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# Synthesis and Evaluation Nanoinsecticidal Activity of Silicadioxide Nanoparticles Combined with *Euphorbia peplus* and *Euphorbia helioscopia* Extracts to Control *Tribolium confusum*

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**Abstract:** To develop a new type of insecticide that differs from conventional insecticides, the present study included the synthesis of nanoinsecticide by adding silica dioxide nanoparticles ($SiO_2$ NPs) to the aqueous extracts of plants *Euphorbia helioscopia* and *Euphorbia peplus* and assessing their toxicity against larvae and adults of the flour beetle *Tribolium confusum*. By the surface treatment method and depending on the $LC_{50}$ after 24, 48 and 72 h of treatment, HERO (40% WDG) was used in dilutions (0.09, 0.07, 0.05, 0.03, 0.01 μg/ml) as a standard for comparison, the control group was treated with distilled water only .The $LC_{50}$ values varied with the difference of the type of insecticide, the extract, the developmental stage, and the exposure period. The results showed that both the nanoinsecticides and the alcoholic extracts of the two plants had a toxic effect against both larvae and adults, especially after 72 h. The $LC_{50}$ values of the nanoinsecticide prepared from *E. peplus* plant was better than the $LC_{50}$ values of the nanoinsecticide prepared from the plant *E. helioscopia*. In general, the third instar larvae were the most sensitive and showed the fastest response to toxicity than the fifth instar larvae and adults after 24, 48 and 72 h of treatment. From the comparison of the $LC_{50}$ values of the alcoholic extracts of the two plants, it was found that the alcoholic extract of *E. helioscopia* was more toxic to insects by about 2.4, 4.3 and 6.6 times after 24, 48 and 72 h, respectively. When comparing the $LC_{50}$ values of the plant nanoinsecticide *E. peplus* with the $LC_{50}$ values of the alcoholic extract of *E. helioscopia*, especially after 72 h of treatment, *E. peplus* was the best and the most toxic by about 3.4 times after 72 h. In addition, some clear morphological and behavioral effects were observed on worker insects, which may be attributed to the fact that the two plants contain many alkaloids and phenolic compounds that are effective against larvae and adults of the flour beetle.

**Keywords:** Nanoinsecticide, *Euphorbia helioscopia*, *Euphorbia peplus*, *Tribolium confusum*, Nanoparticles, Flour beetle, $LC_{50}$

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## Introduction

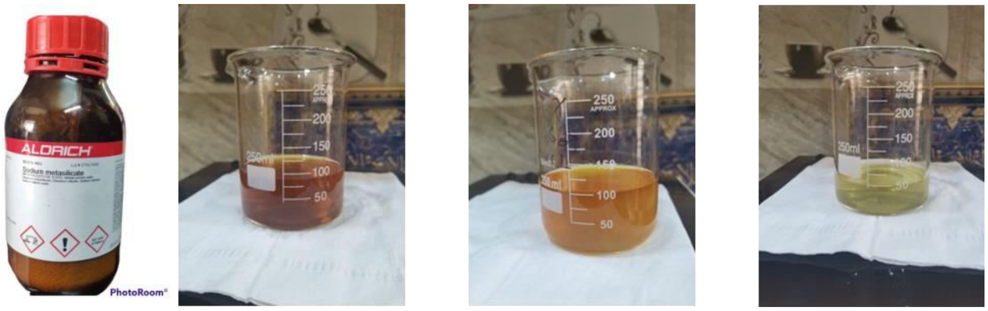
Investing and properly exploiting plants is one of the easiest ways to protect the environment. The concept of "green projects" is the first step taken by many to develop modern methods in the manufacture of green bio-insecticides and in the control of insect pests to reduce the indiscriminate use of chemical insecticides and search for other alternatives that are less dangerous to human health and environmental friendly (El-Helaly *et al*., 2016; Chen *et al*., 2022). These alternatives should eliminate insects and pests that kill agricultural crops and stored materials in a selective manner that does not harm the non-target beneficial living organisms that exist side by side with harmful ones (Samia *et al*., 2020). Nanotechnology has become one of the fastest spreading technologies at the global level and has been called the next technical revolution in various industrial, medical and agricultural fields because of its great advantages that can be applied in various fields and can provide solutions for the control of agricultural and economic insect pests. Nanotechnology occupies a prominent place among the innovative ways to develop agricultural transactions and food production. The wide variety of methods for preparing nanoparticles in material sciences, energy, medicine and life sciences research gave a clear facilitation to expand the areas of using nanotechnology and its applications in agricultural chemical production techniques. The use of plant aqueous extracts to prepare nanoparticles is safest and important method. A number of plant extracts have been used in the preparation of silver nanoparticles, which may be environmentally friendly. The size of the nanoparticles can be modified by using different amounts of the extract because silver nanoparticles are one of the most recently used nanomaterials in the fields of plant growth and disease resistance. A mixture of nanocomposites are used to combat store pests, the most famous of which are the red flour beetles *Tribolim ccstcineum*, hairy grain beetle and other types of insects (Park *et al*., 2007; Yang *et al*., 2009; Ahmed *et al*., 2021), Many researchers have indicated the possibility of benefiting from nanotechnology in improving the characteristics and properties of many biological control agents such as plant extracts, fungal and bacterial preparations, and their insecticidal by-products, as well as preparations used in the control of various plant pathogens, inhibitors and antibiotics, which are among the promising biological control agents. The present study was aimed to evaluate the toxicity of alcoholic extracts of plants *E. peplus* and *E. helioscopia* and preparation of nanoinsecticides by adding silica dioxide nanoparticles ($SiO_2$ NPs) to extracts of these two plants and assessing their toxicity against larvae and adults of flour beetles *Tribolium confusum*

