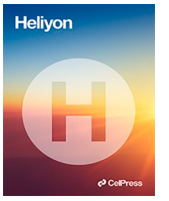
Heliyon 10 (2024) e35659

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon



Research article

Insecticidal formulation based on essential oil from *Ocimum basilicum* Linn. Herb supported onto modified kaolinite for stored maize protection

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ARTICLE INFO

Keywords:
Ocimum basilicum
Essential oil
Modified kaolinite clay
Insecticidal formulation
Control released
Sitophilus zeamais

ABSTRACT

In this study, essential oil was obtained by hydrodistillation from the leaves of Ocimum basilicum and it was analyzed by GC-MS. Eucalyptol (11.19 %), *trans*-iso eugenol (13.12 %), hexadecanoic acid methyl ester (19.26 %) and 9-octadecenoic acid (z)-methyl ester (25.12 %) had been the leading four main components of the plant leaves of the essential oil. The unmodified and modified kaolin was characterized and analyzed by XRD, FT-IR, TGA and SEM/EDX and thus the principal mineral of the nanoclay was proved to be kaolinite. The hydrodistiled essential oil in the absence of the clay support was evaluated within 24 h of exposure time and the outcome revealed that it was insecticidally active against the maize weevil, S. zeamais adults. Moreover, the exposure time effect, the formulation efficiency, the effect of remnant and stability of the prepared formulations were investigated and the results indicated an enhancement of bioinsecticides for a long period with upgraded persistence against the S. zeamais. Finally, the results recommend that O. basilicum essential oil - modified kaolinite formulations should be used as best options to chemical insecticides in pest control of stored products like stored maize grain insects, *S. Zeamais*.

1. Introduction

In Ethiopia, the primary factor of yield losses in storage is the destruction produced by storage insects. Among several insect species, the maize weevil, *Sitophilus zeamais* (Motschulsky) (Coleoptera: Curculionidae) is one of the greatest harmful insects of stored grains, and losses due to this insect have become a significant problem in Ethiopia [1,2]. To combat this insect constraint, the use of chemical insecticides has been practiced by producers all over the country till the present. However, the exhaustive use of these synthetic products can cause several health problems for humans including animals as a whole [3]. There is so, an increasing interest in familiarizing harmless, suitable, eco-friendly and low cost options to reduce post-harvest loses. Various plants have been assessed and known to show insecticidal properties all over the world. Considerable use of local herbs, trees and shrubs, principally from Lamiaceae, Maliaceae, Rutaceae, Fabaceae, and Verbenaceae has been experienced as insect repellents traditionally [4].

Essential oils are the most significant components of plants that have shown potential for use as natural pesticides. The *Ocimum*

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https://doi.org/10.1016/j.heliyon.2024.e35659
Received 4 December 2023; Received in revised form 30 July 2024; Accepted 1 August 2024
Available online 2 August 2024

basilicum Linn. herb, also termed as sweet basil, is an essential oil-rich species which is one of the prominent spices from the Lamiaceae family. This medicinal herb is initially innate to India and other Asian districts. Currently, it is cultured all over the world including Ethiopia. It comprises biologically-active essential oil constituents which possess antimicrobial, insect repellent and fumigants, antioxidant and nematicidal properties [5,6].

Even though several plants and herbs have been confirmed to have insecticidal properties and activities, the persistence of the energetic constituents of the essential oil vanished quickly within a very short period. This is due to their volatile properties; they would lose their active components through evaporation and consequently a loss of insecticidal action against the pests. To solve this quick loss of activity, controlled discharge of essential oils would be a viable option using clay materials. The clay, which is a common constituent of soils and sediments, is used in numerous formulations of insecticides, drugs and cosmetic powders Moreover, the potentials of kaolin clay as adsorbents for volatile terpenic compounds is well documented [7,8].

However, due to the isomorphous substitutions in the aluminosilicate layers, natural clay minerals usually have a net negative charge, which is balanced by alkali metal and alkaline-earth-metal cations such as K^{+}, Na^{+} and Ca^{2+}. The strong hydration of these inorganic cations creates a hydrophilic environment on the surface and in the interlayer region of natural kaolin clay. Thus, the substitution of those inorganic cations by organic quaternary ammonium cations at the exchangeable sites of natural clays results in organoclay derivatives with organophilic properties. This modification of natural clay with organic cations significantly improving the adsorption capacity for essential oil components, terpenes by enhancing the interlayer space of the clay and by generating a better organophilic atmosphere. The experiment is, hence, to investigate a formulation that can preserve active ingredients of essential oils against insects for an extended period by applying modified nanoclay adsorbents via organic surfactants, cetyltrimethylammonium (CTMA) cation [7,9,10,11].

To the best of our knowledge, no insecticidal formulation studies have been conducted with essential oil adsorbed on nanoclay materials. As a result, the present study has focused on insecticidal formulation of *Ocimum basilicum Linn (O. basilicum* L.). against maize weevil, *Sitophilus zeamais* (*S. zeamis)*, by immobilizing the plant essential oils onto modified kaolin to upgrade the persistence of the active ingredients of essential oils using the concept of controlled release mechanism. In this paper, *O. basilicum* essential oil has been first analyzed to determine their main components. Secondly, structural and textural characterizations of clays have been carried out before and after modification of the clay with CTMA by using FTIR, XRD, TGA and SEM/EDX techniques. In a third part, the insecticidal activity, stability and remnant effect of the different formulation has been studied. The result extracted from this work provides additional insight on the importance of environmentally benign persistent biopesticides from plant active ingredients over synthetic insecticides.

2. Materials and methods

2.1. Collection and extraction of essential oil from leaves

The *O. basilicum* L. herb was collected to the chemistry department research laboratory from eastern Ethiopia at the farmlands of Haramaya (Bate), Eastern Hararghe Zone, near Haramaya University. The identification of this widely used herb was done and its voucher specimen has been placed at the Herbarium of the school of Plant Sciences, Haramaya University. Subsequently, the fresh leaves of *O. basilicum* L. (1 kg) were washed repeatedly and hydrodistilled at atmospheric pressure for 4 h. The aromatic yellowish oil was produced and dried by adding anhydrous sodium sulphate (Na_2SO_4). Finally, the hydrodistiled essential oil was stored at lower temperature in the refrigerator (4 °*C*) until analysis and used for insecticidal formulation test.

2.2. Analysis of essential oil

A mixture of the essential oil and dichloromethane (DCM) was examined by an Agilent Technology 7820A GC system coupled with an Agilent Technology 5977E MSD equipped with an auto-sampler. The chromatographic isolation was performed at a flow rate of 1 mL/min on a DB-1701 micro-column (30 m long, 0.25 mm internal diameter and 0.25 μm particle size). The carrier gas that had been used at constant flow was ultra-pure helium (99.999 %). 1 μL of the sample mixture was injected with a splitless injection mode into the inlet of an Agilent G4567A autosampler that was warmed up to 275 °C with a entire run phase of 15.00 min. The temperature of the oven was automated at 60 °C with 2 min hold-time and the temperature of the column was enlarged until it reached 200 °C at the rate of 10 °C/min, moreover the boiling was continued till the temperature reached 240 °C at the rate of 3 °C/min. Actually during the first 4 min of the solvent delay the mass spectra were not gathered. The temperature of the ion source was reserved at 230 °C and the temperature of the transfer line was kept at 280 °C. The EI source of ionization energy was 70 eV and from the range of 40–650 *m/z* the mass spectra data were gathered. Finally, elucidation of the components in the essential oil was done by comparing the obtained mass spectra data with those of reference compounds documented in NIST 2014 mass spectral library accessible in the literature MH\Mass Hunter\Library search\NIST (National Institute of Standard 19 and Technology).

2.3. Insect rearing

Five kilogram maize grain was obtained from Maize Improvement Analysis Program of Haramaya University. The collected maize was then cleansed to get rid of grain with detectable harm symptoms. The cleansed grains were kept in an exceedingly deep-freezer at -20 ± 2 °C for 2 weeks to eradicate storage invasion [12]. Then, the maize beetle, S. *zeamais* were gathered from the store of Haramaya University farm management and were nurtured on the cleansed maize grains in five glass jars. Every jar contained 500 g maize

grains, to those, one hundred adult insects were transferred. Afterwards, each glass jar was enclosed with muslin cloth to permit aeration and stuck with elastic band to avoid escape of weevils. The infested grains were reserved in an incubator adjusted at best condition for weevil growth and multiplication, 28 ± 2 °C and a relative humidity of 70 ± 5 %. All parent insects were off from every jar after 10 days of oviposition and consequently the grains remained free from weevils were preserved in an incubator at similar optimum conditions. When the insertion of weevils in every glass jars containing grains reached forty days, the developed offspring weevils were escaped daily and shifted to contemporary maize grain in glass jar and used for the experiment to get indistinguishable insects having 3–6 days aged adult *S. zeamais* [13].

2.4. Preparation of unmodified kaolinite clay

Kaolin clay was collected from Hawassa Ceramic factory, Hawassa, Ethiopia. In order to eliminate the non-clay portions, the obtained clay was then broken into smaller particles and separated via a sieve. A hundred grams of clay was then spread in deionized water and using a magnetic stirrer it was stirred ceaselessly for 6 h. Subsequently, the denser layer is improved by natural process (centrifugation) after totally decanting the colloidal suspended layer. Moreover, by adding 30 % hydrogen peroxide (H_2O_2) to the recovered solution, it was cleansed and stirred uninterruptedly till all foaminess has completely stopped. To oxidize carbonaceous substance, the solution was then kept stirred overnight and any organic matters were eliminated. The mineral clay then was washed completely with deionized water and the supernatant decanted to eradicate traces of H_2O_2. Finally, the unmodified kaolin was prepared (Kao) by oven drying the recovered kaolin at 80 °C [9,10,14–16] and it was ground and sieved to prepare the preferred size of clay particles. Additionally, to replace all cations in the kaolin by sodium ions, 50 g of the prepared kaolin was preserved with 1 mol L^{-1} sodium chloride (NaCl) solution. The mixture was stirred persistently by using magnetic stirrer for 24 h and the prepared sodium kaolinite (Kao-Na) clay was then centrifuged till it becomes completely free of chloride ion using silver nitrate ($AgNO_3$) test [7].

