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Effectiveness and Persistence of Some Synthetic Insecticides and their Nanoformulation against Whitefly (*Bemisia tabaci)* and Aphids (*Aphis craccivora*) on Fennel Plants and Soil

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Abstract

Fennel *Foeniculum vulgare* Mill. is one of the most important herbal plants in Egypt due to its medicinal properties. Aphids and whiteflies are considered from the major pests which attack the crop, their control using synthetic pesticides caused many problems from which is the presence of pesticide residues at levels higher than Maximum residue limit (MRL) values. This study aims to compare synthetic and (non-conventional) nano form of the pesticides used for controlling these pests, to help in decreasing the persistence and resistance problems of pesticides. The LC_{50} values of acetamiprid, dinotefuran and their nano-form were recorded 5.085, 3.355, 0899, and 0.760 ppm against whitefly, while for aphids they were 3.566, 4.068, 0.590 and 0.705 ppm, respectively. Two field trials were conducted during 2018-2019 in a fennel farm in the Governorate of Fayoum, Egypt, to test the efficacy of four insecticides; thiamethoxam (Actara 25%WG), dinotefuran (Oshin 20%SG), acetamiprid (Mospilan 20%SP) and thiocyclam hydrogen oxalate (Evisect 75%WG) (thiocyclam hydrogen oxalate) against aphid adults and whitefly nymphs. Dinotefuran caused the highest percent reduction against whiteflies, while acetamiprid caused the highest reduction against aphids. A third season was lunched to measure the efficacy of dinotefuran, acetamiprid and their nano forms against whiteflies and aphids. Nano-mospilan was the most effective insecticide during the third season with 94.19% reduction against aphids, while nano-dinotefuran was the most effective compound against whiteflies with 99.13% reduction. Residues were determined in plant and soil using, a QuEChERS (quick, easy, cheap, effective, rugged, and safe) based protocol coupled with liquid chromatography-tandem mass spectrometry (LC–MS/MS) with a recovery percentage of 99.9 and 99.7%, for dinotefuran and acetamiprid. Comparing the initial amounts showed that acetamiprid and nano-acetamiprid were 0.95 and 0.27 mg/kg, in plant and 1.3 and 0.31 mg/kg in soil, respectively. Dinotefuran and nano-dinotefuran initial were 6.77, 0.69 mg/kg in plant and 3.9, 0.88 in soil, respectively. Tested insecticides dissipated differently and results showed that acetamiprid was not detected in 10 days, while its nano form in 5 days and dinotefuran in 15 days and for its Nano form 7 days in plant. However, in soil they were not detected 21 days for synthetic and 10 days for nano form of both pesticides.

Keywords: Fennel; aphid; whitefly; Nano-formulation; efficacy and dissipation.

1. Introduction

Medicinal and aromatic plants were considered very important crops through direct and indirect uses in manufacturing of flavours, medicine, perfume, cosmetics and insecticides [1]. Many human diseases had been treated with medicinal plants. Ancient Egyptians were from the first nations to use these plants, Greeks and Romans also used them [2]. Egypt is one of the major countries in planting aromatic and medicinal plants such as (Marjoram, Anise, Chamomile, ect.,). Egyptian Exporting Council of Agriculture Crops reported that the amount of medicinal and aromatic plants in the first quarter of the year 2018-2019 were 12.5 thousand ton with 20 million American dollars including 29 kind of aromatic and medicinal plants [3].

Foeniculum vulgare Miller (Fennel) is one of the important aromatic and medicinal plants, which belong to the Mediterranean region; recently it has been cultivated nearly around the world [4]. Fennel is cultivated around Egypt especially in Fayoum, Menia and Bani-sweif governorates [5].There are many pests which attack fennel during the planting season or post-harvest causing a lot of damage in the quantity or the quality of the extracted material consequently economic loss, most of them are sucking insects [6].

From the major pests of fennel are aphids and whiteflies, which are considered major pests that

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destroy the volatile oil extracted from seeds [7]. Many aphids attack the fennel, from which are the *Aphis gossypii* (Glover), *Aphis craccivora* (Koch) and the fennel aphid *Hyadaphis foeniculi* (Passerini) [8], [9], [10], [11].

Whitefly, *Bemisia tabaci* Gennadius (Hemiptera: Aleyrodidae) is a major pest of economically important crops worldwide, it damages crops by feeding on phloem sap and the large amounts of sticky honeydew produced can lower the rate of leaf photosynthesis. Most of the important emerging virus diseases are whitefly vectored resulting in yield reductions and economic losses of hundreds of millions of dollars annually in the affected regions [12].

Whitefly is one of the major pests on fennel crops and could make a serious damage to the crop [13], [14].