## Materials and Methods

### *Preparation of Nanoinsecticides*:

The plants *E. peplus* and *E. helioscopia* were collected and washed thoroughly with water. The vegetative part of the two plants was cut into small parts and placed in a 250 ml beaker and mixed with 100 ml of distilled water. The beaker was tightly closed with aluminum foil and placed on a magnetic stirrer at 60 °C, and then placed in the oven for 18 h at 100 °C. Then the solution was filtered more than once using filter papers. After re-filtering, sodium silicate [1 M Sodium metasilicate (Aldrich)] was mixed with the plant extract. The color was changed from yellow to coffee color (Fig. 1) and formed a precipitate at the bottom which was left for an hour at 80 °C with stirring, then the beaker containing the material was placed with ice until the solution is homogeneous. Then it was placed in the oven for 18 h at 100 °C, after which the samples were sent to conduct the tests.

UV-Vis analysis was performed to determine the absorption band of the two plants extracts. Morphology and average particle size analysis of silica dioxide ($SiO_2$) NPs was done by using field-emitting scanning electron microscopy (FE-SEM) using plant extracts by hydrolysis method. X-ray patterns; XRD patterns of $SiO_2$; preparation of NPs




D C B A

Fig. 1: A, B, C showing the color change of plant extract and (D) the nanomaterial used.

using extracts of *Euphorbia helioscopia* and *E. peplus* by hydrothermal method were also performed.

*Hero ® commercial insecticide*:

It belongs to the group of new nicotine analogs, Neonicotinoides, and it is in the form of wettable granules, the active substance percentage is 40%, and it is produced by Synginta with Molecular formula $C_9H_{10}C_lN_5O_2$.

*Insects*:

In the present study, adults and larvae of flour beetle *Tribolium confusum* (Duval) were collected from colonies in the research laboratory of the Biology Department of Education for Girls College at the University of Mosul. Insects were reared in media consisting of sterilized wheat flour by freezing for two weeks to ensure that it is free of insect larvae and eggs, in addition to dry yeast at a ratio of 200:1 (yeast: flour). Equal amounts (200 g) of the culture medium (food) were placed in each vial 600-capacity glass. 100 adult insects were placed in each bottle and kept after covering the mouths of the bottles with sterile gauze and fixing them with rubber bands in the incubator at a temperature of 30-35˚C and a relative humidity of 60-70%, taking into account the exchange of the breeding media every 30 days (Saleem *et al.*, 2013). First, the whole insects were isolated from the larvae by means of a sieve with openings of diameters of 800 micrometers that allowed the passage of the breeding medium and the larvae only. Then the adults were collected in the sieve then transferred on a filter paper and determined the larval age depending on the length of the body and the width of the head capsule (Brindley, 1930). The rest of the larvae were returned with the culture medium at the same aforementioned condition until needed. In glass bottles under the aforementioned rearing conditions, they were checked daily and the newly-emerging adults (several hours - 24 h after emergence) which were characterized by their creamy white color were collected using a sieve with openings (diameter 800 micrometers). These adults were kept with a quantity of culture medium in the nursery until they reached 7 days old.

*Preparation of Test Solutions*:

Stock solutions of the insecticide were prepared by placing the required weight in a graduated cylinder of 10 ml, and completing the volume with distilled water to 10 ml (of which five concentrations were prepared as 0.1, 0.3, 0.5, 0.7, 0.9 µg/ml), by adding (9 ml of distilled water to 1 ml of the concentration of the basic solution). In the same way, the required concentrations (µl/ml) of nanoinsecticides and alcoholic extracts of plants were prepared using appropriate solvents for each of them. The solutions were kept in 30 ml glass bottles with tightly closed lids in the refrigerator at 4 °C until use.

Vital tests included toxicity tests for larvae and adults of flour beetles which included the following:

(i) Estimation of the toxicity of the commercial insecticide Hero.

(ii) Estimation of the toxicity of alcoholic extracts of two plants

(iii) Estimation of the toxicity of nanoinsecticides.

The biological tests were carried out by topical application.

An initial experiment showed that the appropriate amount of solvent to carry the tested materials (µl or µg) for each insect (larva or adult) was 10 ml, so the insects were treated with the addition of 10 ml of each test solution applied to the upper surface (dorsal side) of the insect's thorax using a 10 µl microsyringe. Insects of the control group were treated with distilled water or ethanolic solvent depending on the solvent used in dissolving the tested material and after 15 min examined to ensure the safety of the insects. The treated insects were placed in petri dishes and the dishes were placed in the nursery, and the percentage of deaths was recorded after 24 h, 48 h, and 72 h. In all tests, adults of 7 days of age and larvae of the third and fifth ages were treated with three replicates for each concentration of 10 homogenous insects (larvae or adults) for each replicate.

