, the sorption process of NPE in the Un-modified clay was best described by Langmuir isotherm as the system had homogeneous sites. Sorption involved electrophilic interactions between the NPE molecules and cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) in the clay gallery spaces.

Sorption of NPE in both HDTMA and TMPA modified clays was best described by Freundlich adsorption isotherm (Fig. 9) as the correlation coefficients were in the range of $0.97 \leq R^2 \leq 0.99$ with valid sorption of adsorbent-adsorbate

system concluded from $\frac{1}{n}$ between 0 and 1 that indicates favorable sorption. Of the three samples, HDTMA modified clay had the lowest $\frac{1}{n}$ value of 0.2060 indicating more favorable sorption of NPE molecules [48]. The fact that clay surfaces are hydrophilic and on modifications with these organic cations they become hydrophobic, results to effective sorption of hydrophobic NPE molecules. This further proves the necessity of modification of clay surfaces for the sorption of pesticide molecules as intensely observed by many researchers [19,55]. Of the three samples, HDTMA modified may be the best adsorbent for the NPE pesticide molecules.

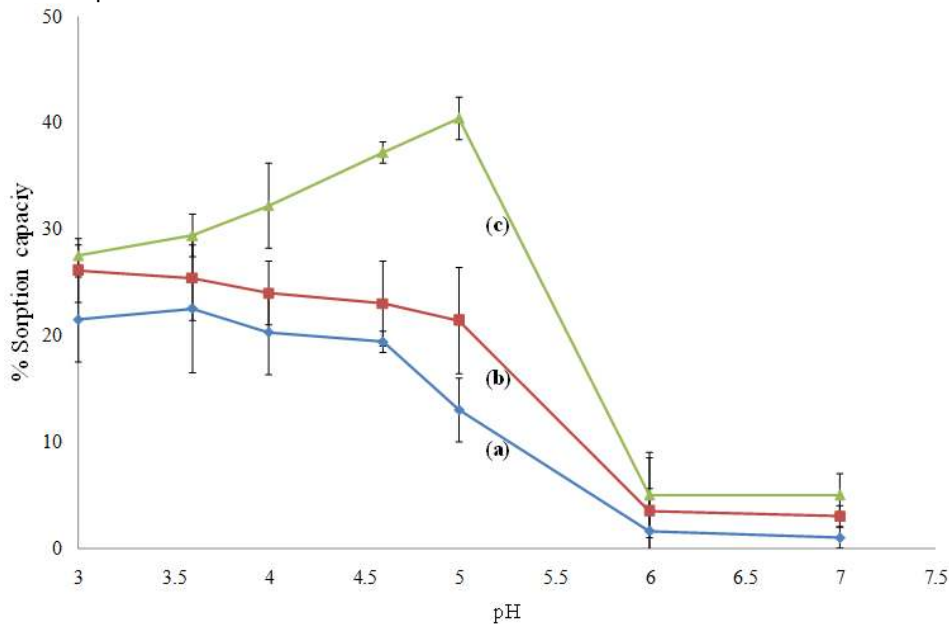


Fig. 5. The effect of pH on the sorption of NPE into different clay materials; (a) Un-modified (b) TMPA modified and (c) HDTMA modified clay materials

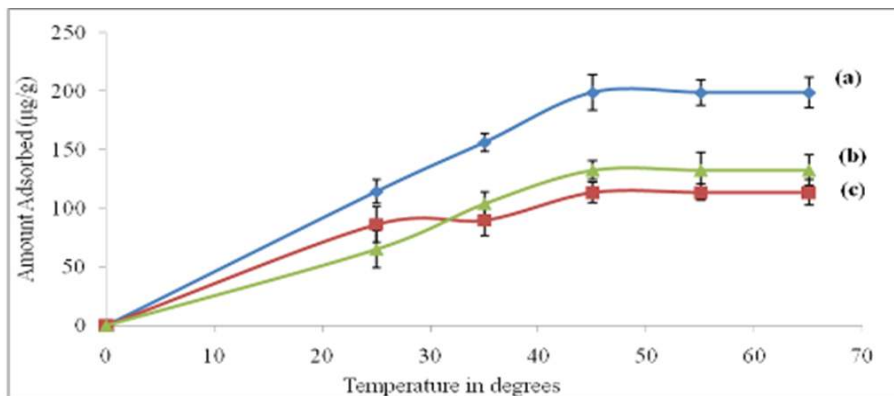


Fig. 6. Effect of temperature on sorption of NPE into different clay materials; (a) Un-modified clay, (b) TMPA modified clay and (c) HDTMA modified clay