Different insecticides with different modes of action were used in controlling sucking piercing insects causing evolution of resistance and problems of persistence in the environment. Neonicotinoid insecticides being from the most widely used insecticides globally, with the advantages of favourable toxicological properties, flexible use, and systemic activity. They are used to control aphids, whiteflies and thrips in many agricultural crops. There are many studies were made to show the effect of pesticide residues in decreasing the quality of the crop [15]. They selectively act as agonists of insect nicotinic acetylcholine receptors (nAChRs), causing impairment of the nervous system and the death of insect. These insecticides besides direct killing, exhibited sublethal effects on the physiological and behavioural traits of insect pests [16].

These neoniconitoid pesticides have many generations and different chemical structures. Acetamiprid (Mospilan 20% SP), thiamethoxam (Actara 25% WG), and dinotefuran (Oshin 20% SG) belong to first, second and third neonicotinoid generations, respectively. Acetamiprid and dinotefuran are non-cyclic compounds, while thiamethoxam is a six-membered ring system [17]. Acetamiprid is a carboxamidine, monochloropyridine, a nitrile that has a chloropyridinyl group. From the necotinoids that has potential activity against insects resistant to other insecticide groups is the dinotefuran molecule [18].

The dissipation behaviour of dinotefuran and its metabolites in different plants like rice, apple, lettuce, potato etc., and also the various pathways of transformation in different commodities had been studied [19].

Thiocyclam hydrogen oxalate (Evisect 75% WG) belongs to Nereistoxin analogue group which is used to control major sucking pests such as aphid and whitefly, is similar to neonicotinoids that acts on the nicotinic acetylcholine (nACh) receptor as a partial agonist at low concentrations with little difference at high concentrates as channel blocker [20], [11].

These medicinal plants are generally consumed in the raw form. Therefore, the pest management should be in such a way that there is very low or no pesticide residues at the time of harvest [21]. To achieve high crops yields, pesticides application is likely to increase, resulting in serious environmental impacts in terms of soil, water resources, biodiversity, and ecosystem [22]. Pesticides pose a potential risk to humans and the frequent use of them against pests lead to development of resistance and many environmental problems [23]. The wrong timing of pesticide usage or the quantities would cause more residues of pesticides in the extracts and will not be allowed to be used as fresh seeds, in medical purposes and as animal food [24]. Besides exceeding the MRL values (Codex, European Union MRLs), which cause considerable rejection percentage in the process of exporting these plants.

Public awareness is increasing regarding the effects of pesticides on the environment, raised the need to hold many trials to solve these problems. Therefore, the development of alternatives, new pesticides, or novel modes of action could minimize the undesirable effects of exposure on human health [25].One of them is converting the synthetic formulation into a nano-form to reduce the amount entering the environment and persisting in its components.

Nanotechnology is used to enhance the efficacy or reduce the environmental footprint of pesticides through nano pesticides. They represent a technological development having benefits including durability, increased efficacy, and reduction in active ingredients used quantities. They also have considerable decomposition in soil or plant, solubility and controlled release [26]. Nanotechnology applications in agriculture have recently attracted increasing attention worldwide [22].

The main focus now is directed towards assessing whether or not the presence of the nano formulation introduces potential differences relative to the synthetic active ingredients [27]. Thus, this study aims to compare effectiveness of the synthetic and non-conventional (nano form) of some insecticides (acetamiprid and dinotefuran) used for controlling aphids and whitefly, in fennel plant and to study their persistence differences on fennel plants.

2. Materials and Methods

2.1. Tested insecticides

Four insecticides have been chosen; Actara 25% WG (thiamethoxam), Oshin 20% SG (dinotefuran), Mospilan 20% SP (acetamiprid) and Evisect 75% WG (thiocyclam hydrogen oxalate); according to

Egyptian Agricultural Pesticides Committee (APC) recommendation on targeted pests Whitefly (*Bemisia tabaci*) Gennadius and Aphid (*Aphis craccivora*) Koch with considering the chemical group and generation for each insecticide (Table 1).

Table (1): Tested insecticides, common name, chemical group and rate of application

No.	Insecticides	Common Name	Chemical Group	Generation	Rate of application (100L)
1	Mospilan 20% SP	Acetamiprid	Neonicotinoids	1st	25 g
2	Actara 25 %WG	Thiamethoxam	Neonicotinoids	2nd	20 g
3	Oshin 20% SG	Dinotefuran	Neonicotinoids	3rd	125 g
4	Evisect 75% WG	Thiocyclam hydrogen oxalate	Neriestoxin analogue	-	125 g

Chemical structures of the tested insecticides are shown in Figure 1.