*Statistical Analysis*:

In cases where the homicide rates in the control group exceeded 10%, the homicide percentages in the transactions were corrected by applying Abbott's equation (Abbot, 1925). Determine the LC value for half of the 50% number of insects tested. The values of concentrations, lethal doses for 50% of 50 tested insects, slope, and upper and lower confidence limits were determined using MSDOS system based on probability program, Probit. Exe, Propit program for the statistical analysis of the results of toxicity tests according to the method (Finney, 1952).

## Results and Discussion

*Field Emitting Scanning Electron Microscopy (FE-SEM) of $SiO_2$ Nanoparticles Using E. helioscopia*:

The morphology and average particle size of silica dioxide ($SiO_2$) NPs were analyzed using FE-SEM images using *E. helioscopia* extract by a chemical method (hydrolysis) at 100°C. Figure 2 shows a microscopic image of prominent nanoparticle structure observed with average grain sizes ranging from 22 to 40 nm. The results show that the nanoparticles are in spherical shape. FE-SEM analysis reveals the shapes (Figs. A, B, C, D) for the samples. The samples have a spherical shape with minimal aggregation (22 nm) (Dias and Alves, 2022).

*Field-Emitting Scanning Electron Microscopy (FE-SEM) of $SiO_2$ Nanoparticles Using E. peplus*:

Morphology and average particle size of silica dioxide nanocomposite images are presented using FE-SEM images using a plant (*E. peplus*) by a chemical hydrolysis method at 100 °C. Figure 3 A-C shows that the nanoparticles are in panels like-structure. It has been shown that individual flakes of the oxide gap can be seen. Silica oxide flakes have a reasonably large surface area and three-dimensional silica oxide are clearly defined and interconnected. These plates unite to form a porous network that resembles a loose sponge in appearance and has a size range of 15 to 71 nm (Fig. 3).

*Optical Characterization:*

*UV-Vis properties of SiO2 NPs by hydrothermal method using plant extracts E. helioscopia and E. peplus*:

UV-Vis spectrophotometer can explain the special features in the spectrum in the absorption region. UV-Vis analysis was performed to determine the absorption band in *E. peplus* and *E. helioscopia* extracts. Figures 4 and 5 show the optical absorption spectra of $SiO_2$ NPs using an extract at 100 °C that was deposited on a glass substrate. It is clear that all films show variation in absorption due to the difference in material thickness, with increasing thickness increasing absorption. All films show an increase in absorbance at

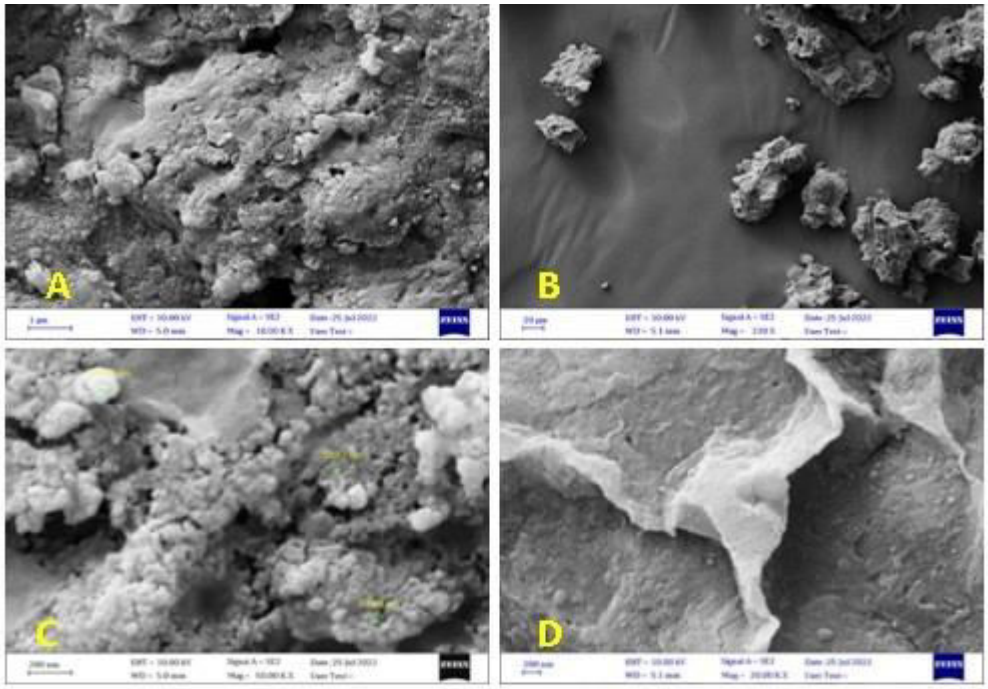



Fig. 2: Scanning electron microscopy images of ($SiO_2$ NPs) prepared using an extract of *E. helioscopia* plant**.**