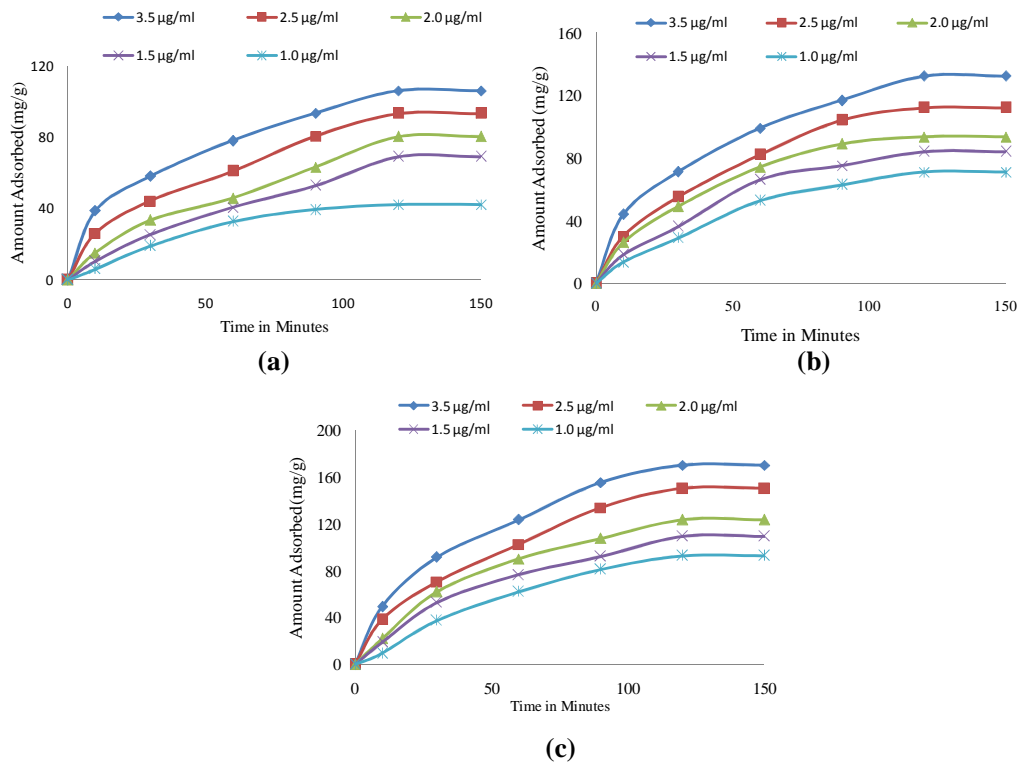


Fig. 7. Effect of initial concentrations at different contact time on the sorption of NPE into; (a) Un-modified clay, (b) TMPA modified clay and (c) HDTMA modified clay

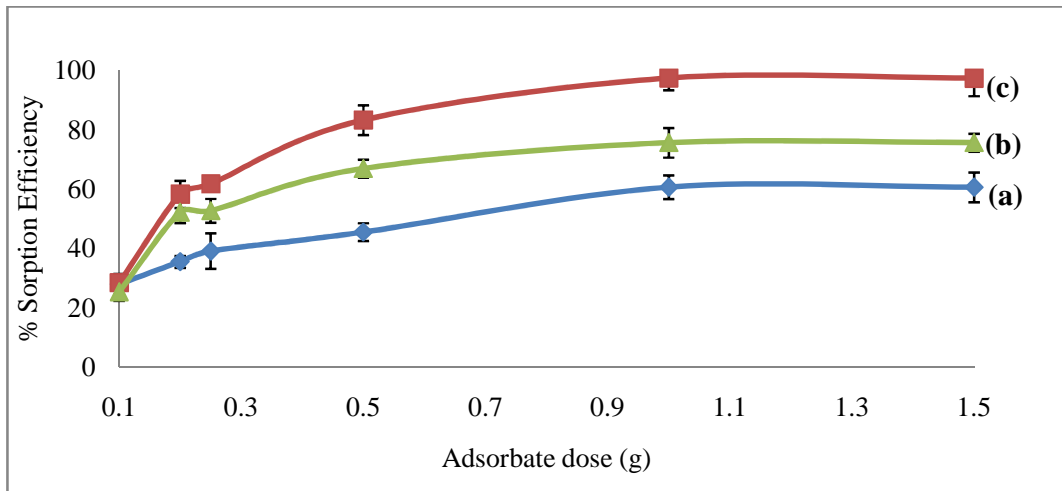


Fig. 8. Sorption of NPE in relation to different clay adsorbate dose; (a) Un-modified clay, (b) TMPA modified clay and (c) HDTMA modified clay

3.2.6 Kinetic sorption models

High correlation coefficient values, (Table 1), suggested that the sorption of NPE into clay materials fitted well in pseudo-second order