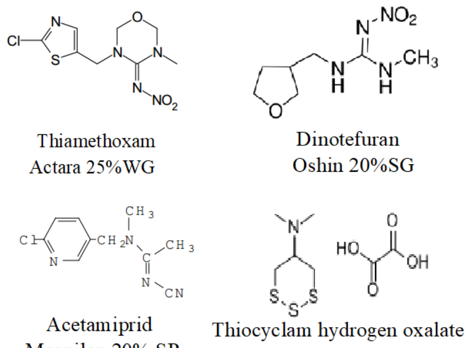

Fig. (1). Tested insecticides chemical structure, active ingredient, trade name and formulation

2.2. Nano preparation

Methods and processes of nano particles were prepared [15], [28], [29], [30], [31], with some modifications.

a.Chemicals used for the preparation of nano form insecticides

Chitosan (MW 71.3 kDa, degree of deacetylation (89%) was purchased from Aldrich (Germany). All reagents were of analytical grade, Chloride in the form of hydrochloric acid (HCl), orthorhombic bravais and sodium chloride NaCl. Nitrite salt NH_4NO_3, HCN and NaCN were purchased from Sigma Chemical Co. (St. Louis, USA). Acetamiprid and dinotefuran were obtained by top to bottom molecular chemical method.

b. Preparation of Acetamiprid:

Nano-chloride: Diethoxy (oxo) silane; tetraethyl silicate and methoxymethane; triethoxysilicon reagents (1:1) v: v were mixed, added to the acetamiprid (1:36) (v:v) , then centrifuged at 1200 rpm for 10 minutes, subsequently 2 ml of tetraethyl silicate; hydro fluoride was added slowly, centrifuged at 500 rpm for 5 minutes, then the precipitate was filtered and exposed to 1.5 psi pressure for 6 hours continuously (product a).

Nano-suspension of chloride (top to bottom molecular chemical method); was prepared from aqueous solution of HCl and MnO_2 (v:v), then hydrochloric acid and manganese oxide were added slowly , the molar ratio was (3:2) in the presence of PVA (stabilizing agent) under vigorous stirring for 5 h.The precipitate was filtered and washed thoroughly with deionized water. The obtained suspension was added to 16 ml of NaCl 0.2 M aqueous solution under vigorous stirring for 40 min., followed by stirring for 3more hours at room temperature. The precipitate was then mixed with orthorhombic bravais v: v (2:1) in presence of HCl 90%, and exposed to 1.5 psi pressure for 6 hours continuously (product b). The end product (b) 2µlwas mixed with acetamiprid (a) in a ratio of 1:200 (v: v) then centrifuged at 1500 rpm for 20 minutes 48 hours discontinuously [28], [29].

c. Preparation of Dinotefuran

Nano-CN and NO_2:Tetraethoxy-tetrasiloxane reagent was added to the dinotefuran (1:32) (v:v) , centrifuged at 1500 rpm for 20 minutes, followed by adding 2 ml of tetraethyl silicate; hydro fluoride slowly, centrifuging at 1000 rpm for 10 minutes, then exposed to 1.5 psi pressure for 12 hours discontinuously after being filtered (product a).

Nano No_2 was prepared from aqueous solution of NH_4NO_3 and NO 2:3 (v: v). Sodium hydroxide and nitrous oxide solutions (1:1) were added slowly in a molar ratio of 1:3 under vigorous stirring for 8 h .The obtained precipitate was washed thoroughly with deionized water in a mixed water/toluene system using a high-speed stirrer, and then washed again with ionized water for 3 hours. Polymerizing methacrylic acid in chitosan solution as carrier coated in buffer solution for 5 hours at room temperature in two-steps processes. In the first step, 0.23 g chitosan was dissolved in methacrylic acid aqueous solution (0.5%, v/v) for 18 h using magnetic stirring. In the second step, the precipitate was mixed with 0.2 mmol of K2S2O8 until the solution became clear. Then trimethylammoniumbromide compound solution was added (molar ratio 1:3) at (33 C°) and slowly stirredfor 6 hours then a drop of silver nitrate (0.15 M), the end solution was exposed to 1.5 psi for 3 days discontinuously (7 hours per day). The solution was dried in an oven at 90º C for 3 days continuously; deionized water was added to the end product to form nano-suspension which was left on shaker for 2 days at 20º C [30]. Nano CN was prepared from aqueous solution of HCN and NaCN 1:3 (v: v), then potassium hydroxide and methacrylic acid aqueous (0.5%) solutions were added (1:1) under magnetic stirring for 18 h, the end solution was exposed to 1.5 psi for 2 days discontinuously (3 hours per day), then HCl solution (Merck, 28%) was added at a temperature between 60–70 °C in a heater-magnetic stirrer to remove solid by-products. The final product was obtained after centrifuging at 500 rpm for 30 min, decanting, washing (deionized water, 4 h, 100 °C) and drying in an oven at 50 °C for 12 h (product b).

1µl from the end product (b) was mixed with dinotefuran (a) in a ratio of 1:300 (v: v) then centrifuged at 1500 rpm for 48 hours discontinuously. The end precipitate washed thoroughly with deionized water filtration [30].

Nano-acetamiprid and nano dinotefuran Fig. 2 were characterized by scanning electron microscopy (SEM).

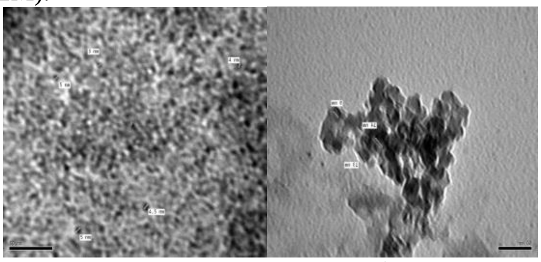

Fig. (2). Nano-acetamiprid and nano dinotefuran were characterized by scanning electron microscopy (SEM).