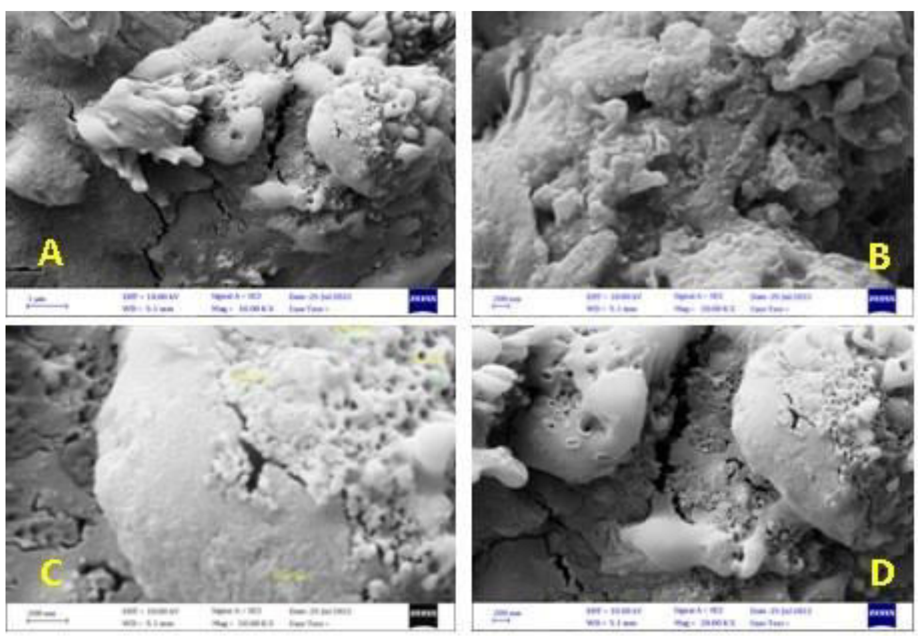



Fig. 3: Scanning electron microscope images of (SiO2 NPs) prepared using (E. peplus) plant extract.. shows scanning tunneling electron microscope images of silica dioxide nanoparticles ($SiO_2$ NPs) (A,B, C) the color change of the two plants *E. helioscopia* and *E. peplus* and (D) the nanomaterial used.

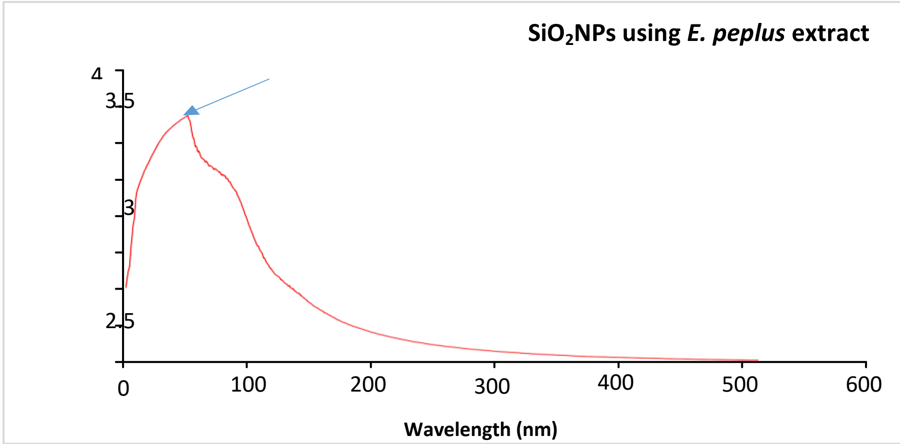



Fig. 4: UV-Vis absorbance spectrum of $SiO_2$ NPs as-prepared by a hydrothermal method using *E. peplus* extract at 100 °C.

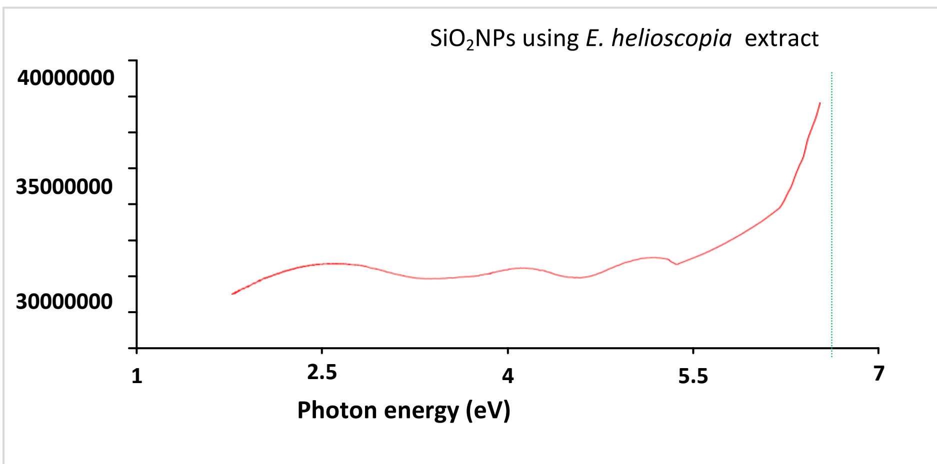



Fig. 5: UV-Vis absorbance spectrum of $SiO_2$ NPs as-prepared by a hydrothermal method using *E. helioscopia* extract at 180 °C.