2.5. Preparation of modified kaolinite clay

At room temperature, 10 g of Kao-Na was mixed in 200 mL of deionized water and then the mixture was stirred and solubilized for 2 h. 0.03 mol L^{-1} CTMA solution was prepared and it had been added slowly to the water dissolved Kao-Na. Subsequently, by using stirrer in a thermostated water bath at a temperature of 50 °*C*, the mixture was slowly stirred for 24 h. The prepared modified kaolin, cetyltrimethylammonium kaolinite (Kao-CTMA) was centrifuged till completely free of bromide using $AgNO_3$ test. Finally, it was oven dried at 80 °*C* and crushed in order to get the desired particle size [7,9,10,16].

2.6. Characterization of the modified and unmodified kaolin

The oxide composition of the kaolin had been identified by concrete analytical methods including $LiBO_2$ fusion, HF attack, colorimetric, gravimetric and atomic absorption spectroscopy (AAS). Both the unmodified clay (Kao and Kao-Na) and modified clay (Koa-CTMA) were also characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR), thermogravimetric analysis (TGA) and scanning electron microscope (SEM-EDX).

2.7. Essential oil effects on S. Zeamais adults

The pesticidal effects of *O. basilicum* L. essential oil against *S. zeamais* adults has been investigated via glass jar [12]. 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 μ L of the *O. basilicum* hydrodistilled essential oil was diluted by acetone as a solvent to obtain 3 mL of unlike concentrations of essential oil solutions [7]. Consequently 1 mL of each solution sample having unlike concentration was unvaryingly introduced into separate glass jars containing 20 g of maize seeds and carefully mixed by shaking to effectively coat the grains with the diluted oil. The glass jars had been opened to allow the evaporation of solvent for 2 h [17]. Subsequently for each treatment, 20 *S. zeamais* adults were transferred and were put at optimum conditions for weavil growth in an incubator [13]. To permit adequate ventilation and to avoid outflow of the insects, each jar was enclosed with muslin cloth and tied with rubber bands. Malathion 5 % dust had been taken at the suggested rate of 0.5 g/kg as positive control (0.01 g chemical insecticide for 20 g maize) and the acetone treated check was used as negative control in which neither chemical insecticide nor botanical had been applied. Each trial was replicated three times and the rate of mortality of *S. zeamais* adults had been evaluated and estimated using Abbott's formula after 24 h [18].

2.8. The essential oil remnant effect on maize

Two hundred grams of maize was coated with 6 mL of acetone diluted hydrodistilled oil. The essential oil concentrations that had been used was the lethal concentration for 95 % of mortality (LC_{95}) (176.84 μgmL^{-1}) calculated for the bioassay assessment. Acetone was left to evaporate for 2 h after the maize had been coated and the negative control was the acetone coated maize seeds. Subsequently, 20 g of essential oil coated maize seeds had been transferred into cleaned glass jars every two days. Then after, the glass jars containing adult insects and the coated maize seeds was enclosed using muslin cloth and rubber bands. Finally, each glass jar had been placed under the same situations used for assessing the entire essential oil effect on the adult insects. Survival test had been noted in three replicates, one day after treatment [7].

2.9. Formulation of kaolin clay-O. Basilicum essential oil

Formulation of kaolin clay-*O. basilicum* Essential Oil in this investigation had been prepared with both modified (Kao-CTMA) and unmodified kaolin clay (Kao-Na) by using the ratio of:

$$\frac{\text{Mass of } O.\ basilicum \text{ essential oil in gram}}{\text{Mass of modified or unmodified kaolin nanoclay in gram}} = 0.1 \quad (1)$$

Ten grams of powdered kaolin (Kao-Na or Kao-CTMA) had been introduced in a 100 mL flask and the calculated amount of acetone diluted (10 mL) *O. basilicum* essential oil was transferred to formulate 10 g of formulation of kaolin clay-*O. basilicum* essential oil. To evaporate the solvent, acetone in the formulation, it had been kept at 30 $^{\circ}C$ in a water bath for 1:30 h after 5 min of manual shaking of the mixture. Finally, the formulation (Kao-Na-*O. basilicum* and Kao-CTMA-*O. basilicum*) had been placed in containers firmly covered with aluminum foil [7].

2.10. The effect of formulation exposure time on the S. Zeamais adults

In order to evaluate the influence of formulation exposure time, 1.25 g of Kao-Na and Kao-CTMA formulations including 1.25 g of acetone formulated Kao-Na and Kao-CTMA as negative control with the positive control (0.01 g Malathion 5 % dust) were randomly used to select the exposure time for the bioassay as well as for the stability and remnant effect study of the formulations. Twenty grams maize were added into 5 glass jars for one replication and then the randomly selected mass of formulation were used to coating the maize on each glass jars. After the maize were coated, 20 adult *S. zeamais* were added on each glass jars and mixed well and these jars were enclosed with muslin cloths and maintained with rubber bands. Each trial was done with three replications in an incubator. The data were assessed on the first six days with one day interval and mortality was estimated using Abbot's formula.

2.11. Formulation effects on S. Zeamais adults

Bioassay assessments had been carried out by transferring 20 g of maize and 20 insects in eight glass jars, with different modified and unmodified kaolin supported essential oil formulation mass (0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75 and 2.00 g). Each glass jar were tightly enclosed with muslin cloths and secured with rubber bands. As a positive control, 0.01 g chemical insecticide, Malathion 5 % dust per 20 g of maize seeds and as the negative control, acetone formulated Kao-Na and Kao-CTMA was used, respectively. Each trial had been done with three replications in an incubator and the mortality rate of adults had been evaluated using Abbot's formula after five days of contact [7].

2.12. Stability of formulation

1.50 g of the unmodified and 1.25 g of the modified kaolin-essential oil formulation had been introduced to 30 glass jars (90 glass jars for both formulations and Malathion, positive control (5 %)) to examine the formulations stability. Among the 30 glass jars for each kind of the formulation plus positive control, Malathion, 15 had been firmly closed and the other 15 left glass jars had been just enclosed with muslin cloths and maintained with rubber bands. Subsequently, 20 g of maize and 20 *S. zeamais* adults had been transferred into each glass jars containing the formerly stored formulation after 1, 8, 15, 22 and 29 days formulation age for both of the unmodified and modified kaolin-essential oil formulation including the chemical insecticide, Malathion,. Like in the previous assessment trials, mortality of insects had been estimated 5 days later [7,15].

2.13. Remnant effect of formulation on maize

Twenty grams of maize mixed with both modified (1.25 g) and unmodified kaolin-essential oil formulation (1.50 g) plus Malathion (5 %) conserved for different period of time via glass jars and covered with muslin cloths to examine the remnant effect of the two formulations including the chemical insecticide. Like in the previous assessments, 20 insects had been added to 20 g of maize seeds formerly preserved for the periods of 1, 8, 15, 22, 29, 43, 57, 71 and 85 days. The experiment was carried out with three replications in an incubator (9 glass jars per day for the two formulations plus Malathion). Similarly in each case the mortality rate of adult insects had been estimated 5 days later [7].

2.14. Statistical analysis

Adult maize weevil, *S. zeamais* insect corrected rate of mortality had been estimated in percent of the introduced entire amount of insects in each replication and was calculated by using Abbott's formula [18].

$$\text{CM } (\%) = 1 - \frac{\text{n in T after treatment}}{\text{n in Co after treatment}} \text{ X } 100 \quad (2)$$

where, CM is corrected mortality, n is insect population, T is treated and Co is control.

In this regard, One-way analysis of variance (ANOVA) had been done using the general linear model method of the statistical

analysis system, SAS version 9.00 (SAS Institute Inc., 2002) at 5 % significance level to decide there significant difference between the outcomes gained for each assessments on adult insects. Subsequently to assess the *O. basilicum* essential oil mean lethal concentration (LC_{50}, LC_{95}), lethal mass (LM_{50}, LM_{95}) and the storage time (ST_{50}, ST_{90}) for 50 % and 95 % or 90 % mortality of *S. zeamais*, probit analysis had been done.

3. Results and discussion

3.1. Percentage yield of essential oil

O. basilicum fresh leaves were hydrodistilled and 42.73 g light pale yellow oil was obtained. Accordingly, on the basis of fresh leaves the yield of the essential oil was calculated as 4.27 % where the mass of the collected fresh leaves were 1 kg using the following equation [19].

$$\text{Yield of Essential oil (\%)} = \frac{\text{Extract of essential oil in gram}}{\text{Sample of fresh leaves in gram}} \text{ X } 100 \quad (3)$$

3.2. GC-MS analysis of essential oil

The essential oil components of *O. basilicum* leaves are tabulated below in Table 1. A total of 40 natural compounds were identified representing 99.99 % of *O. basilicum* essential oil. Among 40 constituents on the essential oil of this mostly used traditional medicinal herb, eleven monoterpene hydrocarbons and oxygenated monoterpenes (sabinene, α-pinene, β-myrcene, cyclohexane, diprene, eucalyptol, β-ocimene, Eugenol, Estragole, α-terpineol and 3-methoxyamphetamine) and four sesquiterpenes (*trans*-α-bergamotene, Humulene, β-bisabolene and *cis*- α-bisabolene) were identified. In general, 9-octadecenoic acid (z)-methyl ester (25.12 %), Hexadecanoic acid, methyl ester (19.26 %), *trans*-iso eugenol (13.12 %), eucalyptol (11.19 %), methyl stearate (8.35 %), 11-octadecenoic acid, methyl ester (2.91), 9,12-octadecadienoic acid, methyl ester (2.78 %), methyl tetradecanoate (2.70 %), 9-hexadecenoic acid, methyl ester (2.41 %), β-bisabolene (1.70 %) and estragole (1.69 %) were found as the major compounds of the sweet basil and some of the structures are described in Fig. 1.