The nanoparticles' shape and dimension were examined using a JEOL 1010 transmission electron microscope (TEM) at 80 kV (JEOL, Japan). A single drop of the nanoparticle solution was spread onto a carbon-coated copper grid and was posteriorly dried at room temperature for TEM analysis. The dimensions of the nanoparticles were established directly from the figure using Image-Pro Plus 4.5 software. The rate is a normal size of three parallels.

2.3. Laboratory evaluation

Toxicity testing of Mospilan 20% SP (acetamiprid), Oshin 20% SG (dinotefuran) and their Nano form against aphids and whitefly was conducted [32]. Whiteflies and aphids were collected from the field and reared for two generations. Experiments were done on the third generation. Whiteflies were reared in a greenhouse on cotton plants under conditions of 27± 2°C, 55 ± 5% R.H. and a photoperiod of 18:6 h (light: dark). Aphids were reared in green bean pots under laboratory conditions at 20-30° C, 70 ± 5% R.H. and a photoperiod of 16:8 h (light: dark) [33].

Discs (30 mm diameter) were cut, immersed in serial dilutions of insecticides for 20 seconds, air-dried for one hour and laid in adaxial side, down on a bed of agar-gel (2%), previously poured into the base of a plastic dish petri (30 mm diameter,20 mm high) with 4 holes, covered with a metal screen for good ventilation. Control discs were dipped in water for only 20 seconds. About 20 *B. tabaci* adults were removed from the rearing cages using mouth aspirator and placed in each Petri dish, while 10 adults of aphids were transferred onto treated leaf discs using suitable brush. The result was recorded after 24 hours from application at 25 ±2º C with a photoperiod of 18:6 h (light: dark). Any movement from the insect was calculated as alive on counting the result. Results have been corrected [34]. The slope, LC_{50} and LC_{90}values for each insecticide were calculated [35].

2.4. Field Evaluation

a. Two Field trials were conducted in 2018 and 2019 growing seasons

Field experiments were conducted to evaluate the efficacy of tested insecticides against whitefly nymphs and aphid adults infesting fennel in Fayoum governorate. The candidate insecticides for the two seasons; Actara 25% WG (thiamethoxam), Oshin 20% SG (dinotefuran), Mospilan 20% SP (acetamiprid) and Evisect 75% WG (thiocyclam hydrogen oxalate); were applied at their recommended rates of application Table (1).

In Fayoum governorate, fennel was planted during seasons 2018 and 2019 and all cultivating and fertilizing methods were followed as commonly practiced. The area chosen for the experiment was divided into blocks according to a complete randomized block design including four replicates for each treatment. Each replicate was 42 m^2 (1/100 fed.). A knapsack sprayer (CP-3) was used in applying the insecticides dissolved in water as foliar treatment for one time throughout the season. The control was treated with water only. 100 plants were examined for the infestation and the population of each target pest before spraying and after 1, 3,5,7,10,14 and 21 days of application was recorded. The reduction percentage was calculated [36].Then the most effective compounds against aphids and the whitefly were chosen to be prepared into a nano-scale according to their chemical structure.

b. Field trial for comparing tested insecticides and their nano-form

According to the results of the two previous seasons Oshin was the most effective against whitefly, while mospilan was the most effective against aphid. These two compounds were converted into their nano form. The third season 2020 was conducted using four insecticides namely Oshin 20% SG (dinotefuran), Mospilan 20% SP (acetamiprid) and their nano forms to compare efficacy between the synthetic forms with the normal rate of application 125g and 25 g respectively and the nano-form with a rate of 10% of the synthetic (12.5g and 2.5g) according to the bioassay results. A knapsack sprayer (CP-3) was used in applying the insecticides for one time through the season, four replicates were treated for each insecticide with an area of $42m^2$ (1/100 fed.). The same procedure was followed as in the previous field trials conducted in 2018 and 2019 growing seasons.The reduction percentages were calculated [36].

2.5. Analytical procedures

a. Chemical and reagents

The chemicals used were: acetonitrile (ACN) (chromatographic grade), formic acid and methanol (HPLC grade), magnesium sulfate anhydrous (MgSO4), sodium chloride (NaCl), disodium hydrogen citrate sesquihydrate, and trisodium citrate dehydrate all were purchased from Merck (Darmstadt, Germany). Deionized water was obtained from a Milli–Q water purification system (Millipore, USA). The purity of acetamiprid and dinotefuran standards was 99.7% and99.9 %, respectively, obtained from Dr. Ehrenstorfer, Augsburg, Germany. Stock solution of acetamiprid and dinotefuran (1000 mg L^{-1}),working standard solution of 10 mg $L^{-1}$and calibration standards were prepared in acetonitrile .Stock solution was stored at - 20 °C).