wavelength below 242 nm due to the strong absorbance of the films in this region, which is consistent with the optical properties of ($SiO_2$) metal in the UV-Vis range (Nandanwar *et al*., 2015). Figures 4 and 5 show the optical absorption spectra of $SiO_2$NPs as prepared by hydrothermal autoclave method using extracts of *E. peplus* and *E. helioscopia*. These figures show a high absorption rate (242, 240, and 271 nm), indicating the strong absorption of $SiO_2$ in this region and the spectral range 200-900 nm (Verma and Bhattacharya, 2018; Mutesher and Kadhim, 2021). The energy bandgap of $SiO_2$NPs prepared using extracts of *E. peplus* and *E. helioscopia* by hydrothermal method at 100 °C for 18 h in an oven was estimated by plotting the square ($ahu^2$) versus the photon energy (hu). A straight line extrapolation to $ahu^2$ gives the value of the energy gap. The energy band gap values (eg) depend on the crystal structure of the film and the arrangement and distribution of atoms in the crystal lattice. The band gap was different when different temperature was used. The optical band gap is increased for SiO2 NPs which differ in *E. peplus* and *E. helioscopia* due to their nano-size composition (Maroušek *et al*., 2022). The optical band gap values of $SiO_2$ NPs range as 502, 302, and 208 eV depending on the working temperature used as shown in Figures 4 and 5, and this result is consistent with (Ghosh *et al.*, 2022).

*Structure properties*:

*XRD patterns of $SiO_2$ NPs preparation using Euphorbia peplus and E. helioscopia extracts by hydrothermal method*:

The x-ray diffraction (XRD) carried out to investigate the crystal structure type and the crystalline size of prepared $SiO_2$NPs using different plant (*E. peplus* and *E helioscopia*) extracts by hydrothermal method at 140 °C for 18 h. Figures 6 and 7 demonstrated the formation of pure cubic $SiO_2$NPs crystal structure with space group (Fm-3m), crystal dimensions (a = b = c = 9.4 A°) and crystal angles (α = β = γ = 90°), corresponding with the cubic structure (JCPDS 14-0054). The XRD results revealed that the cubic phase of $SiO_2$ NPs formed at calcination temperature 300°C for 3 h, and then the peaks became more sharp and intense, this is a common behavior for all synthesized samples by hydrothermal method. The XRD patterns referred that the crystalline growth of $SiO_2$NPs was in the same cubic crystal structure at the different plant extracts (*E. peplus* and *E. helioscopia*).

The following Scherrer's equation was used to compute the crystalline size (D):

$$D\ (nm) = K\lambda / \beta Cos\theta,$$

Where k stands for form factor (0.98), λ denotes the wavelength (1.54), β denotes the full width at half maximum.

The dislocation density is calculated by the equation:

$$\delta = 1/D2\ (Line2/m2)\ x\ 1015$$

Where δ is the dislocation density, and the micro strain of the film were estimated using the equation:

$$\varepsilon = \beta \cos \theta / 4$$

Tables 1 and 2 show results of the crystalline size, dislocation density, and microstrain of $SiO_2$NPs prepared using the *E. peplus* and *E. helioscopia* by hydrothermal method at 140 °C for 18 h.

The XRD results revealed that the cubic phase of $SiO_2$ formed at different plant (*E. peplus* and *E. helioscopia*) extracts by hydrothermal method at 140 °C for 18 h and then the peaks became more sharp and intense with increasing the *E. peplus* at 14**0** °C for 18 h. This is a common behavior for all synthesized samples by hydrothermal method with the calcination temperature at 300 °C for 3 h. The XRD patterns referred that the crystalline growth of $SiO_2$ NPs was in the same cubic crystal structure at the different plant extracts.

*Effect of Nanoinsecticides and alcoholic extracts of the study plants against fifth larval instar of flour beetle*:

Tables 3-7 indicate that the alcoholic extracts and the nanoinsecticides prepared from addition silicadioxide nanoparticles ($SiO_2$ NPs) to the extracts of two plants *E. pelplus and E. helioscopia* have a toxic effect against the adults and fifth larval instar of the flour beetle, and the toxicity increased with increasing the exposure period. $LC_{50}$ values show that the toxicity percentage with *E. pelplus* was higher about 1.0, 1.5 and 1.8 times after 24, 48 and 72 h of exposure than the toxicity percentage with *E. helioscopia*. But, we note that the nanoinsecticide of *E. pelplus* was more toxic to the fifth larval instar than *E. helioscopia* about 1.8 times, especially after 72 h of treatment. Alcoholic extract of *E. helioscopia* had a more toxic effect than the alcoholic extract of *E. pelplus* about 1.4, 1.7 and 1.5 times after 24, 48 and 72 h, respectively.

$LC_{50}$ values are shown in the Tables 4-7. After comparing the $LC_{50}$ values of the nanoinsecticide of *E. pelplus* with the values of the $LC_{50}$ of the nanoinsecticide of *E. helioscopia*, it was found that the toxicity percentage was higher for *E. pelplus* by 1.9, 5.3 and 2.5 times, respectively during 24, 48