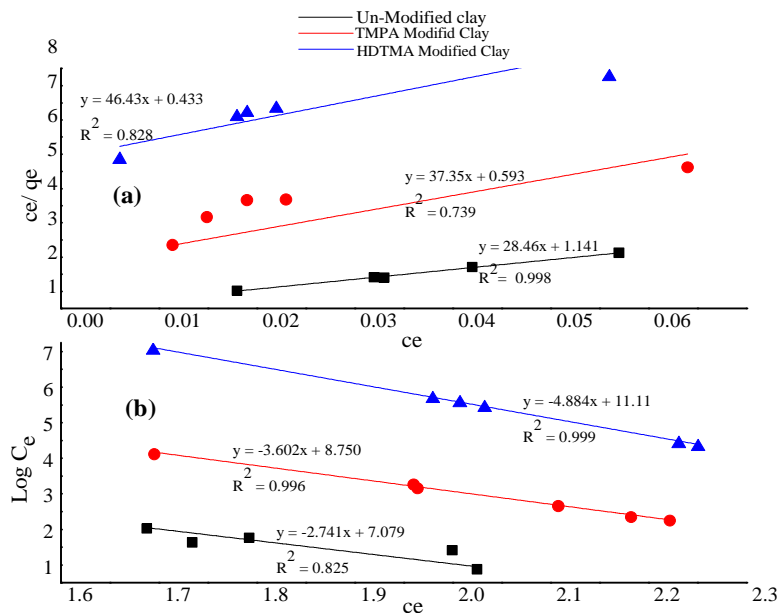
model better than pseudo-first order (Figs. 10 and 11) in all the concentrations tested. Moreover, the Q_e estimated by pseudo-second order model (Table 1) gave closer values to those of experimental Q_e values in comparison

with pseudo-first order model. According to pseudo second order kinetics principle this suggested that the rate limiting step may have been sorption on a heterogenous/ multiple surfaces; clay and organo-clay surface, through exchange of electrons between the positively charged organic cations and negatively charged NPE molecules. Moreover the sorption involved electrophilic interactions between the NPE molecules and cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+) in the clay galley spaces [32].

3.3 Intercalation of NPEs in Clay Materials

There was successful intercalation of NPEs as evidenced by enhancement in FT-IR

peak intensities attributed to overlapping of the functional groups from NPE and the clay materials (Fig. 12). Two peaks in the range of 2860 cm^{-1} - 2930 cm^{-1} were attributed to C-H asymmetrical and symmetrical stretching vibrations of both Jasmolin and Cinerin in NPE were observed to cause shifts in the absorption bands of the clay materials [56]. New peaks at 2856.1 cm^{-1} and 2927.7 cm^{-1} were observed on intercalation of NPE in Un-Modified clay, reduced peak intensity was observed in TMPA Modified Clay shifting from 2966.3 cm^{-1} and 3031.9 cm^{-1} to 2925.8 cm^{-1} and 2960.5 cm^{-1} and on HDTMA Modified clay shift from 2856.4 cm^{-1} and 2927.7 cm^{-1} to 2858.3 cm^{-1} and 2925.8 cm^{-1} respectively.



Clay Material	Langmuir Parameters		Freundlich Parameters			
	b	Q_{\max} (mg/g)	R^2	K_f	$1/n$	R^2
Un-Modified	0.02486	0.02837 ± 0.0001	0.998	0.0018	0.2941	0.825
TMPA Modified	0.07266	0.04309 ± 0.0003	0.739	2.5×10^{-4}	0.2822	0.996
HDTMA Modified	0.12043	0.05214 ± 0.0013	0.828	1.306×10^{-5}	0.2060	0.999

Fig. 8. Langmuir adsorption isotherms plots (a) and Freundlich adsorption isotherms plots (b), together with inset table for Langmuir and Freundlich parameters