b. Extraction and cleanup

A Hobart Food Chopper (Hobart, Canada) was used to homogenize samples and a sample of 10±0.1 g was weighted into a 50-mL polypropylene centrifuge tube for analysis. Extraction was performed using QuEChERS method [37], [38]. An aliquot of 10±0.1 g was weighed, 10 mL of acetonitrile was added and vortexed for 2 min. Then 4.0 g of $MgSO_4$ anhydrous, 1.0 g of NaCl, 1.0 g trisodium citrate dehydrate and 0.5 g disodium hydrogen citrate sesquihydrate were added and the tube was hand shaken intensively for 2 min. The sample was then centrifuged at 4800 rpm for 5 min and an aliquot (200 µL) of the supernatant was diluted with 800 µL acetonitrile and filtered through a PTFE (0.2 µm) syringe filter prior to analysis.

c. Analytical method and equipment

Quantitation and identification were performed with a QTRAP mass spectrometer coupled with an Exion HPLC system (QTRAP 6500+, AB Sciex). A Synergy C_{18} column, 2.5 µm Fusion-RP 100 Å, 3.0×50 mm (Phenomenex, Egypt) was used. The mobile phase consisted of 10 mM $HCOONH_4$ in H_2O/methanol (90:10, v/v) (phase A) and methanol (phase B), with injection volume of 2 µL and a flow rate of 0.4 mL min^{-1}.

The gradient elution of the mobile phase was as follows: 0 min, 100% A; 1–15 min from 100% to 5% A; 15–18 min 5% A; 18–20 min 100% A. with a flow rate of 0.4 mL min⁻1 [39] with a total run time of 20 min. Mass was operated at positive mode. Gas parameters and sources were as follows: ion spray voltage 5500 V for ESI (+);curtain gas 20 psi; collision gas medium; nebulizer gas and auxiliary gas 35 psi and ion source temperature 400 ºC.

2.6. Statistical evaluation

The residues were calculated with the following equation [40]:

mg/kg = (Ps × B × V)/(Pst × G × C) × F;

where: F (recovery factor) = 100/R, R: average of recovery, Ps: sample peak area, B: amount of standard injected (ng), V: final volumes of samples (mL), Pst: standard peak area, G: sample weight (g), C: amount of sample injected (µL).

Residues half-life values (RL_{50}) were calculated mathematically according to this equation: RL_{50} = Ln2/K = 0.6932/K [41].

2.7. Recovery

The recovery study was conducted by fortifying five replicates of untreated fennel samples with tested pesticide standards at three levels 0.01, 0.1 and 1 mg/kg. Recovery percentages were calculated using the following equation: % Recovery = [(µg) found/(µg) added] × 100.

Accuracy is calculated as the percentage between the obtained and the known concentrations, while Precisions as the relative standard deviation (%RSD) and is calculated as the ratio between standard deviations and average obtained concentrations.

Table (2): Recovery percentages of dinotefuran and acetamiprid in fennel plant.

Spiking level (mg/kg^{-1})	Acetamiprid	RSD %	Dinotefuran	RSD %
	Rec %(n=3)		Rec% (n=3)	
0.01	89.12	4.33	97.01	5.22
0.1	105.0	6.50	99.16	6.12
1.0	96.50	5.20	92.07	3.23

The tested spiking levels (0.01, 0.1 and1) resulted in percent recovery from (89.12 to 105) for acetamiprid and (92.07 to 99.16 for dinotefuran at n=3.

3. Results and Discussion

3.1. Laboratory evaluation of the chosen insecticides for each Bemisia tabaci and Aphis craccivora and their Nano-form

a. Whitefly (*Bemisia tabaci*)

Results in Table (3) showed that Nano-Dinotefuran was the most effective pesticide against *Bemisia tabaci* adults, followed by nano-acetamiprid, dinotefuran (Oshin 20% SG) and then acetamiprid (Mospilan 20% SP).

The LC_{50} values for the tested pesticides arranged in ascending order were as follows: nano-dinotefuran (0.76 ppm), nano-acetamiprid (0.899 ppm), dinotefuran (3.355 ppm) and acetamiprid (5.085 ppm).

The toxicity index was employed comparing the efficiency of all tested compounds at a fixed level (LC_{50}) to their most effective pesticide. The toxicity index values were 84.5, 22.7 and 14.9% as toxic as nano-dinotefuran for nano-acetamiprid, dinotefuran and acetamiprid, respectively. However nano-forms had the steepest slope with 2.607 and 2.583 which indicates that the least change in pesticide concentration caused high mortality, compared to the slope values for dinotefuran and acetamiprid in their normal / synthetic form; which needed more concentration to give the same effect (percent mortality); 1.592 and 1.298, respectively.

The mortality in whitefly adults treated with imidacloprid was double whiteflies treated with dinotefuran [42]. LC_{50} for acetamiprid was 2.3 ppm in laboratory strain of Whitefly [43].