Table 1
The compounds identified from the essential oil of the leaves of *O. basilicum* by GC-MS analysis.

Peak	RT	Chemical formula	Identified Compound name	Area %	Peak	RT	Chemical formula	Identified Compound name	Area %
1	5.356	$C_9H_{15}Cl$	(4Z)-5-chloro-3,4-dimethyl-2,4-heptadiene	0.27	21	14.262	$C_{15}H_{24}$	*Cis*-α-bisabolene	0.30
2	6.015	$C_{10}H_{16}$	Sabinene	0.12	22	14.850	$C_{16}H_{34}$	Hexadecane	0.20
3	6.082	$C_{10}H_{16}$	α-pinene	0.33	23	14.910	$C_{13}H_{21}NO$	N-desmethyltapentadol	0.13
4	6.260	$C_{10}H_{16}$	β- myrcene	0.25	24	15.626	C3H7NO	N-ethyl formamide	0.07
5	6.927	$C_{10}H_{18}$	cyclohexane,1-methyl-5-(1-methylethenyl)-(R) or diprene	0.17	25	15.998	$C_9H_{18}N_2O_3$	dl-alanyl-DL-norleucine	0.12
					26	16.297	$C_{15}H_{30}O_2$	methyl tetradecanoate	2.70
6	6.993	$C_{10}H_{18}O$	Eucalyptol or cineole	**11.19**	27	17.165	$C_6H_{13}N_5O_4$	N, φ-nitro-L-arginine	0.31
−7	7.198	$C_{10}H_{16}$	β –ocimene	0.78	28	17.525	$C_{16}H_{32}O_2$	Pentadecanoic acid, methyl ester	0.62
8	9.161	$C_{10}H_{15}NO$	3-methoxyamphetamine	0.21	29	18.625	$C_{17}H_{32}O_2$	9-hexadecenoic acid, methyl ester	2.41
9	9.329	$C_{10}H_{16}$	γ-terpinene	0.42	30	18.907	$C_{17}H_{34}O_2$	Hexadecanoic acid, methyl ester	**19.26**
10	9.519	$C_{10}H_{18}O$	α-terpineol	0.83	31	19.743	$C_9H_{13}NO_2$	DL-phenylephrine	0.16
11	9.613	$C_{10}H_{12}O$	Estragole	1.69	32	19.876	C9H13N	Dextroamphetamine	0.18
12	10.371	$C_{14}H_{23}N_3O_2$	1-(3,5-dimethyl-1-adamantanoyl)semicarbazide	0.18	33	20.019	$C_8H_{22}N_4$	N,N′-bis(3-aminopropyl) ethylenediamine	0.29
13	11.894	$C_{10}H_{12}O_2$	*trans*-isoeugenol	**13.12**	34	20.112	$C_{10}H_{15}NO$	5-(2-aminopropyl)-2-methylphenol	0.30
14	12.356	$C_9H_{12}N_2O$	2-methylamino-N-phenyl-acetamide	0.22	35	20.477	$C_6H_9N_3O$	2-formylhistamine	0.21
15	12.834	$C_8H_5N_3O_4$	pyrido(3,4,d)imidazole,1,6-dicarboxylic acid	0.36	36	21.694	$C_{19}H_{34}O_2$	9,12-octadecadienoic acid, methyl ester	2.78
16	12.949	$C_{15}H_{24}$	*Trans*- α –bergamotene	0.30	37	21.797	$C_{19}H_{36}O_2$	9-octadecenoic acid (z)-, methyl ester	**25.12**
17	13.278	$C_{15}H_{24}$	Humulene	0.23	38	21.960	$C_{19}H_{36}O_2$	11-octadecenoic acid, methyl ester	2.91
18	13.633	$C_{15}H_{32}$	Pentadecane	0.86	39	22.243	$C_{19}H_{38}O_2$	methyl stearate	8.35
19	13.857	$C_{15}H_{24}$	β –bisabolene	1.70	40	25.281	$C_{13}H_{20}N_2O_6$	N-methyl-Benzeneethanamine	0.16
20	13.952	$C_{13}H_{26}O_2$	Dodecanoic acid, methyl ester	0.18					

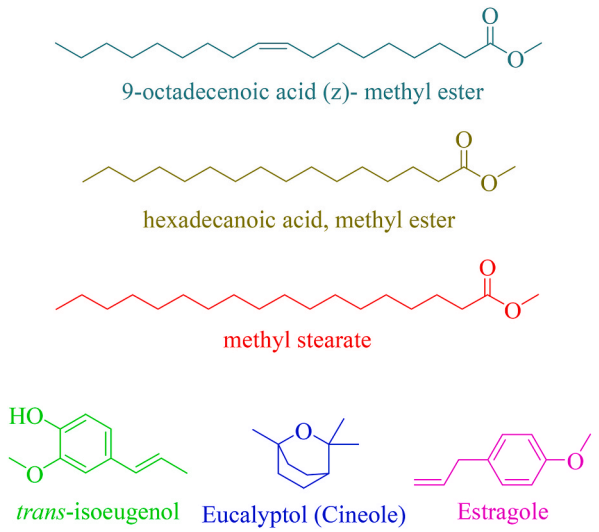

Fig. 1. The Structures of some of the major compounds of *O. basilicum* essential oil.

3.3. Chemical analysis of raw kaolin clay

The chemical compositions of oxides of kaolin in weight % had been illustrated in Table 2 using concrete analytical methods ($LiBO_2$ fusion, HF attack, Colorimetric, Gravimetric and AAS). The chemical analysis of the unmodified raw kaolin clay shows silica (SiO_2) and alumina (Al_2O_3) in major quantities and other elements in minor quantities. The analysis result also shows due to the absence of carbonates, the amount of calcium oxide (CaO) and magnesium oxide (MgO) is very low. Thus, the kaolin clay that has been used as adsorbent for essential oil formulation is principally composed of the kaolinite ($Al_2O_3.2SiO_2.2H_2O$) as indicated by the result of oxide composition. The results obtained in the present investigation are very close to what is expected for other kaolinites according to different reports [20,21,22].

3.4. Analysis of XRD patterns

The intensive peaks appearing in the XRD pattern are characteristics of the kaolinite minerals in kaolin clay as depicted in Fig. 2. The diffraction peaks at scattering angles (2θ) around 12.35, 19.89, 20.37, 23.09, 24.86, 34.97, 35.92, 38.40, 45.41, 54.97, 59.88 and 62.27° are clear indication for the presence of kaolinite in major quantity from the sample kaolin clay. Similar diffraction profiles were reported by Zen et al. (2018) and this guides that the kaolin clay used in our research is indeed kaolinite with anorthic (triclinic) lattice structure. The diffraction minor peaks at 2θ around 21.26, 23.72, 26.37, 39.23, 49.50, 51.00, 56.74 and 59.88° shows the presence of quartz ([23–25]; Maite et al., 2020). Therefore, most of the peaks can be accounted by the kaolinite minerals with quartz as minor impurities on the raw kaolin.

The basal distance (d) and the average crystallite size (D) of unmodified (Kao, Kao-Na) and modified kaolinite (Kao-CTMA) were calculated using Bragg's Law {$2\lambda = d\sin\theta$} and Debye Scherer Equation {$D = K\lambda/\beta\cos\theta$}, respectively; where, K is the shape factor constant taken as 0.90, λ is the X-ray radiation wave length (0.15406 nm), β is a broadening of the diffraction line measured at the full width at half maximum (FWHM) and θ corresponds to the Bragg's diffraction angle in radians. The most intense peak at $2\theta = 24.86°$ for Kao and Kao-Na and at $2\theta = 24.76°$ for surfactant modified kaolinite (Kao-CTMA) has a profile similar to that of the intense peak of kaolinite diffraction pattern in literature [23]. β were 0.003506, 0.004674 and 0.02688 for raw kaolinite (Kao), sodium treated kaolinite (Kao-Na) and modified kaolinite by CTMA (Kao-CTMA), respectively.

Thus, the calculated average crystalline sizes of Kao, Kao-Na and Kao-CTMA were estimated to be 40.49, 30.38 and 5.28 nm, respectively. The average crystal size of the Kao-CTMA is less than the Kao and Kao-Na as the result revealed and this directs the intercalation of the organic surfactants on the kaolinite surface. The basal distance of the unmodified (Kao and Kao-Na) at $2\theta = 24.86°$ and the modified kaolin (Kao-CTMA) at $2\theta = 24.76°$ are 1.43 and 1.44 nm, respectively. It is therefore evident that the intercalation of organic surfactant increases the distance of the kaolin layers thus signifying the successful preparation of modified kaolinite using organic surfactant, CTMA. Overall, the major differences in the X-ray diffraction pattern of unmodified and modified kaolinite are their interlayer space (basal distance) and average crystal size. The intensification in the value of basal spacing depends upon the presence of

Table 2
Chemical composition of unmodified (raw) kaolinite using concrete analytical methods.

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LOI
Weight %	75.84	16.58	0.75	<0.01	0.20	<0.01	<0.01	0.02	0.12	<0.01	1.21	5.70

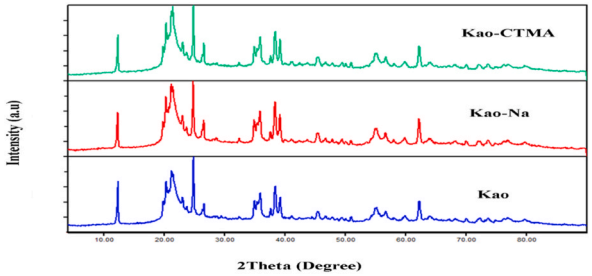

Fig. 2. X-ray diffraction pattern of unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA).

large hydrophobic groups on surfactants and the decrease in surface energy of kaolinite clay after modification [26].