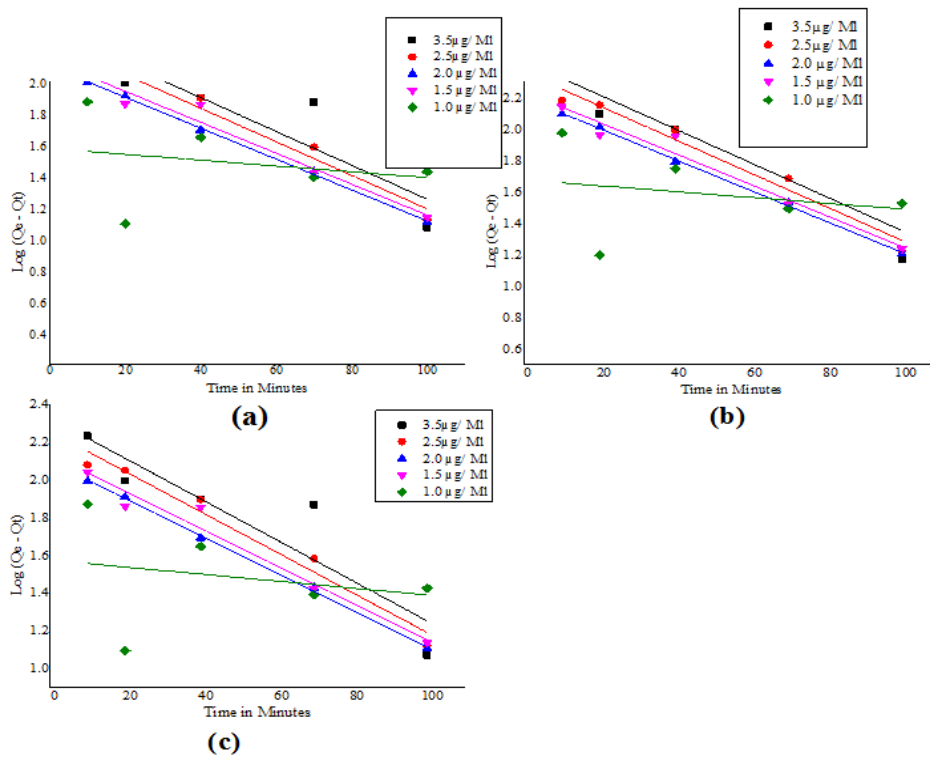


Fig. 9. Pseudo-first order kinetics model for the sorption of NPE into (a) Un-modified clay, (b) TMPA modified clay and (c) HDTMA modified clay

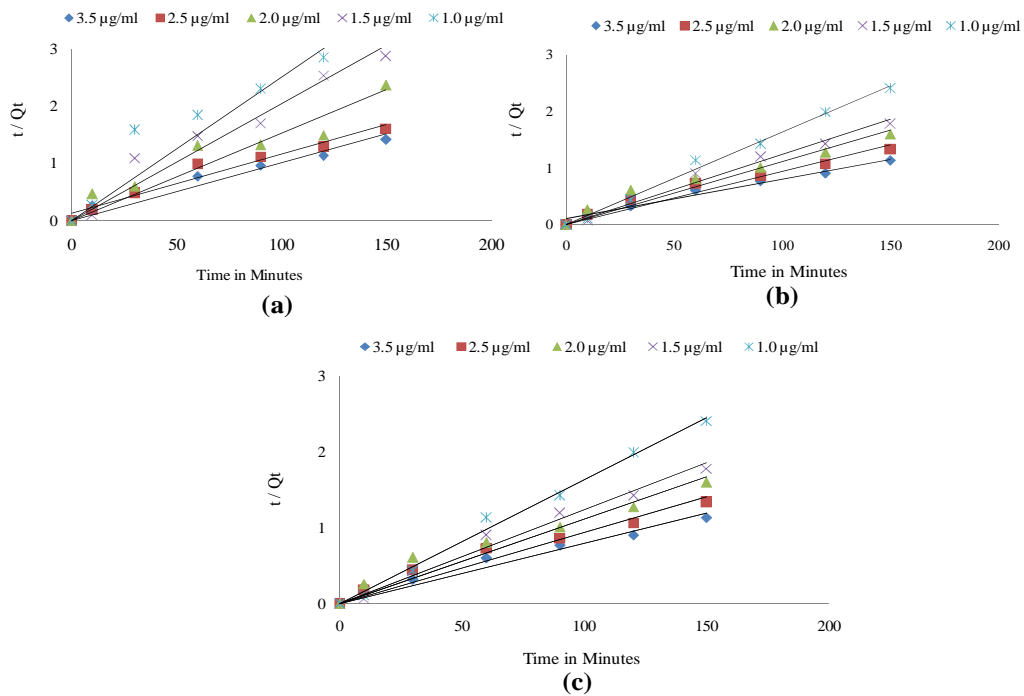
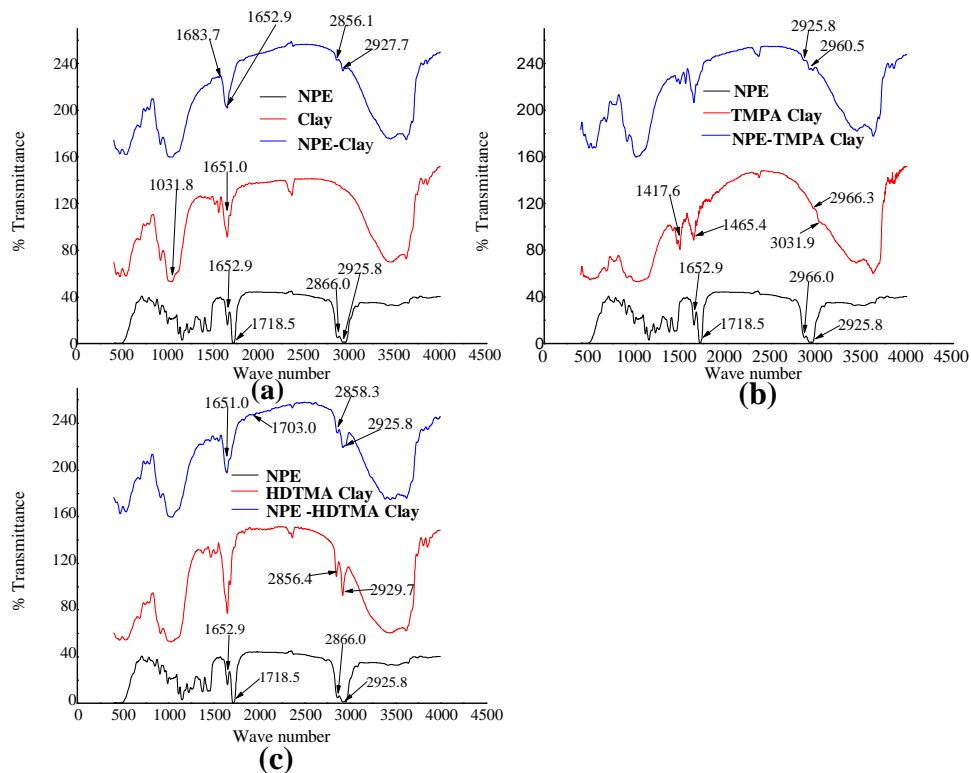