Table (3) Susceptibility levels of *Bemisia tabaci* adult to tested insecticides after 24 hours

Pesticides	LC levels of the tested pesticides (ppm)			Slope	χ2	Toxicity index at LC_{50}
	LC_{25}	LC_{50}	LC_{90}			
Nano-Dinotefuran	0.302	0.760	2.346	2.583	9.52	100.00
Nano-Acetamiprid	0.360	0.899	2.787	2.607	9.78	84.50
Dinotefuran	0.745	3.355	21.272	1.592	10	22.70
Acetamiprid	0.809	5.085	49.359	1.298	9.1	14.90

b. Aphids (*Aphis craccivora*)

Based on data in table (4) the results of tested insecticides against *Aphis craccivora* adults the Nano-acetamiprid was the most effective at the LC_{50} level (0.59 ppm), followed by Nano-dinotefuran (0.70), acetamiprid (3.57) and dinotefuran(4.07).

Table (4) Susceptibility levels of *Aphis craccivora* adult to tested insecticides after 24 hours

Pesticides	LC levels of the tested pesticides (ppm)			Slope	χ2	Toxicity index at LC_{50}
	LC_{25}	LC_{50}	LC_{90}			
Nano-Acetamiprid	0.26	0.59	1.596	2.97	7.35	100.00
Nano-Dinotefuran	0.27	0.70	2.346	2.46	8.81	83.70
Acetamiprid	1.47	3.57	19.113	1.76	5.7	16.50
Dinotefuran	1.84	4.07	18.339	1.96	4.01	14.50

Nano-acetamiprid was used as a standard in calculating the toxicity index due to its highest effect.Data in table (4) illustrated that Nano-dinotefuran was 83.7% followed by acetamiprid with 16.5% the least was dinotefuran with 14.5% when compared to Nano-acetamiprid.

As in the case of testing these pesticides against whitefly in Table (3), the slope was steeper for the nano pesticides (2.97 and 2.46) than their synthetic forms (1.76 and 1.96).Nano-acetamiprid showed the steepest toxicity line slope and highest efficiency. It is obvious that the Nano products are much more effective than the synthetic forms but also had the steepest slope comparing with their synthetic compounds. In tables 3 and 4 the sequence of LC_{25} and LC_{90}values was in accordance with LC_{50} value order.

Different concentrations were tested to measure the toxicity and guide to estimate the rate of application for the Nano-pesticides that will be used in the third season.

Nano-acetamiprid LC_{50} value was lower three times than the commercial compound in a laboratory evaluation [44] while the most toxic insecticide against the cowpea aphid, *Aphis craccivora* was thiamethoxam followed by acetamiprid while dinotefuran was the least [45]. LC_{50} of dinotefuran was 4.016ppm confirming our results according to table (4) [46]. The toxicity of acetamiprid against Soybean Aphid *Aphis glycines* was estimated as LC_{50} value of 6.742 mg a.i./L with a confidence interval of 5.133–8.629 mg a.i./L [47]. The bio-assay of Nano-acetamiprid shows better results when compared to the normal commercial acetamiprid [26].

The lethal effect of dinotefuran was the highest against *B. tabaci* different species , followed by imidacloprid and thiamethoxam. The highest toxicity was exerted by dinotefuran (5.54 mg/L and 6.01 mg/L of LC_{50}) followed by thiamethoxam (8.77 mg/L and 24.26 mg/L of LC_{50}), imidacloprid (9.74 mg/L and 20.37 mg/L of LC_{50}) for the species MEAM and MED, respectively [48]. The obtained results are also in agreement with [49] and [50] who measure the mortality percentages of *Glyphodes pyloalis's* larvae which increased in leaf dip bioassay method using nano-imidacloprid with a clear reduction in insecticide ratios and LC_{50} decreased to 4.82 and 9.05-fold much more less than the commercial trade size of imidacloprid; respectively.

The nano-pesticide of imidacloprid was much more effective around five times higher than synthetic with reducing LC_{50} values from 2.56 ppm with imidacloprid to 0.512 ppm with nano-imidacloprid after 24 hours of application against tobacco aphids in laboratory bioassay [51]. The results showed that nano-pesticides are more effective in comparison of insecticides. The new nanotechnology with materials having unique properties than their macroscopic or bulk counterparts, has promised applications in various fields.

3.2. Field evaluation of tested insecticides against Bemisia tabaci nymphs and Aphids craccivora adults in two seasons (2018 – 2019)

3.3. 1. Field trials season 2018 and 2019

The efficiency of four pesticides under two chemical groups; Neonicotinoids and Neriestoxin analogue was conducted against whitefly *Bemisia tabaci* nymphs in Fayoum Governorate, through two consecutive seasons (2018) and 2019. The reduction of infestation on fennel plant was calculated before and after application in the two seasons and tabulated in table (5).