3.5. TGA analysis

The stability and structural integrity of unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA) clay was characterized by thermogravimetric analysis (TGA) as shown in Fig. 3 and the thermal analysis data are represented in Table 3. From the thermograms and Derivative thermogravimetric analysis (DTA) curves shown, there are two distinct mass loss steps observed for Kao and Kao-Na prior to the formation of the final oxides. The first step of decomposition shows 1.58 % and 1.45 % weight loss of raw kaolinite and sodium treated kaolinite, respectively in the temperature range of 25–150 °*C* and this corresponds to the surface adsorbed water molecules dehydration. The thermogram curve of both Kao and Kao-Na displays a stability plateau in the range of 150–450 °*C* where the mass is relatively constant and this gives clear information to the high thermal stability of the unmodified kaolin sample under the given conditions. In the temperature range of 450–600 °*C*, a second step of additional 6.73 % and 6.25 % weight loss resulting in the formation of metakaolinite on Kao and Kao-Na, respectively attributed to water loss via dehydroxylation of OH on the kaolin sample [26]. Previous studies assert that when unmodified kaolinite dehydroxylation occurs from 400 to 650 °*C*, it is practically the main endothermic mass loss transformation in this temperature range [27] and this supports the present study.

However, there are three distinct weight loss events for Kao-CTMA. The first step of decomposition with minor weight loss (0.83 %) for Kao-CTMA occurring between 25 and 150 °*C* is due to the disappearance of surface adsorbed water molecules without any alteration of the kaolin structure. This minor weight loss is an indication for the intercalation of organic surfactant cations on kaolin clay due to the less adsorption of surface water as the organophilic properties of the modified kaolin rises. The second decomposition step of the Kao-CTMA in the temperature range of 200–300 °*C* shows 7.40 % weight loss attributed to the desurfactant of organic cations (CTMA) which were intercalated with the kaolinite during the modification process. The last weight loss of Kao-CTMA (6.12 %) occurring between 450 and 600 °*C* is as a result of OH dehydroxylation on the kaolinite structure. The weight loss corresponds to OH dehydroxylation on the Kao-CTMA is relatively lower than the unmodified kaolin and this specifies the relative stability of the modified kaolin by the organic surfactants [27].

After 600 °*C*, the kaolin structure completely decomposed and resulting to the formation of oxides. The residual weights after heating the samples, at 750 °*C* were 91.69 % and 92.30 % for Kao and Kao-Na. But the residual weights after heating the Kao-CTMA at 750 °*C* were 85.65 % and are lower than the unmodified kaolin attributed to the replacement of the metal ions by organic surfactant cations. The amount of water drops from 1.58 % to 1.45 % for unmodified kaolinite (Kao and Kao-Na) to 0.83 % for Kao-CTMA. This feasible result directs the substitution of mineral cations by CTMA cations and thus changing the surface of kaolin from hydrophilic to organophilic/hydrophobic properties.

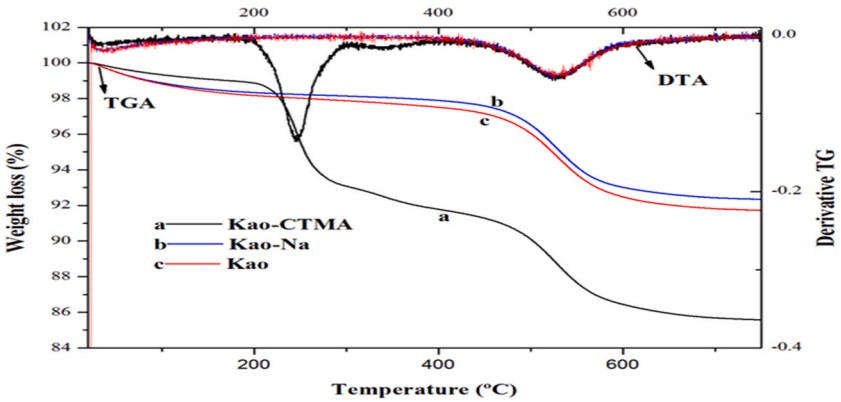

Fig. 3. Thermogravimetric analysis of unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA).

Table 3
Thermal analysis data of unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA).

Sample	Temperature range, °C	Mass loss, %	Residue weight, %
Kao	25–150	1.58	91.69
	450–600	6.73	
Kao-Na	25–150	1.45	92.30
	450–600	6.25	
Kao-CTMA	25–150	0.83	85.65
	200–300	7.40	
	450–600	6.12	

3.6. FT-IR characterization

The FT-IR spectra of unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA) are illustrated in Fig. 4. The bands at 3623 cm^{-1}, 3666 cm^{-1} and 3695 cm^{-1} is attributed to the internal hydroxyl groups of the kaolinite, hydroxyl groups at the surface of the octahedral layers of alumina that interact with the oxygen atoms of the adjacent tetrahedral layers of silica and the hydroxyl groups sitting at the edges of the platelets, respectively ([24,28]; Maite et al., 2020). Furthermore, the band around 1638 cm^{-1} is credited to the bending vibrations of free water (moisture) adsorbed to the surface of kaolin. The presence of bands in the 1800-400 cm^{-1} range at 1104, 1031, 916, 793, 685, 533 and 472 cm^{-1} shows the clay is kaolinite type. The bands at 1104 cm^{-1}, 1031 cm^{-1} and 916 cm^{-1} are responsible for the stretching vibrations of asymmetric *Si*–O, the stretching vibrations of alternating *Si*–O–Si plus Al–O–Al and the Al–O–H bending vibrations (hydroxyl groups sitting on the alumina faces), respectively. The *Si*–O–Si symmetric stretching vibration is accountable for the bands around 793 and 685 cm^{-1}. Lastly the bands around 533 cm^{-1} and 472 cm^{-1} are due to Al–O–Si vibration and the O–Si–O bending vibrations ([24,29–31]; Maite et al., 2020).

The FTIR spectrum of Kao-Na was found to be similar with Kao. In the case of the Kao-CTMA, similar absorption peaks with Kao and Kao-Na have been observed. Besides, new absorption band were also detected around 2851 and 2922 cm^{-1} which are representatives of the asymmetric and symmetric stretching vibrations of the methylene (CH_2) and methyl groups (CH_3) of the aliphatic chain of the organic surfactant, CTMA as clearly observed in the FT-IR spectrum of Kao-CTMA. The broad band centered around 3428 cm^{-1} on the spectrum of raw and sodium treated kaolin is due to the typical O–H stretching hygroscopic moisture. The occurrence of the H–O–H bending mode at 1638 cm^{-1} definitively confirms the constant existence of adsorbed water and demonstrating the hydrophilic nature of the unmodified kaolinite. However, the H–O–H bending and stretching modes decreased in modified kaolinite by surfactant, CTMA which shows that organic surfactant modifications of the kaolinite reduce the hydrophilic properties of the adsorbent surface and enhance organophilic character instead.

3.7. SEM-EDX analysis

The morphology and the weight (%) of elements in the unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA) was determined by scanning electron microscopy (SEM) merged with the EDX results as indicated in Fig. 5a, b and c. All the three micrographs show irregular sized particles. However, the Kao-CTMA materials appeared to have less aggregates with formation of flake like materials the formation of which is pronounced with the organo modified kaolinite. The morphology of Kao and Kao-Na are relatively thick stacks (massive and aggregated morphology with sparse large flakes observed on the Kao and Kao-Na) possibly due to particles bound together by intermolecular forces [32] whereas flake like dispersed structures of smaller size predominate the organoclay samples (Kao-CTMA). This relative difference on the surface morphology suggests the incorporation of organic molecules (CTMA) in the layer of kaolin [33].

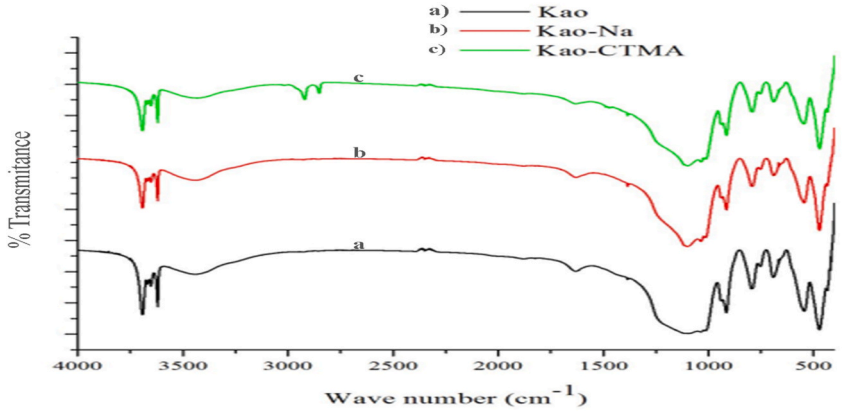

Fig. 4. The FT-IR spectrum of the unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA).