Fig. 10. Pseudo-second order kinetics model for the sorption of NPE into; (a) Un-modified clay, (b) TMPA modified clay and (c) HDTMA modified clay at different concentrations

Table 1. Pseudo-first and pseudo-second orders reaction kinetics for the sorption of NPE by the Un-modified, TMPA modified and HDTMA modified clays

Clay	Initial NPE conc (µg/mL)	Q _e (experimental) (mg/g)	Pseudo first-order kinetics			Pseudo second-order kinetics		
			R ²	K ₁ (1/min)	Q _e (calculated) (mg/g)	R ²	K ₂ (g/mg/min)	Q _e (calculated) (mg/g)
Un-modified	1.0	0.0420	0.883	2.90 X 10 ⁻⁵	0.621	0.941	0.5745	0.0425
	1.5	0.0643	0.881	4.52 X 10 ⁻⁵	0.0994	0.957	1.4312	0.0692
	2.0	0.0841	0.007	6.73 X 10 ⁻⁵	0.0292	0.924	1.1790	0.0828
	2.5	0.0932	0.785	8.51 X 10 ⁻⁵	0.0741	0.958	3.0398	0.0935
	3.5	0.1071	0.664	9.56 X 10 ⁻⁵	0.0693	0.966	7.0890	0.1052
TMPA	1.0	0.0711	0.899	2.43 X 10 ⁻⁵	0.0893	0.993	7.3780	0.0741
	1.5	0.0844	0.886	2.56 X 10 ⁻⁵	0.0901	0.982	1.6703	0.0841
	2.0	0.0941	0.887	2.84 X 10 ⁻⁵	0.0912	0.984	6.9178	0.0923
	2.5	0.0932	0.821	3.23 X 10 ⁻⁵	0.1324	0.973	1.3142	0.1108
	3.5	0.1321	0.882	2.32 X 10 ⁻⁵	0.1042	0.976	2.2751	0.1297
HDTMA	1.0	0.0930	0.892	3.11 X 10 ⁻⁵	0.0721	0.999	7.7091	0.0932
	1.5	0.1093	0.901	2.64 X 10 ⁻⁵	0.0932	0.997	6.9000	0.1094
	2.0	0.1232	0.926	2.47 X 10 ⁻⁵	0.1043	0.999	1.4482	0.1205
	2.5	0.1504	0.931	2.96 X 10 ⁻⁵	0.1240	0.999	1.7236	0.1543
	3.5	0.1702	0.826	2.50 X 10 ⁻⁵	0.1511	0.999	1.4592	0.1709

**Fig. 11. FTIR spectra of; (a) NPE intercalated into Un-Modified clay; (b) NPE in TMPA Modified clay and (c) NPE in HDTMA Modified clay**

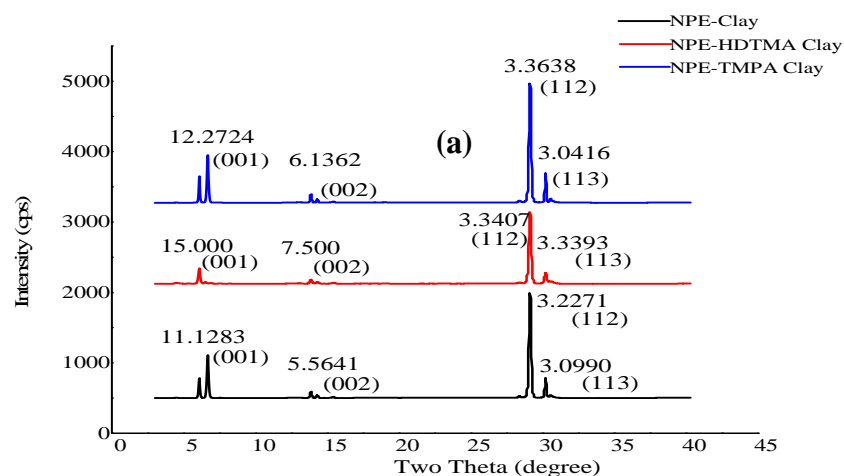
Intercalation of NPEs in clay gallery spaces was confirmed by the increase in the basal spacing of the main Un-modified and modified clays (Fig. 13). All the samples sorbed NPEs, however,