The percent reduction in infestation caused by oshin was 100% for 1and 3 days after application. Even through the rest of the experiment the reduction was considerably high 97.34, 94.68, 92.59, 91.48 and 88.60 after 5, 7, 10, 14 and 21 days respectively. Actara reduction values were nearly close, as it started with 100% reduction also for 1, and 3 days after spraying, followed by slow gradual decrease reaching 84.33% after 21 days of application. Evisect was also effective with reduction percentages of 94.48, 93.24, 93.72, 90.78, 87.05, 85.64 and 79.46. While mospilan values were the least during the whole experiment with 86.59, 83.89, 79.20, 80.75, 74.08, 72.29, 69.31%. During the experiment there was no significant difference in the values of percent reduction for each tested pesticide, but the difference was between the different pesticides. The mean values of the percent reduction during the experiment were 94.96, 92.94, 89.25 and 78.06 % for oshin, actara, evisect and mospilan, respectively. The same trend/ was obtained during 2019 season Table (5).

These values showed that Oshin was the most effective insecticide against whitefly nymphs in field in this experiment, followed by actara, evisect then mospilan with the least effectiveness.

(Table 5)

Our findings can be compared to the work of different researchers who reported that acetamiprid was effective for the control of whitefly adult on cotton crop [52]. Acetamiprid (Mospilan 20% SP) was found to be an effective insecticide, which resulted in significant reduction of whitefly adult populations, with mortalities of 84.51% in the first season and 84.0% in the second season, 168 hours (7 days) after spray [53]. Maximum mortality of whitefly was recorded with (mospilan 20%SP) i.e., 82 and 86% 1 and 7 days after spray significant reduction of whitefly adult populations as compared to all other insecticides. These results are in accordance with ours, which were 80.75and 85.66% reduction of nymphs' infestation in the first and second season, respectively. Also chemical control of whitefly by acetamiprid was successful for managing the *B. tabaci* on various crops [54].

First season, data in Tables (6) indicate those five days after spray, mospilan, evisect, actara and oshin at the recommended rate of application induced high infestation reduction of aphid adults. They gave more than 95.46% reduction in the population. The percent reduction in infestation of aphid adults after five days of application was 99.15, 96.30, 93.26 and 93.14% by using mospilan, evisect, actara and oshin respectively. The corresponding values after 7 days were 98.03, 89.10, 92.17, and 91.79% respectively. After ten days of application, percentage of reduction in aphid infestation reached to 96.20, 78.26, 90.54 and 90.05 respectively. After 14 days of application, percentage of reduction in aphid infestation slightly decreased to 90.61, 68.51, 85.12 and 86.92 respectively.

The field evaluation data of tested insecticides are set out in Tables (6). The tested insecticides against aphid adults can be arranged according to the residual effect values. Mospilan, oshin, evisect and actara with 95.88, 90.73, 85.58 and 82.79% respectively, at the second season and 96.00, 90.48, 90.27 and 83.04% respectively, at the second season.

The field evaluation data of tested insecticides are showed that there are no differences between the efficacy of tested insecticides in the evaluation seasons 2018 and 2019. The tested compounds could be arranged according to their reducing the population of aphid adults in the following descending order: mospilan, oshin, actara and evisect.

(Table 6)

Many researchers stated that neonicotinoid insecticides as acetamiprid and thiamethoxam were effective against whitefly and aphids [55], [56]. *B. tabaci* varied in vulnerability to acetamiprid, and thiamethoxam in *Cucumis melo* areas [57]. Neonicotinoids are compelling against piercing-sucking creepy crawlies such as aphids and whiteflies [58], [59]. Thiamethoxam can be more effective against whiteflies and aphids than other pesticides [60], [61]. The impact of neonicotinoids acetamiprid, imidacloprid and thiamethoxam on youthful stages and grown-ups of *B .tabaci* was tall hence; these bug sprays may be considered promising in controlling whitefly with a lower impact on their predators [62]. The impact of the neonicotinoids compound thiamethoxam against Cabbage aphid, *Brevicoryne brassicae* in Pakistan [63], [64], [65]. The effect of thiamethoxam caused tall impact on the whitefly in cucumber and cucumis crops [66].

3.4. Third field trial 2020

To evaluate synthetic and Nano-form of tested insecticides against *Bemisia tabaci* nymphs and *Aphis craccivora* adults in field during season 2020

a. Whitefly (*Bemisia tabaci*)

Considering the results in the two previous seasons, the main aim of third field evaluation was to assess the efficacy of acetamiprid, dinotefuran and their nano-form (according to the concentrations/ dosages which were previously tested in the laboratory) against *Bemisia tabaci* nymphs on fennel plant (*F. vulgare* Mill) under field conditions. In the third season, all tested insecticides caused high effect where the mean reduction ranged from 90.78 to 98.99 % (Table 7). Mostly all the treatments resulted in 100% mortality one day after application. Dinotefuran N (oshin N) has higher effects on *Bemisia tabaci* nymphs than nano acetamiprid (mospilan N) with 98.99% and 94.24% respectively. The treatment with dinotefuran N caused the highest mortality, killing all nymphs in the study with percent reduction 100% until 10 day from the treatment with a mean of 98.99%. The least effectiveness was recorded with acetamiprid (90.78%).

b. Aphid (*Aphis craccivora*)

The third season of field evaluation data of tested insecticides are set out in Table (7). The tested insecticides against aphid adults had relatively close residual effect values. Oshin 92.91% reduction, mospilan 94.50% and the nano forms were nearly the same values 95%.