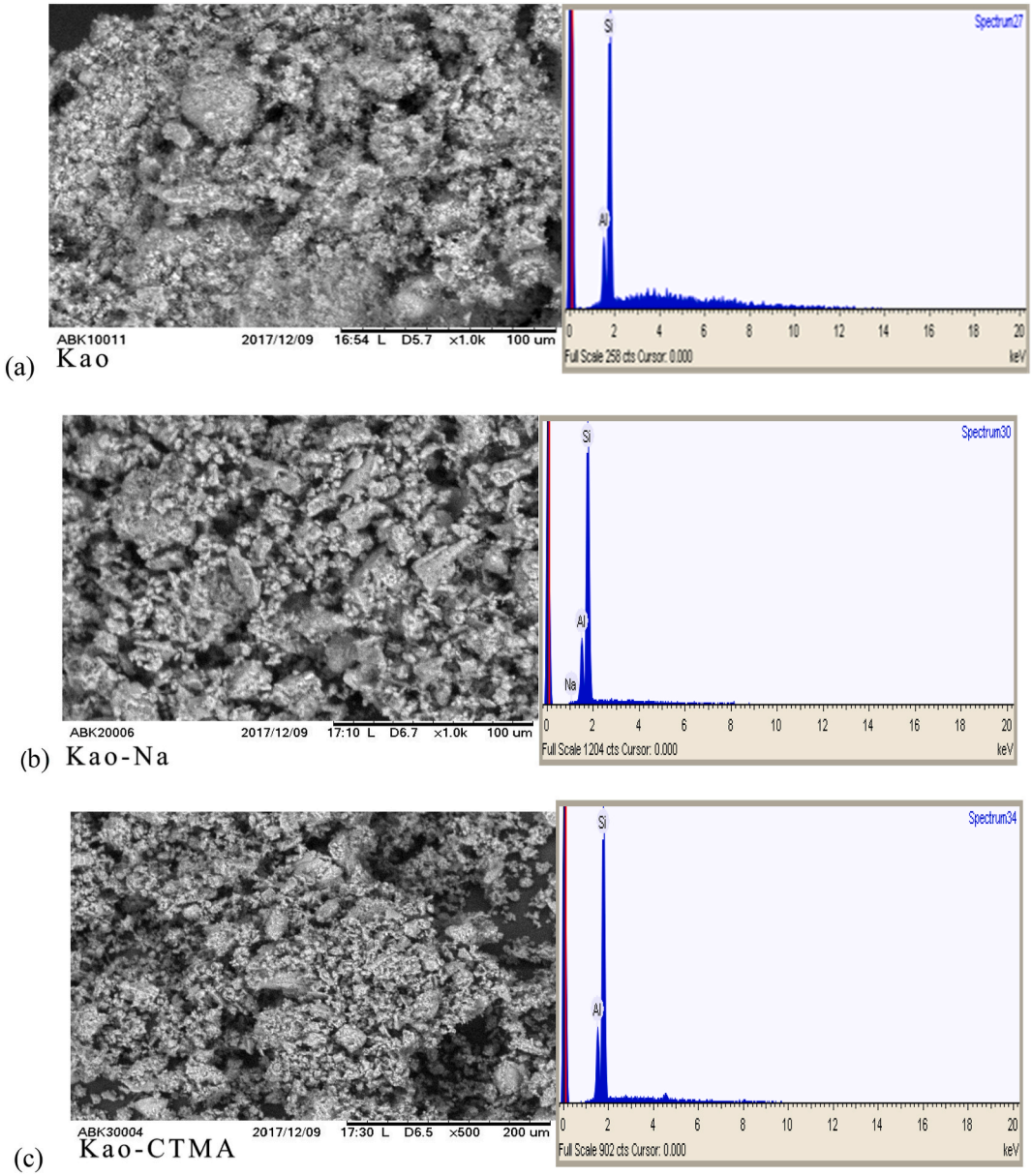

Fig. 5. SEM-EDX picture of the raw kaolinite (a, Kao), sodium treated kaolinite (b, Kao-Na) and the modified kaolinite by CTMA (c, Kao-CTMA).

Table 4
EDX elemental analysis results of the unmodified (Kao and Kao-Na) and modified kaolinite (Kao-CTMA).

Sample code	Element	Range of weight (%)	Average weight (%)
ABK-1 (Kao)	Aluminium	14.5–21.9	17.2
	Silicon	78.1–85.5	82.8
ABK-2 (Kao-Na)	Sodium	0.0–0.5	0.16
	Aluminium	14.3–15.7	15.1
	Silicon	84.3–85.7	84.74
ABK-3 (Kao-CTMA)	Aluminium	15.6–17.5	16.55
	Silicon	81.9–84.4	83.13
	Copper	0–1.3	0.32

Silicon (Si) and aluminum (Al) are the major elements of kaolin as indicated by the elemental analysis performed using EDX (Table 4), confirming the results obtained from chemical composition analyses. The intense Si peak could be ascribed to kaolin clay minerals possibly free SiO_2 (quartz) in addition to the kaolinite mineral [28,34]. Only Al and Si signals are observed in the EDX spectrum of raw kaolin clay (Kao) which has been recognized as the fundamental elements of unmodified kaolin. Whereas the presence of sodium signals in the EDX spectrum of Kao-Na clay sample indicates the treatment and intercalation of sodium ion on the raw kaolin sample. The absence of sodium signals in the EDX spectrum of Kao-CTMA suggests the replacement of sodium ions by the organic CTMA surfactant ions and the presence of copper signals on this spectrum may be due to the impurities detected from the copper grid.

3.8. Insecticidal activity of O. Basilicum essential oil

Results on insecticidal activity of adult maize weavil, *S. zeamais* during 24 h exposure time after the application of *O. basilicum* leaves essential oil at different concentrations has been presented (Fig. 6 and Table 5). 47.46 % and 100.00 % corrected mortality of *S. zeamais* adults were found at concentrations of 32.67 and 228.67 μgmL^{-1} of *O. basilicum* leaves essential oil, respectively. The computed lethal concentration for 50 and 95 % mortality of *S. zeamais* adults (LC_{50} and LC_{95}) were 40.17 and 176.84 μgmL^{-1}, respectively. This observed result is an indication of the maize weavil, *S. zeamais* adult mortality increases with the quantity of *O. basilicum* essential oil. The results of maize weavil mortality by *O. basilicum* essential oil compared favourably with Malathion (5 %) after 24 h treatment against *S. zeamais*. Concentrations of *O. basilicum* (196.00 μgmL^{-1}) show higher significant mortality (98.33 %) as compared with the percent mortality of Malathion (5 %, 0.01 g) dust (91.67 %) with in the period of 24 h time of exposure. Similar observations has been reported from previous findings [7,9,10,35,36]).

The higher pesticidal efficiency of the *O. basilicum* leaves on *S. zeamais* adults is generally due to the synergetic effect of bioactive terpenic compounds (monoterpene hydrocarbons, sesquiterpenes and oxygenated monoterpenes). For instance, 1,8-cineole (eucalyptol) and terpineole which were identified from the GC-MS analysis of this important herb has been reported with good toxicity against adult maize weevils [37,38].

3.9. Remnant effect of O. Basilicum essential oil on maize

The pesticidal efficacy of *O. basilicum* essential oil against *S. zeamais* adults rapidly dropped with the essential oil and maize contact time increased before exposure (Fig. 7). The corrected mortality of *O. basilicum* essential oil against *S. zeamais* adults diminished from 100.00 % to 15.18 % eight days later, maize and essential oil being impregnated and no toxicity had been observed from the 12th day on wards (Fig. 7). The essential oil of the *O. basilicum* storage time for 50 % of its insecticidal activity is about 5 days and 7 h after the essential oil and maize being impregnated and before the infestation of the maize weavil. However, the essential oil of *O. basilicum* toxicity had been enhanced for around six days with 49.04 % of mortality on *S. zeamais* by being treated on grain compared to the insecticidal effects of direct infestation. This obtained result was compared with the reported studies by Nguemtchouin et al. [7] and shown a slightly higher storage time by impregnating the *O. basilicum* essential oil on maize than the reported one. The reason might be attributed to the difference in the persistence of the active ingredients between the two *Ocimum* herbs.

3.10. The effect of formulation exposure time on S. Zeamais

For both of the two formulations, 1.25 g Kao-Na- *O. basilicum* and Kao-CTMA-*O. basilicum* essential oil were randomly used. The obtained result shows the *S. zeamais* adult mortality considerably increasing ($P < 0.05$) with the exposure time of the introduced formulation in the glass jars containing insects and maize (Fig. 8) until five days of the exposure time. However, the effect was found to be insignificant after five days of exposure as shown in Fig. 8. Five days of exposure time had been, therefore, selected for all the other formulation evaluation. For the negative controls (1.25 g acetone formulated Kao-Na and Kao-CTMA), the mortality of *S. zeamais* were not significant and the effect of the negative control is very less even when the exposure time is increased. To the contrary, for the

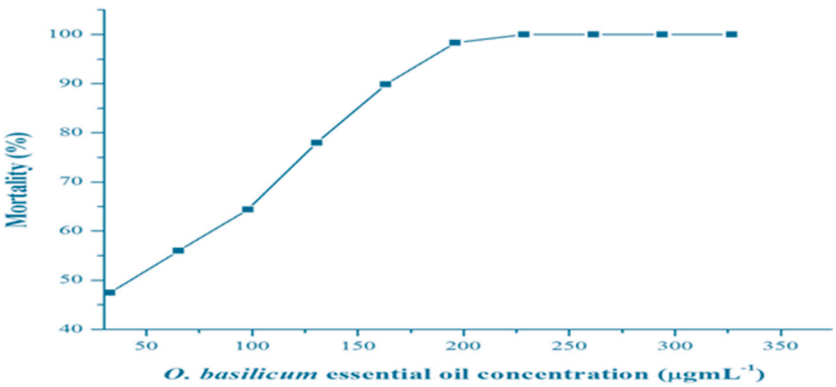

Fig. 6. Assessment of the insecticidal activities of essential oil of *O. basilicum* leaves on *S. zeamais* adult insects.

Table 5
Leaves of *O. basilicum* essential oil insecticidal toxicity against *S. zeamais* on the concentration variation within 24 h of exposure time.

Concentration of essential oil (μgmL^{-1})	Mean corrected mortality (%) ± SD
Control (acetone treated)	1.67 ± 2.89^{g}
32.67	47.46 ± 2.50^{f}
65.33	55.97 ± 1.67^{e}
98.00	64.39 ± 1.06^{d}
130.67	77.98 ± 2.64^{c}
163.33	89.83 ± 0.30^{b}
196.00	98.33 ± 2.89^{a}
228.67	100.00 ± 0.00^{a}
261.33	100.00 ± 0.00^{a}
294.00	100.00 ± 0.00^{a}
326.67	100.00 ± 0.00^{a}
Malathion	91.67 ± 2.89^{b}

Mortality values followed by the same superscript letters within the same column (concentration variation) are not significantly different by using one-way ANOVA ($P \leq 0.05$) followed by LSD test.