HDTMA modified clay composite was more efficient as shown in the inset-table. This may have resulted from increased electrostatic attractions between the electrophilic HDTMA cations (long chain cation) covering the whole interlayer space and the nucleophilic NPEs molecules in comparison with TMPA organo-clay. The sorbed NPEs pesticide molecules may have formed monolayer coverage on all the clay materials. Similar results were found in case of benzene and pyridinium rings (have related structures) attaching into clay interlayer spaces [41,50]. The decrease in peak intensity also signified intercalation of the molecules.

3.4 Accelerated Stability Tests

Standard curve for NPEs standards was drawn and the unknown concentrations of NPE in the clay samples and amount degraded determined. Natural sunlight caused the highest degradation of the NPE molecules compared with the artificial UV radiations (Fig. 14), this may be ascribed to

the influence of other environmental factors such as moisture, oxygen and temperature [9]. Other losses may have been as a result of evaporation rather than photo-degradation of these NPE molecules. HDTMA modified clay had the highest photo-stabilization effect. About 63.4% and 11.13% NPEs in NPE-HDTMA clay and unprotected NPE (control) respectively were undecomposed on exposure to sunlight (Fig. 15). This may have been as a result of more NPE intercalation in the gallery space and consequently more protection from UV light and active oxygen species degradation. Moreover, according to Yasser et al. [57], the cationic organic chromophores; HDTMA and TMPA intercalated in clay materials may have acted as energy/charge acceptor to the photo-excited NPE pesticide molecules, that returned to the ground state and became photo-stabilized or may have absorbed light and prevented photo-excitation of the NPE pesticide molecules and this lengthened its degradation lifetime.



Original Sample(Å)	Increase in Basal Spacing on pyrethrins intercalation (Å)		
	Un-Modified Clay	HDTMA Modified Clay	TMPA Modified Clay
9.6849	1.4434	2.8096	0.1059
4.8424	0.7217	1.9944	0.0530
3.2283	-0.0012	0.0528	0.1277
3.1393	-0.0403	0.1110	0.0977

Fig. 12. (a) XRD patterns of NPE intercalated in different clay materials and (b) inset table of basal spacing variations on NPE intercalation in clay gallery spaces

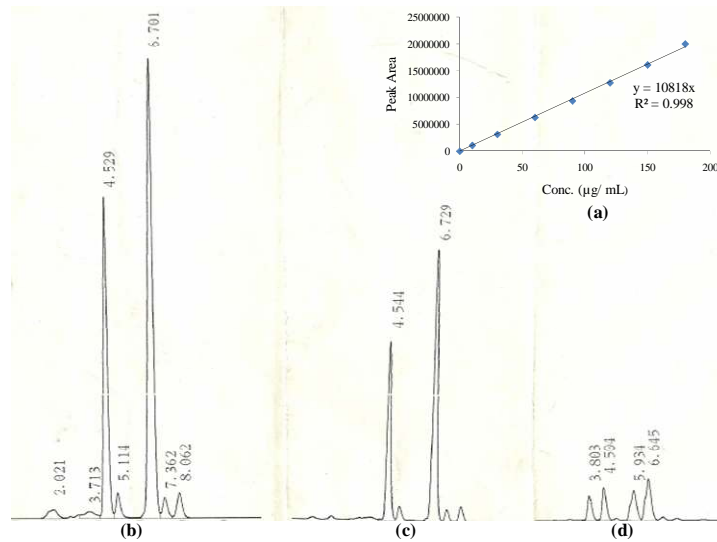


Fig. 13. (a) NPE calibration curve and chromatograms for; (b) NPE standard (c) NPE- HDTMA clay after 4hrs exposure to sunlight, (d) unprotected NPE after 4hrs exposure to sunlight

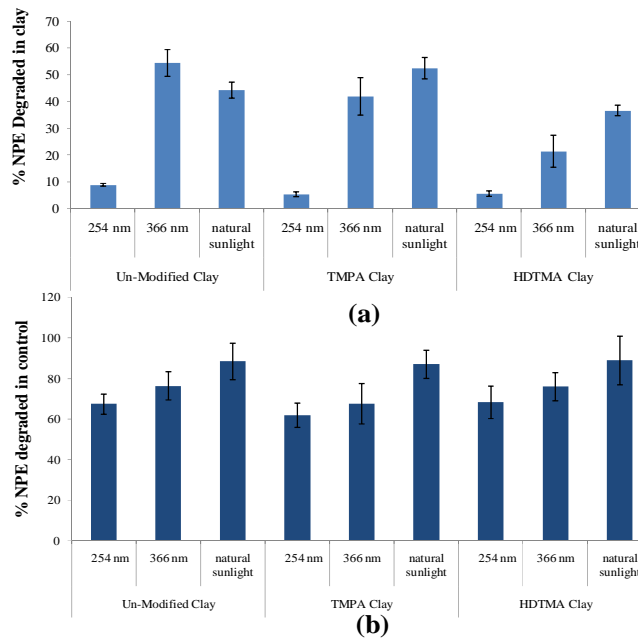


Fig. 14. NPE content (%) degraded after exposure to different UV radiations and sunlight; + (a) NPE- clay composites and (b) unprotected NPE equivalent