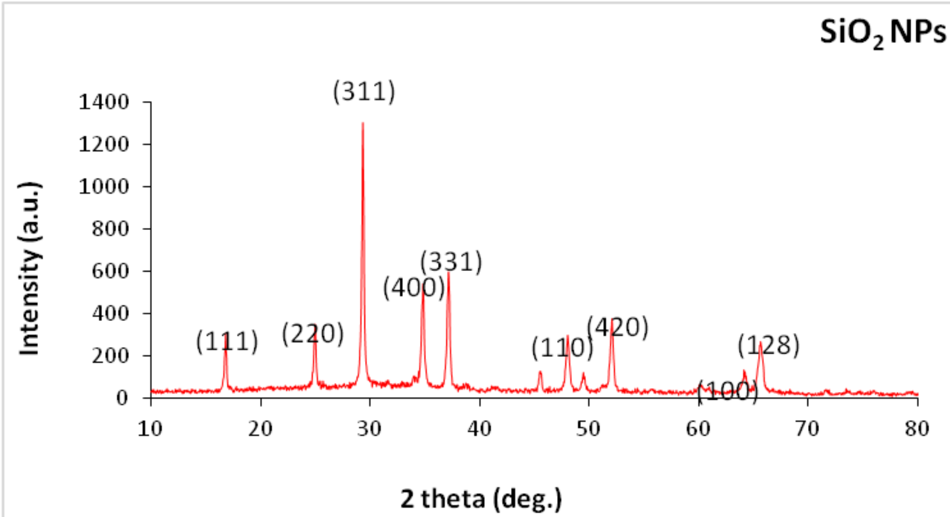



Fig. 6: XRD patterns $SiO_2$ NPs at 140 °C for 18 prepared using the *E. peplus* extract by hydrothermal method.

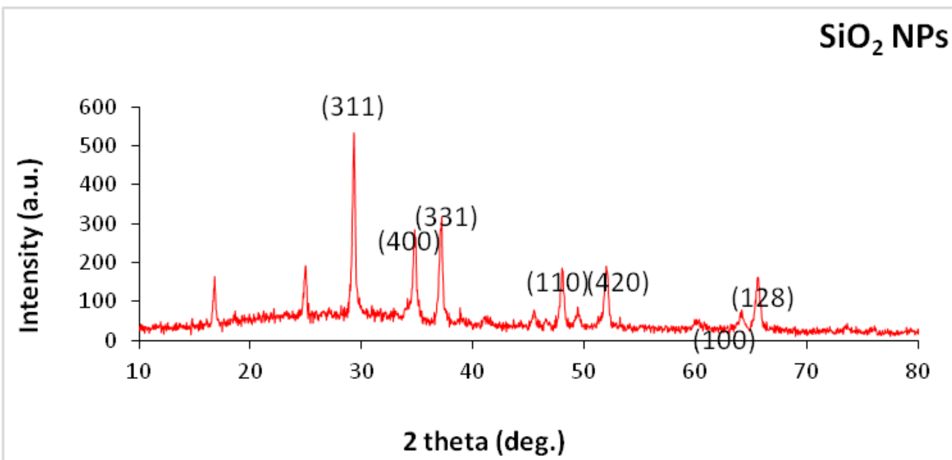



Fig. 7: XRD patterns $SiO_2$NPs at 140 °C for 18 prepared using the *E. helioscopia* extract by hydrothermal method.

Table 1: XRD measurements of $SiO_2$NPs using extract by hydrothermal method

| Material | 2ϴ (deg) Practical | 2ϴ (deg) Standard | FWHM (deg) | Crystalline size (nm) | Dislocation density δ(line²/m²) x10¹⁵ | Micro strain ξx10⁻³ | (hkl) |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 17.04 | 17.01 | 0.23 | 34.73602 | 8.287814 | 9.975237 | (111) |
| | 25.16 | 25.17 | 0.22 | 36.80268 | 7.383139 | 9.415074 | (220) |
| | 29.60 | 29.71 | 0.21 | 38.92475 | 6.600066 | 8.901791 | (311) |
| | 34.96 | 34.97 | 0.88 | 9.416841 | 112.7689 | 36.79578 | (400) |
| | 37.32 | 37.33 | 0.28 | 29.79749 | 11.26265 | 11.6285 | (331) |
| | 48.32 | 48.90 | 0.31 | 27.95862 | 12.79289 | 12.39332 | (110) |
| | 51.92 | 51.99 | 0.30 | 29.32294 | 11.63014 | 11.81669 | (420) |
| | 64.44 | 64.91 | 0.29 | 32.26022 | 9.608715 | 10.74078 | (100) |
| | 66.08 | 66.21 | 0.40 | 23.60651 | 17.94471 | 14.67816 | (128) |

Table 2: XRD measurements of $SiO_2$NPs using extract by hydrothermal method

| Material | 2Θ (deg) Practical | 2Θ (deg) Standard | FWHM (deg) | Crystalline size (nm) | Dislocation density δ(line²/m²) x10¹⁵ | Micro strain ξx10⁻³ | (hkl) |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 17.04 | 17.01 | 0.27 | 29.58994 | 11.4212 | 11.71006 | (111) |
| | 25.16 | 25.17 | 0.28 | 28.91639 | 11.95946 | 11.98282 | (220) |
| | 29.60 | 29.71 | 0.29 | 28.18689 | 12.58652 | 12.29295 | (311) |
| | 34.96 | 34.97 | 0.50 | 16.57364 | 36.40526 | 20.90669 | (400) |
| | 37.32 | 37.33 | 0.33 | 25.28272 | 15.64417 | 13.70501 | (331) |
| | 48.32 | 48.90 | 0.34 | 25.49168 | 15.38874 | 13.59267 | (110) |
| | 51.92 | 51.99 | 0.40 | 21.99221 | 20.67581 | 15.75558 | (420) |
| | 64.44 | 64.91 | 0.29 | 32.26022 | 9.608715 | 10.74078 | (100) |
| | 66.08 | 66.21 | 0.38 | 24.84896 | 16.1951 | 13.94425 | (128) |