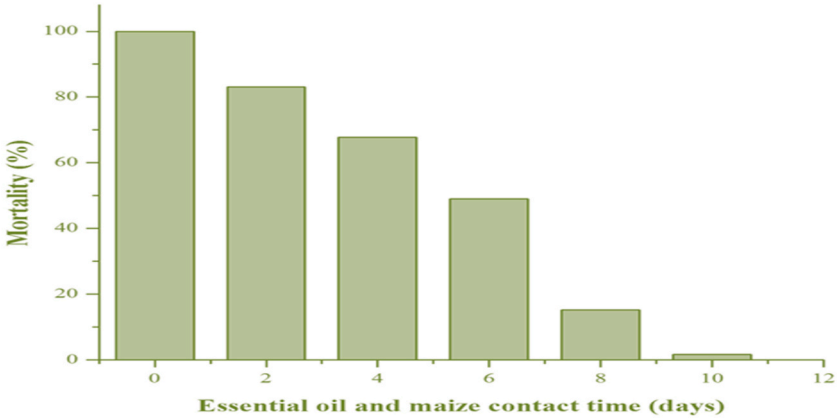

Fig. 7. Remnant efficacy of the *O. basilicum* essential oil against *S. zeamais* adults.

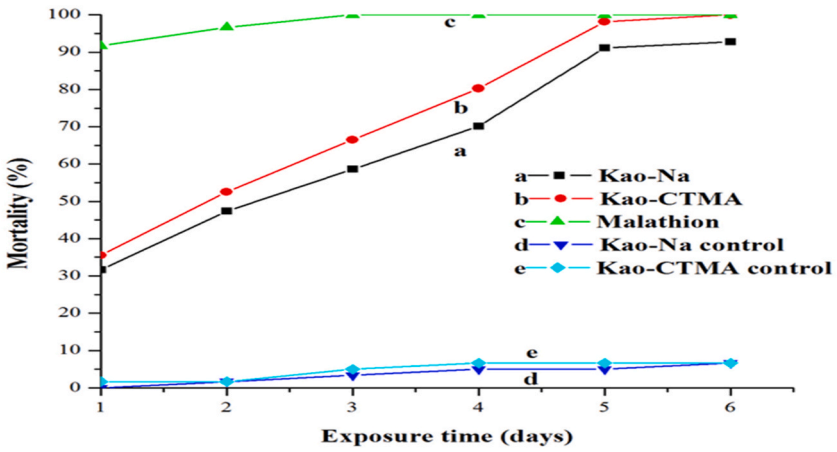

Fig. 8. The effect of exposure time on the mortality of *S. zeamais* at constant mass of formulation.

Malathion dust (5 %, 0.01 g), the mortality of the *S. zeamais* significantly increased with the first three days of exposure time but the effect appeared less significant beyond evidencing the pronounced effect on the mortality of *S. zeamais* at short period of exposure time. Thus, when compared with the synthetic insecticide, higher exposure time needs for higher mortality of *S. zeamais* adults in the case of the two formulations. This might be due to delayed release of the active ingredients that are sorbed on the nanoclay, kaolin.

3.11. The formulation efficiency on Sitophilus zeamais

For both of Kao-Na-*O. basilicum* and Kao-CTMA-*O. basilicum* formulations, the insecticidal activity on *S. zeamais* adults improved ($P < 0.05$) when the quantity of formulation increased till a certain optimum mass significantly. Further increase in formulation mass, however, showed no pronounced effect (Fig. 9 and Table 6). Also the negative control result revealed that there is no significantly observed toxicity by Kao-Na and Kao-CTMA. Insect mortality varied from 33.30 to 37.52 % with 0.25 g–100.00 % with 1.50 and 1.25 g of formulation mass for Kao-Na and Kao-CTMA based formulations, respectively. Moreover the calculated formulation mass needed to destroy 50 and 95 % of adult maize weevil (LM_{50} and LM_{95}) had been 0.59 and 1.43 g (Kao-Na- *O. basilicum) and* 0.39 and 1.17 g (Kao-CTMA-*O. basilicum*), respectively. Hence, when compared with the formulation based on unmodified kaolinite, the formulation prepared by *O. basilicum* with modified kaolinite confirmed to show strong activity to destroy the infestation of maize by adult insects and demonstrating that extra bioactive terpenoids had been fused. The main reason for this is due to the enhancement of kaolinite adsorption capability prompted by the preliminary treatment with organic surfactant, CTMA, which improved the crystallographic arrangement of the kaolinite and raise the organophilic properties of the modified clay material.

The efficiency of the presnt formulation was compared with other formulation which was reported by Nguemtchouin et al. [7]. According to their findings, the *S. zeamais* adult mortality meaningfully enhanced with the formulation mass in line with the present study. However, this investigation requires less amount of formulation for 50 % of *S. zeamais* adult mortality when compared with previous reported formulation [7,9,10]. This could be due to the presence of highly insecticidal active ingredients in *O. basilicum* essential oil. Therefore, this study confirms the significance of the insecticidal formulation efficiency of *O. basilicum* essential oil by using modified kaolinite adsorbent as a means of environmentally friendly insecticide for maize weavil, *S. zeamais* adults.

3.12. Stability of formulations

The stability the two prepared modified (1.25 g) and unmodified (1.50 g) kaolinite formulations preserved for various days before the contact of maize and insects in both closed and open glass jars against the maize weevil adults after five days of exposure has been denoted on Fig. 10(a and b). On the first day of the formulation age, the *S. zeamais* adult mortality had been 96.39 and 98.33 due to the ingestion of the Kao-Na-*O. basilicum* formulation and 98.25 and 100.00 due to Kao-CTMA-*O. basilicum* formulation in open and closed jars, respectively, 5 days later. Thus, in both open and closed jars; insecticidal activity caused by the two formulations including Malathion had been insignificant on the first day of the formulation age. When the storage time increased, however, there was significantly different *S. zeamais* adult mortality between the modified and unmodified kaolinite-*O. basilicum* formulations plus Malathion used in both closed and open glass jars ($P < 0.05$).

The insecticidal activity caused by Kao-Na-*O. basilicum* essential oil falling more quickly with the age of formulation and losing about 70 and 25 % of its activity in open and closed jars at 29 days of the formulation age, respectively. Whereas at the same time of the formulation age, about 52 and 18 % of the insecticidal activities were lost in open and closed jars, respectively for Kao-CTMA-O. *basilicum* essential oil formulation. From this the formulation in closed boxes has been more stable and declined its activities slowly than those in open boxes. This investigations has been consistent with Nguemtchouin et al. [15] reported results. However, the insecticidal activity caused by the positive control (Malathion) reduced very slowly than by the two formulations as storage time increased in both open and closed jars as it has been shown on Fig. 10(a and b). The reason behind this is most probably due to the stability of organophosphorus formulations of Malathion is well established. This finding has been supported by different reported studies [7,9,10,15].

For formulations with unmodified clay (Kao-Na-*O. basilicum*), modified clay (Kao-CTMA-*O. basilicum*) and finally Malathion preserved in open jars, 50 % of their insecticidal strength had been lost later 19 days and 8 h, 28 days and 16 h and 30 days and 14 h, respectively (Table 7). However, the significant variation between each kaolinite formulations in the period dropping 10 % efficiency (prompting 90 % death) was much minor with storage time of 8 days and 23 h, 7 days and 2 h and 6 days and 1 h for Malathion, Kao-CTMA and Kao-Na-*O. basilicum* formulation, respectively in the open jars. Moreover formulations preserved in closed glass jars missing 10 % of their pesticidal efficiency (ST_{90}) later 19 days and 1 h, 15 days and 8 h and 9 days and 4 h for Malathion, Kao-CTMA and Kao-Na, respectively as observed in Table 7. But 30 days later no formulation had lost rapidly its activity and as a consequence very large periods of time were estimated for ST_{50} of each formulation in the closed jars. The obvious slight loss of active constituents in the kaolinite formulations with firmly closed glass jars might have been as a result of sorption of the active constituents of the formulation into the closed jars. Generally, the kaolinite-*O. basilicum* formulation half-life time shows considerably enhanced stability over the unmodified kaolinite formulation and this finding supported by the result of Nguemtchouin et al. [7] and Noudem et al. [10].

3.13. Remnant effect of formulations

Both of the two formulations previously mixed with grain before infestation including the positive control, Malathion and infested after 1, 8, 15, 22, 29, 43, 57, 71 and 85 days, had been investigated as insecticidally energetic on maize adult insects. As shown in Fig. 11, for the two kaolinite-essential oil formulations and Malathion dust (5 %, 0.01 g), mortality of *S. zeamais* gradually reduced in

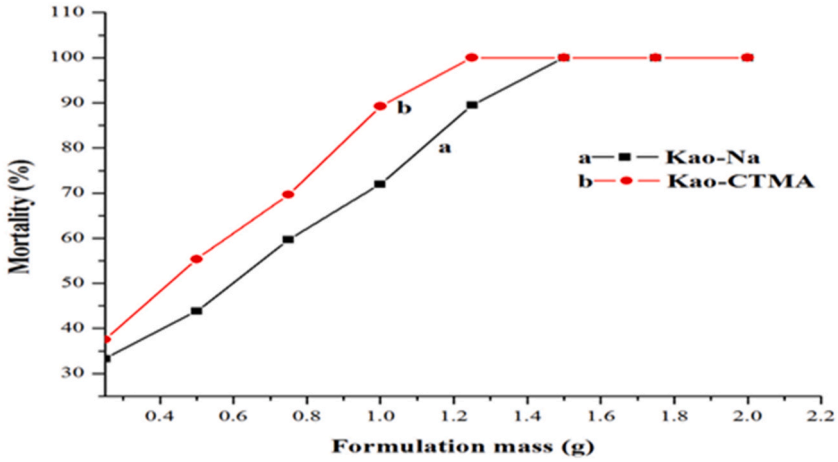

Fig. 9. Influence of mass of powder formulations with modified and unmodified kaolinite clays on *S. zeamais*.

Table 6
The unmodified (Kao-Na) and modified (Kao-CTMA) formulation efficacy of on *S. zeamais* mortality (%) after corrected using abbot's formula and after 5 days of exposure time.