3.5 Bio Assay Tests on Maize Weevils

There was a significant difference ($p = 0.05$) in the weevils' mortality rate attributed to the different clay treatments. The un-degraded NPE was the most effective closely followed by NPE-HDTMA clay at 100% and 58% respectively when applied at 0.5 g / 30 g maize grain after 48 hrs of exposure (Fig. 16). The effect of time

factor did not have a significant effect on the weevils' mortality rate. However, the effect of both the dosage and dosage*time factors had significant effect of the mortality rate (Table 2). This was due to the increased exposure time and dosage in all the different sample treatments (Fig. 16). This may have been due to the increased contact poison for a prolonged period of time. Similar observations of increased

mortality at increased treatment concentration were made by Abdullahi et al. [58] in *Sitophilus zeamais* control using *Acacia nilotica* bark and root powders. NPEs are contact poison that rapidly penetrated to the weevils' nervous system, block the nerve junction and the action of sodium channels causing knock-down effect, paralysis and later death [59]. There was a significant difference ($p = 0.05$) in the mortality rate for NPE-HDTMA clay, NPE-TMPA clay and NPE-clay treatments at 48 hrs exposure (Table 3). Un-degraded NPE pesticide present in the clays was responsible for the death of the weevils. However, NPE present in HDTMA clay was in large quantities in comparison to both TMPA clay and Un-modified clay even after 4 hrs of exposure to sunlight.

There was no significant difference between HDTMA clay, TMPA clay and Clay in weevils'

mortality rate. This further proofed that the cations added to clay had no effect on the weevils' death and only acted as surfactants that increased the NPE sorption into clay. However, according to Masiwa [36], the clays killed the weevils through physical means of massive water absorption from the weevils' body. High clay concentrations resulted to higher chances of the weevils' dust pick up and consequent desiccation of the insects (Fig. 16). Degraded NPE had the lowest maize weevils' mortality rate attributed to its unprotected state from the UV light. According to Antonious [60], NPEs degrade from 100 - 1% on exposure to field conditions within 5 hrs. Combination of two effective samples; clay and NPE proofed to have the best results in maize weevils' eradication and farmers should embrace this technology. As expected, there was no mortality in the untreated.

Table 2. Two way Analysis of Variance (ANOVA) for the mortality rates of *Sitophilus zeamais* on treatments with clay composites at two dosages

Within sample subject effects	Sum of squares	Mean square	Degree of freedom	Probability >F
Dosage	110.4500	110.4500	1	0.0030
Time	778.3620	194.5905	4	1.2728 x 10 ⁻⁶
Dosage	39.6250	9.9063	4	0.0052
	4207.9005	4207.9005	1	0.01209

Table 3. Cumulative means of *Sitophilus zeamais* mortality rate on different clay treatments