and 72 h of treatment. When comparing the $LC_{50}$ values of the alcoholic extract of *E. peplus* plant with the $LC_{50}$ values of the alcoholic extract of *E. helioscopia* plant, the highest toxicity was observed for *E. helioscopia* plant with 1.1, 4.3 and 5.1 after 24, 48 and 72 h, respectively. Thus, the $LC_{50}$ values of the plant nanoinsecticide *E. pelplus* were compared with the $LC_{50}$ values of the alcoholic extract of the plant *E. helioscopia*, especially after 72 h of treatment, as they were somewhat similar in terms of toxicity, with 0.44 for the nanoinsecticide and 0.467 µl/ml of the alcoholic extract**.**. These results are in agreement with Abbas (2013) that the larvae of the fourth age of the flour beetle, the red rusty flour beetle, and the long-headed flour beetle are more sensitive to the insecticides Actaer and Lannate than their adults, and this is probably due to the activity of oxidation enzymes mixed with the function of metabolizing insecticides. In larval ages it is less than in adults, which makes it less susceptible to detoxification reactions, or this may also be attributed to size, due to the existence of a relationship between toxicity and size, and this conclusion is confirmed by many studies on larvae and adults. Martin *et al*. (2000) found that smaller first-instar larvae of *Helicoverpa armigera* were more sensitive to cypermethrin than larger, subsequent successive instars. It was also found that the smaller third-instar larvae of the red flour beetle are more sensitive to the insecticides Coopex, Decis, and Vapcocidin than the larger fifth- and seventh-instar larvae (Al-Attar and Abbas, 2003).

*Effect of nanoinsecticides and alcoholic extracts of the plants against flour beetle adults*:

The results showed that when comparing the $LC_{50}$ values of the nanoinsecticide of *E. pelplus* with the values of the $LC_{50}$ of the nanoinsecticide of *E. helioscopia*, the toxicity percentage was higher for the *E. peplus* plant in the adult insect, as previously mentioned in Table **4** for the Fifth larval instar, but with different proportions, as it came in different proportions for each period of 24, 48, and 72 h of treatment with 1.2, 1.0, and 1.6, respectively. The mortality of flour beetle reached the lowest percentage after 48 h, while the highest percentage of mortality was recorded in the first 24 h as dead, but it looked like this, as it was subjected to temporary paralysis due to the presence of alkaloids of an anesthetic nature to the insect. We obtained a high toxic effect after 72 h. Thus, a comparison of the $LC_{50}$ values of the alcoholic extract of *E. pelplus* was made with the $LC_{50}$ values of the alcoholic extract of *E. helioscopia*, where the toxicity was also higher for *E. helioscopia* by 2.4, 4.3 and 6.6 times after 24, 48 and 72 h, respectively. When comparing the $LC_{50}$ values of the *E. peplus* plant nanoinsecticide with the $LC_{50}$ values of the alcoholic extract of the plant *E. helioscopia,* especially after 72 h, it was 3.4 µl/ml **.** The results of the $LC_{50}$ nanoinsecticides of

Table 3: Effect of Hero against larvae and adults of the baffled flour beetle *T. confusum* after 24, 48 and 72 h of treatment

| Time | Fifth larval instar | | | | Adult stage | | | |
|---|---|---|---|---|---|---|---|---|
| | $LC_{50}$ | 95% confidence limits | | Slope | $LC_{50}$ | 95% confidence limits | | Slope |
| | | Upper | Lower | | | Upper | Lower | |
| **24h** | **0.006** | **0.012** | **0.003** | **1.594** | **0.005** | **0.012** | **0.003** | **1.785** |
| **48 h** | **0.002** | **0.004** | **0.003** | **1.995** | **0.003** | **0.010** | **0.002** | **1.706** |
| **72 h** | **0.001** | **0.002** | **0.006** | **1.759** | **0.001** | **0.002** | **0.000** | **1.416** |

Table 4: Effect of Nanoinsecticides and alcoholic extracts of *E. peplus* against Fifth larval instar of *T. confusum* after 24, 48 and 72 h of treatment

| Time | Nanoinsecticides | | | | Alcoholic extracts | | | |
|---|---|---|---|---|---|---|---|---|
| | $LC_{50}$ | 95% confidence limits. | | Slope | $LC_{50}$ | 95% confidence limits | | Slope |
| | | Upper | Lower | | | Upper | Lower | |
| **24 h** | **0.083** | **0.055** | **0.102** | **2.581** | **0.290** | **0.147** | **0.572** | **1.807** |
| **48 h** | **0.045** | **0.026** | **0.079** | **1.637** | **0.264** | **0.128** | **0.562** | **1.747** |
| **72 h** | **0.044** | **0.025** | **0.078** | **1.609** | **0.239** | **0.112** | **0.530** | **1.370** |

Table 5: Effect of Nanoinsecticides and alcoholic extracts of *E. peplus* against Adult of *T. confusum* after 24, 48 and 72 h of treatment

| Time | Nanoinsecticides | | | | Alcoholic extracts | | | |
|---|---|---|---|---|---|---|---|---|
| | $LC_{50}$ | 95% confidence limits | | Slope | $LC_{50}$ | 95% confidence limits | | Slope |
| | | Upper | Lower | | | Upper | Lower | |
| **h24** | **0.207** | **0.104** | **0.503** | **3.049** | **0.348** | **0.171** | **0.089** | **2.170** |
| **48 h** | **0.307** | **0.107** | **0.800** | **1.765** | **0.481** | **0.203** | **0.113** | **1.528** |
| **72 h** | **0.275** | **0.145** | **0.501** | **2.058** | **0.481** | **0.190** | **0.121** | **1.528** |