Formulation mass (g)	Kao-Na (%M)	Kao-CTMA (%M)
Control	a5.00 ± 5.00^{g}	a6.67 ± 2.89^{f}
0.25	b33.30 ± 1.71^{f}	a37.52 ± 1.18^{e}
0.50	b43.85 ± 1.54^{e}	a55.36 ± 2.64^{d}
0.75	b59.67 ± 1.63^{d}	a69.69 ± 2.20^{c}
1.00	b71.97 ± 1.86^{c}	a89.28 ± 0.34^{b}
1.25	b89.45 ± 0.56^{b}	a100.00 ± 0.00^{a}
1.50	a100.00 ± 0.00^{a}	a100.00 ± 0.00^{a}
1.75	a100.00 ± 0.00^{a}	a100.00 ± 0.00^{a}
2.00	a100.00 ± 0.00^{a}	a100.00 ± 0.00^{a}
Malathion (5 %)	a100.00 ± 0.00^{a}	a100.00 ± 0.00^{a}

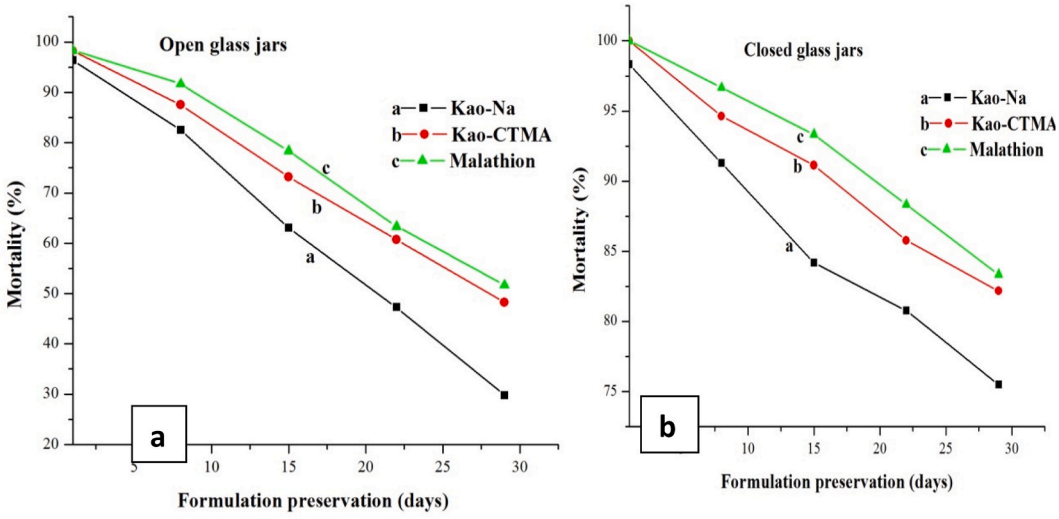

Fig. 10. Stability effect of the formulations and Malathion conserved in open (a) and closed (b) glass jars.

the order: Kao-Na-*O. basilicum* > Kao-CTMA-*O. basilicum* > chemical positive control (Malathion dust 5 %) formulations. The mortalities of *S. zeamais* adults by the insecticidal action of both formulations (Kao-Na-*O. basilicum* and Kao-CTMA-*O. basilicum*) and the Malathion were 98.25, 100.00, and 100.00 % on the first day of the formulation and maize contact time before the infestation of the adult weevils, respectively. However at the end of the 85th day, Kao-Na-*O-basilicum* (1.5 g) induced 17.49 % of insect mortality

Table 7
ST_{50} and ST_{90} values (days) of the formulations and Malathion (synthetic insecticide).

Types of formulation		ST_{50} (day)	ST_{90} (day)	Slope	Intercept	R^2
Open jars	Kao-Na-O. *basilicum*	19.35	6.08	−2.55	8.28	0.986
	Kao-CTMA-O. *basilicum*	28.70	7.08	−2.11	8.08	0.996
	Malathion	30.62	8.98	−2.40	8.57	0.998
Closed jars	Kao-Na-O. *basilicum*	115.36	9.17	−1.17	7.40	0.992
	Kao-CTMA-O. *basilicum*	162.40	15.35	−1.25	7.77	0.985
	Malathion	128.73	19.08	−1.55	8.26	0.987

ST_{50} and ST_{90} represent the number of days (storage time) at which formulation could induce 50 % or 90 % mortality respectively.

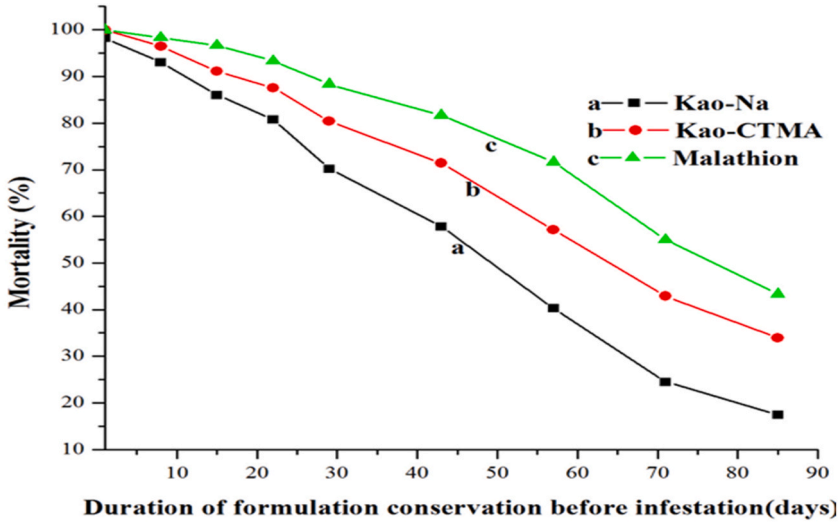

Fig. 11. Remnant effect of the formulations and Malathion previously mixed with maize.

efficiency, on the other hand Kao-CTMA-*O. basilicum* formulation (1.25 g) and Malathion dust (5 %, 0.01 g) induced 33.92 and 43.33 % respectively.

The relatively less preservation of insecticidal activity by the Kao-Na-*O. basilicum* compared to Kao-CTMA-*O. basilicum* formulation had been a result of fewer terpenes being sorbed primarily, and the greater release speed of these ingredients. The Kao-CTMA-*O. basilicum* essential oil formulation had been enhanced initially through the capability for hydrogen bonds to be formed between the kaolinite and insecticidally active terpenic constituents like eucalyptol (1,8 cineole), which is one of the compound in *O. basilicum* essential oil existing in major abundance, and moreover between the organic surfactant combined with sheets of kaolinite and the oxygenated terpenes for example beta myrcene and alpha-pinene of the plant *O. basilicum*. These constituents have been recognized for their synergic activity on insects, *S. zeamais* when they exist together (Tapondjou et al., 2002). Generally the declining of insect mortality in each formulation when the maize and **formulation** contact time increased is due to the declining of essential oil toxicity **described by** the release of the synergistically active terpenic compounds in the plant essential oil [7,10].

The remnant effect of the present finding is in familiar with the reported studies on *Xylopia aethiopica* and *O. gratissimum* plant essential oil formulation using kaolinite and montmorilonite types of clay adsorbent [7,10,15]. The significantly higher persistence of the Malathion when compared with the two prepared formulations is due to the higher release rate of the two formulations. Generally the persistence of the modified and unmodified kaolinite *O. basilicum* essential oil formulation was highly increased when compared with the remnant effect of the essential oil without support.

4. Conclusions

In conclusion, we have successfully extracted essential oil through hydrodistillation and the active components were analyzed via GC-MS. Moreover, the supporting materials both modified and unmodified kaolinite clay were prepared and characterized efficiently for essential oil adsorption. Results confirm that the hydro distilled oil was active towards the maize weevil *S. zeamais*. However, this research displays the persistence of the essential oil without the use of adsorbent is not satisfactory for a long period of time by impregnating it on the stored grain. Thus, the current study solves the quickly released efficacy of essential oils on pest management through use of a formulation based on modified clay with organic surfactants and essential oil. During this study, the formulations preserved for various days before the contact of maize and insects was lead to perceive the stability. However, the formulation was coated and conserved on maize at different durations before infestation of *S. Zeamais* in order to observe the remnant efficacy. The

results of this study displays that the formulation of essential oil using modified kaolin exhibited the higher insecticidal activities, higher stabilities and higher remnant/persistence effects than the formulation using unmodified kaolin. Hence, the formulation based on *O. basilicum* with modified kaolinite proved to be more toxic than the same formulation with unmodified clay, indicating that more insecticidal active compounds were incorporated in the modified formulation. This is due to the improvement of clay adsorption capacity induced by the initial treatment with CTMA solution which modified the crystallographic structure and increased the organophilic properties of the supporting material. Consequently formulating the essential oil of *O. basilicum* with the modified kaolinite clay as support could be vital solution to enhance and upgrade the stability and remnant effect of bioinsecticides. Overall, this research is an involvement for investigation of ecologically harmless means of insect controlling mechanism by using naturally existing plant essential oils supported on modified kaolinite. Thus, the application of plant derived insecticide adsorbed on clay resources could be considered as an alternative choice of synthetic insecticide and could become very crucial elements of integrated pest management strategies as they are easily accessible, ecologically benign and easy to handle.

Data availability

The necessary data are incorporated in the research thesis manuscript. The corresponding author is ready to clarify the data and provides all the required data set as per the request.

CRediT authorship contribution statement

Kendalem Woretaw Worku: Writing – original draft, Methodology. **Abi M. Taddesse:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Solomon Abera:** Investigation, Formal analysis, Data curation. **Muthusaravanan Sivasubramanian:** Writing – original draft, Supervision, Formal analysis, Data curation. **Neelaiah Babu G.:** Writing – review & editing, Supervision, Project administration, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors duly acknowledge the research grant received from Ministry of Education *via* Haramaya University (HURG-2016-03-02 and HURG-2020–03-02–75). The authors would also like to thank Addis Ababa University, Geological Survey of Ethiopia and Instituto de Catálisis y Petroleoquímica (CSIC), Madrid, Spain for characterizing the samples and Hawassa Ceramic Factory for availing the kaoline samples.