Treatments	Dosage (g/30g grains)	24 hrs	48 hrs	72 hrs	96 hrs	120 hrs
NPE-	0.1 g	3±1 ^(a)	7.3±1.2 ^(b)	13±1.6 ^(c)	19±1 ^(d)	20±0.0 ^(d)
HDTMA-	0.5 g	5.3±0.58 ^(a)	11.6±1.6 ^(b)	19.9±0.1 ^(c)	19.9±0.1 ^(c)	19.9±0.1 ^(c)
Clay						
NPE-TMPA-	0.1 g	3.3±0.6 ^(a)	5.6±0.6 ^(b)	9.9±1.6 ^(c)	14.6±0.6 ^(d)	19.9±0.6 ^(c)
Clay	0.5 g	4.3±0.6 ^(a)	8.3±1 ^(b)	15.3±1 ^(c)	18.3±1 ^(d)	19.3±1 ^(c)
NPE-Clay	0.1 g	0.3±0.6 ^(a)	1±0.6 ^(a)	3±1 ^(b)	5.3±0.6 ^(a)	8±0.6 ^(d)
	0.5 g	1.3±0.6 ^(a)	3.3±1 ^(b)	7.3±1 ^(c)	11.9±1.5 ^(d)	16.2±0.6 ^(c)
HDTMA-	0.1 g	0.7±0.6 ^(a)	1±0.6 ^(a)	1.3±0.6 ^(a)	1.6±0.6 ^(a)	2.3±0.6 ^(a)
Clay	0.5 g	0.7±0.6 ^(a)	3.4±1.2 ^(b)	5.4±1 ^(c)	7.4±1 ^(d)	9.1±0.6 ^(a)
TMPA-Clay	0.1 g	0±0.0 ^(a)	0.7±0.6 ^(a)	1.4±0.6 ^(a)	2.1±0.6 ^(a)	2.8±0.6 ^(a)
	0.5 g	0.3±0.6 ^(a)	1.3±1 ^(a)	2.6±1.2 ^(a)	3.6±1.0 ^(a)	4.6±1.0 ^(a)
Clay	0.1 g	0.3±0.6 ^(a)	0.6±0.6 ^(a)	1.3±0.6 ^(a)	2±0.6 ^(a)	2.3±0.6 ^(a)
	0.5 g	0.3±0.6 ^(a)	1.6±1.2 ^(a)	3.6±1.0 ^(b)	4.6±0.7 ^(b)	5.9±0.6 ^(b)
Un-	0.1 g	12.3±0.6 ^(a)	17.6±0.6 ^(b)	17.6±0.6 ^(b)	18.6±0.5 ^(b)	19.9±0.1 ^(b)
degraded	0.5 g	5.3±1.0 ^(a)	19.6±2.1 ^(b)	19.9±2.1 ^(b)	19.9±2.1 ^(b)	19.9±2.1 ^(b)
NPE						
Degraded	0.1 g	0±0.0 ^(a)	0.3±0.6 ^(a)	0.6±0.6 ^(a)	1.3±0.6 ^(a)	1.3±0.6 ^(a)
NPE	0.5 g	0.3±0.6 ^(a)	1.6±1.2 ^(a)	3.6±1.0 ^(b)	4.6±1.0 ^(b)	5.9±0.6 ^(b)

Means with same superscripts in brackets across a row represent no significantly difference at 5 % probability level

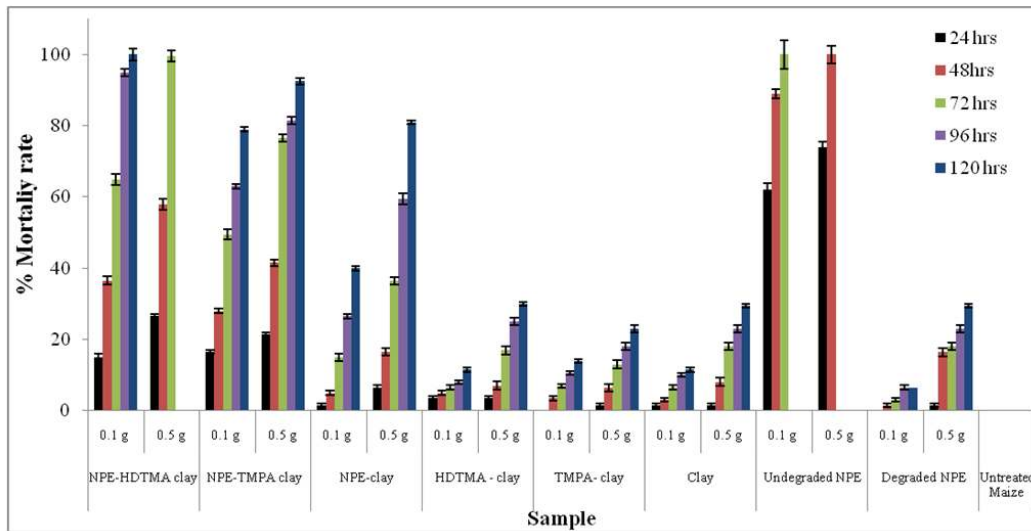


Fig. 15. Percentage maize weevils' mortality rate at different dosages of clay composites

Clay is extremely stable leaving no chemical residues on the treated produce thus has no health problem to the final consumer. Moreover, winnowing, a physical process removes about 98% of this dust from the treated grains. NPEs on the other hand, may be used against a wide range of pests and breaks down easily, leaving no residues to the maize grains hence no chemical toxicity to the final consumer [61].

4. CONCLUSION

NPEs were photo-stabilized with MMT-clay showing a marked increase in photo-protection. HDTMA-clay had the highest photo-stabilizing effect in comparison with other clay materials. Bio assay study showed that NPE-HDTMA clay may be a potential maize grain protectant against maize weevils (*Sitophilus zeamais*). Clay is very stable and winnowing the food products would assist in removing the dust. NPEs on the other hand, may be used against a wide range of pests and breaks down easily, leaves no residues to the food materials. Combination of the two materials resulted to a spectacular pesticide formulation for the control of pests. Successful photo-stabilization of the NPEs pesticides based formulation will improve the marketability of the pyrethrum flowers, improve economic utilization of clay deposits and consequently boost food security globally.

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COMPETING INTERESTS

The authors declare that there is no conflict of interests regarding the publication of this paper.

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