Table 6: Effect of Nanoinsecticides and alcoholic extracts of *E. helioscopia* against Fifth larval instar of *T. confusum* after 24, 48 and 72 h of treatment

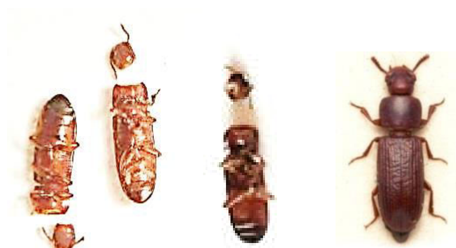
| Time | Nanoinsecticides | | | | Alcoholic extracts | | | |
|---|---|---|---|---|---|---|---|---|
| | $LC_{50}$ | 95% confidence limits | | Slope | $LC_{50}$ | 95% confidence limits | | Slope |
| | | Upper | Lower | | | Upper | Lower | |
| **h24** | **0.164** | **0.103** | **0.262** | **2.488** | **0.080** | **0.058** | **0.112** | **2.985** |
| **48 h** | **0.245** | **0.110** | **0.544** | **1.284** | **0.060** | **0.043** | **0.083** | **2.917** |
| **72 h** | **0.114** | **0.004** | **0.202** | **1.759** | **0.046** | **0.033** | **0.064** | **2.957** |

Table 7: Effect of Nanoinsecticides and alcoholic extracts of *E. helioscopia* against adults of *T. confusum* after 24, 48 and 72 h of treatment

| Time | Nanoinsecticides | | | | Alcoholic extracts | | | |
|---|---|---|---|---|---|---|---|---|
| | $LC_{50}$ | 95% confidence limits | | Slope | $LC_{50}$ | 95% confidence limits | | Slope |
| | | Upper | Lower | | | Upper | Lower | |
| **24 h** | **0.339** | **0.171** | **0.708** | **2.170** | **0.142** | **0.095** | **0.213** | **2.882** |
| **48 h** | **0.351** | **0.157** | **0.781** | **1.433** | **0.111** | **0.070** | **0.177** | **2.140** |
| **72 h** | **0.164** | **0.103** | **0.262** | **2.488** | **0.072** | **0.052** | **0.100** | **2.880** |

Control

Fig. 8: Phenotypic effects of the fifth instar larvae of the flour beetle after 72 h of treatment with a nanoinsecticide of *E. peplus*.



Control

Fig. 9: Phenotypic effects of flour beetle adults treated with *E. peplus* nanoinsectcide after a week in the laboratory.

*E. peplus* and *E. helioscopia*, where the nanoinsecticides of *E. peplus* were more toxic than the nanoinsecticides of *E. helioscopia* by about 1.6 times, especially after 72 h of treatment. The results of the current study for adults were consistent with the results of Soummane *et al*. (2011) that methanolic and dichloromethane extracts from the aerial parts of a number of medicinal plants are toxic to the larvae of the Mediterranean fruit fly *Ceratitis capitata* more than to its adults, and also agree with Saidana *et al*. (2007) that the petroleum ether, methanolic, and chloroform extracts of several types of plants were very effective against the larvae and adults of the flour beetle, but the larvae were more sensitive than the adults, and this variation in toxicity can be attributed to the behavior of the larva due to the fact that its body wall (cuticle layer) is less rigid than it is in the adult, which makes the larvae to absorb more insecticides, and this is consistent with what was previously confirmed by Cercilus and Knowles (1976) in the larvae of the leaf blight insect. The toxicity varied clearly with the sex, developmental stage, and method of treatment. The present study is in agreement with other studies in which the active substance acetamiprid, found in the insecticide Nestor was used against different insects (Zhang *et al*., 2022).

### *Phenotypic and behavioral effects of nanoinsecticides against flour beetle larvae and adults*:

The results showed behavioral and phenotypic effects on the insect through its surface treatment, and it was clearly noted on the larvae a blackening in the midgut region of the digestive canal (Fig. 8), especially in the fifth instar larvae, and this is attributed to the damage to the digestive canal due to the arrival of toxic substances from the extracts through the body wall. In addition to that, phenotypic effects appeared, which are cutting off the heads of adults after treating them with nanoinsecticides after 72 h of treatment (Fig. 9), especially at the highest concentrations of nanoinsecticides of *E. peplus*, where the experiment was repeated more than once and the same results appeared. In order to slow down the development of resistance in target pests among nanomaterials, silica particles have received great attention as an alternative to traditional insecticides. This was agreed upon by Abid and Kadhim (2020), and it is believed that the properties of silica insecticides are due to the direct effect, so that the insect's epidermis is eaten or absorbed through the skin layers. Silica may also have an indirect effect, and the insecticides are affected by pests that feed on treated plants or food. By blocking and stimulating the gut**.**

The results showed behavioral effects, as the insect loses control of its movement due to the occurrence of temporary paralysis that lasts within 48 h of treatment and dies after 72 h of treatment**.**

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