References

[1] Karta Kaske Kalsa, Bhadriraju Subramanyam, Girma Demissie, Admasu Fanta Worku, Nigus Gabbiye Habtu, Major insect pests and their associated losses in quantity and quality of farm-stored wheat seed, Ethiop. J. Agric. Sci. 29 (2) (2019) 71–82.
[2] Waktole Sori, Amsalu Ayana, Storage pests of maize and their status in Jimma Zone, Ethiopia, Afr. J. Agric. Res. 7 (28) (2012) 4056–4060.
[3] M.N. Naqqash, A. Gökçe, A. Bakhsh, M. Salim, Insecticide resistance and its molecular basis in urban insect pests, Parasitol. Res. (2016) 4898–4909.
[4] J.O. Ogendo, S.R. Belma, A.L. Deng, D.J. Walker, Comparison of toxic and repellent effects of *Lantana camara* L. with *Tephrosia vogelii* Hook and a synthetic pesticide against *Sitophilus zeamais* Motschulsky (Coleoptera: Curculionidae) in stored maize grain, Insect Sci. Appl. 23 (2003) 127–135.
[5] S.J. Lee, K. Umano, T. Shibamoto, K.G. Lee, Identification of volatile components in basil (*O. basilicum* L.) and thyme leave (*Thymus vulgaris* L.) and their antioxidant properties, Food Chem. 91 (2005) 131–137.
[6] Aris Giannakasa, Ioannis Tsagkaliasb, Dimitris S. Achiliasb, Athanasios Ladavos, A novel method for the preparation of inorganic and organo-modified montmorillonite essential oil hybrids, Appl. Clay Sci. 146 (2017) 362–370.
[7] M.M.G. Nguemtchouin, M.B. Ngassoum, P. Chalier, R. Kamga, T.L.S. Ngamo, M. Cretin, *Ocimum gratissimum* essential oil and modified montmorillonite clay, a means of controlling insect pests in stored products, J. Stored Prod. Res. 52 (2013) 57–62.
[8] K. Majeed, M. Jawaid, A. Hassan, A. Abu Bakar, H.P.S. Abdul Khalil, A.A. Salema, I. Inuwa, Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites, Mater. Des. 46 (2013) 391–410.
[9] J.A. Noudem, M.G. Nguemtchouin Mbouga, K.G. Kaptso, M. Khalfaoui, G.B. Noumi, Saponins-Clay Modified Materials: A New Approach against *Callosobruchus*, 2017.
[10] Jean Antoine Noudem, Marie Goletti Nguemtchouin Mbouga, Martin Benoit Ngassoum, Tsague, Roli Karole Tsatsop, Insecticidal activities of essential oil of *ocimun gratissimun* in composite of modified saponins-clay montmorillonite and mango seed starch bioplastic, Available at: SSRN: https://ssrn.com/abstract=3949, 2021.
[11] Kamal Essifi, Abdourahim Hammani, Doha Berraaouan, El Bachiri Ali, Marie-Laure Fauconnier, Abdesselam Tahani, Montmorillonite nanoclay based formulation for controlled and selective release of volatile essential oil compounds, Mater. Chem. Phys. 277 (3) (2022) 125569.
[12] Kifle Gebreegziabiher, Mulatu wakgari, Muluken Goftishu, Evaluation of some botanicals oils for the management of Maize weevil, *Sitophilus zeamais* Motsch. (Coleoptera: Curculionidae), Int. J. Life Sci. 5 (1) (2017) 10–20.
[13] Tefera Tadele, M. Stephen, T. Regina, L. Paddy, Mass Rearing of Stem Borers, Maize Weevil, and Larger Seed Borer Insect Pests of Maize, CIMMYT, Nairobi, Kenya, 2010.
[14] M.M.G. Nguemtchouin, M.B. Ngassoum, T.L.S. Ngamo, P.M. Mapongmetsem, J. Siliechi, F. Malaisse, G.C. Lognay, E. Haubruge, T. Hance, Adsorption of essential oil components of Xylopia aethiopica (Annonaceae) by kaolin from Wak, Adamawa province (Cameroon), Appl. Clay Sci. 44 (2009) 1–6.
[15] M.M.G. Nguemtchouin, M.B. Ngassoum, T.L.S. Ngamo, X. Gaudu, M. Cretin, Insecticidal formulation based on *Xylopia aethiopica* essential oil and kaolinite clay for maize protection, Crop Protect. 29 (2010) 985–991.

[16] C.E. Chigbundu, I.O. Omonoh, Adsorption of Acetaminophen from aqueous solutions onto hexadecyltrimethylammonium modified kaolinite, Nat. Sci. 12 (11) (2014) 147–154.
[17] Gemechu Fekadu, S. Waktole, R. Santiago, Evaluation of plant powders and cooking oils against maize weevil, Sitophilus zeamais M. (Coleopteran: Curculionidae) under laboratory conditions, J.World Acad. Sci. Eng. Technol. Mol. Entomol. 3 (2) (2012) 4–14.
[18] W.W. Abbott, A method of computing the effectiveness of an insecticide, J. Econ. Entomol. 18 (1925) 265–267.
[19] M. Mehani, L. Segni, Antimicrobial effect of essential oil of plant Schinus molle on Some Bacteria Pathogens, World Acad. Sci. Eng. Technol. 24 (2013).
[20] M. Garcia-Valles, T. Pi, P. Alfonso, C. Canet, S. Martinez, A. Jimenez-Franco, M. Tarrago, B. Hernández-Cruz, Kaolin from Acoculco (Puebla, Mexico) as raw material: mineralogical and thermal characterization, Clay Miner. 50 (2015) 405–416.
[21] E. Barrachina, I. Calvet, D. Fraga, J.B. Carda, Ceramic porcelain stoneware production with Spanish clays purified by means of the removal of iron compounds and organic matter using physical methods, Appl. Clay Sci. 143 (2017) 258–264.
[22] Maite Garcia-Valles, Pura Alfonso, Salvador Martínez, Núria Roca, Mineralogical and thermal characterization of kaolinitic clays from terra alta (catalonia, Spain), Minerals 10 (2020) 142, https://doi.org/10.3390/min10020142.
[23] N. Worasith, B.A. Goodman, J. Neamp, N. Jeyachoke, P. Thiravetyan, Characterization of modified kaolin from the Ranong deposit Thailand by XRD, XRF, SEM, FTIR and EPR techniques, Clay Miner. 46 (2011) 539–559.
[24] A.A. Salwa, A.T. Mohamed, M.A. Elham, I.Q. Mostafa, Characterization and application of kaolinite clay as solid phase extractor for removal of copper ions from environmental water samples, Int. J. Adv. Res. 3 (3) (2015) 1–21.
[25] J.O. Ogbemudia, E.O. Felix, E.O. David, N.O. Uzoma, Organomodified kaolin as filler for natural rubber, Chem. Ind. Chem. Eng. Q. 21 (4) (2015) 477–484.
[26] J. Fafard, O. Lyubimova, S.R. Stoyanov, G.K. Dedzo, Gusarov, S.A. Kovalenko, C. Detellier, Adsorption of indole on kaolinite in nonaqueous media: organoclay preparation and characterization, and 3D-RISM-KH molecular theory of solvation investigation, J. Phys. Chem. 117 (36) (2013) 18556–18566.
[27] Y. Park, G.A. Ayoko, J. Kristof, E. Horvath, R.L. Frost, Thermal stability of organoclays with mono- and dialkyl cationic surfactants, J. Therm. Anal. Calorim. 110 (2012) 1087–1093.
[28] S. Mustapha, M.M. Ndamitso, A.S. Abdulkareem, J.O. Tijani, A.K. Mohammed, D.T. Shuaib, Potential of using kaolin as a natural adsorbent for the removal of pollutants from tannery wastewater, Heliyon 5 (2019) e02923, https://doi.org/10.1016/j.heliyon.
[29] E. Galan, P. Aparicio, A. Miras, K. Michailidis, A. Tsirambides, Technical properties of compounded kaolin sample from Griva (Macedonia, Greece), Appl. Clay Sci. 10 (1996) 477–490.
[30] S. Sunardi, A. Yateman, Modified kaolin with cationic surfactant for gibberellic acid carrier materials, Indones. J. Chem. 11 (1) (2011) 96–102.
[31] Y.M. Liew, H. Kamarudin, A.M. Mustafa Al Bakri, M. Luqman, I. KhairulNizar, C.M. Ruzaidi, C.Y. Heah, Processing and characterization of calcined kaolin cement powder, Construct. Build. Mater. 30 (2012) 794–802.
[32] R.R. Tiwari, K.C. Khilar, U. Natarajan, Synthesis and characterization of novel organo-montmorillonites, Appl. Clay Sci. 38 (2008) 203–208.
[33] O.E. Theresa, O. Grace, E.O. Felix, T. Funda, Effect of exchanged surfactant cation on the structure of kaolinitic clay, J. Mater. Sci. Appl. 1 (2015) 54–61.
[34] A. Mbaye, C.A.K. Diop, Miehe Brendle, Jocelyne, Senocq, François, Francis Maury, Characterization of natural and chemically modified kaolinite from Mako to remove lead from aqueous solutions, Clay Miner. 49 (4) (2014) 527–539.
[35] G.B. Swella, D.M.K. Mushobozy, Evaluation of the efficacy of protectants against cowpea bruchid *Callosobruchus maculatus* (F.) on cowpea seeds (*Vigna unguiculata* (L.) Walp.), Plant Protect. Sci. 43 (2007) 68–72.
[36] B.R. Raghvani, M.N. Kapadia, Efficacy of different vegetable oils as seed protectants against Callosobruchus maculatus (Fab.), Indian J. Plant Protect. 31 (2003) 115–118.
[37] O. Calmasur, S. Kordali, O. Kaya, I. Aslan, Toxicity of essential oils of vapours obtained from *Achillea* species to *Sitophilus granaries* (L.) and *Tribolium confusum (Jacquelin du Val)*, J. Plant Dis. Prot. 113 (2006) 37–41.
[38] V. Rozmana, I. Kalinovica, Z. Korunic, Toxicity of naturally occurring compounds of Lamiaceae and Lauraceae to three stored-product insects, J. Stored Prod. Res. 43 (2007) 349–355.