(Table 7)

The excessive use of pesticides leads to risks for human health and environmental problems. So nanoscience and nanotechnology allow the development of agricultural fields with high technology (nanoproducts) and that leads to controlled management and less utilization of pesticides. Nano pesticides are from the best alternative to the traditional pesticides. Nano-neonicotinoid insecticides thiamethoxam (Actara 25% WG), imidacloprid (Best 25% WP), acetamiprid (Mospiln 20% SP) are better than commercial formulation in reducing the infestation in leaf miner with a study includes two seasons [67].

Be that as it may, nano formulations appeared more viability in diminishing leaf miners than the commercial formulation at the same recommended rate in both seasons. These comes about might happen since nano formulation increments the effectiveness of insecticides and decreases the measurements level required to control due to the little sizes of nanoparticles which makes insecticides more penetrative into leaf tissue and effortlessly reach to target leaf miner. The ecotoxicity is related to active ingredient concentration, and chance is recognized utilizing comes about of exposure and effects (in terms of mass per mass of active ingredient) [26]. Be that as it may, as for nanopesticides, particle number concentration and particle measure dissemination and the proportion of free and nanoparticle-bound active ingredient are required to decide the pesticide bioavailability and toxicity. Nano-acetamiprid reduces toxicity in agricultural fields and it is highly active at lower level concentration, its formulation enhances the stability and it slowly releases the active ingredient. Generally from the benefits of nano pesticides better efficacy, better control of application and less use of chemicals.

Dissipation of tested pesticides in fennel plants

Results of persistence in the fennel plants were tabulated in table (8). At 3 days after application, the initials of nano were lower than synthetic synthetic even in dinotefuran it was 0.1 of the synthetic. All the tested compounds decreased drastically, with 22.11, 14.81, 27.92 and 39.13 for acetamiprid, nano-acetamiprid, dinotefuran and nano-dinotefuran, respectively. The nano forms of both pesticides were not detected after 5 and 7days for nano-acetamiprid and nano-dinotefuran compared to10 and 15 days for acetamiprid and dinotefuran, respectively. But the rate of degradation in synthetic was higher /faster, resulting in RL_{50} values less than those of their nano forms. Half-live of dinotefuran at the standard and double doses were 2.1 and 2.4 d for fresh chilli peppers, respectively. The corresponding calculated waiting periods were 1.34 and 3.45 d for. The residue in soil reached a half-life of 1.86 and 1.43 d at the standard and the double doses respectively [18].

(Table 8, 9)

Acetamiprid has moderate persistence under natural field conditions, which is likely to be low due to environmental conditions of temperature, exposure to sunlight, etc. [68]. In soil the nanopesticides sorption behavior is studied. The field dissipation study was done to show pesticide persistence in soil as half-dissipation time (DT_{50}), the decrease of concentration in soil measured over time is expressed as DT_{50}. The dissipation trends of the four insecticides in soil are shown in Table 9. The dissipation of acetamiprid was gradual until after 3 days of application with DT_{50} value of 3.73 then it was fast until 21st day it was not detected, its nano form rate of degradation was so close (0.19, 0.188), with RL_{50} value of 3.69 and was not detected 10 days after application. As for dinotefuran the rate of degradation in nano form (0.27) was higher than in synthetic (0.19), with), resulting in DT_{50} values 2.53 and 3.57, respectively. Dinotefuran in both forms was also not detected at 21st, and 10 days after application. The dissipation of insecticides in field is usually controlled by several factors like physio-chemical properties of the pesticide, soil, and environmental factors growth rate, light, plant varieties and dosage [69].

Nano-insecticides are promising tools in management due to their high soluble abilities in water which makes it more absorbable than normal size of pesticides to deliver active ingredients to target pest into leaf mines [70]. From nanopesticides formulations benefits are greater solubility, stability and mobility, reduce the concentration of pesticides and decrease the toxicity to non-target organisms and human [71]. Stable compounds are not easily broken down in the environment due to their low water solubility [72]. The increased surface area of nano particles allows the use of the less quantity of traditional pesticides in the agricultural land. Thus the nano encapsulated acetamiprid was found to have more antifungal activity. Padmavathi, *et al.,* 2020 [26].

Dissipation behavior differences between nano and synthetic form of imidacloprid as the model for neonicotinoids [73]. They stated that the initial deposit in soil for Nano-imidacloprid were less than imidacloprid. Major deterioration of nano-imidacloprid took place through the first week after application, followed by degradation at a slower rate during the next weeks. This was the same behavior of acetamiprid and dinotefuran and their nano forms tested in this work. They also stated that the degradation rate of nano-imidacloprid was higher than imidacloprid under the tested conditions. The obtained differences in the rate of degradation may be due to the variations in the formulations, the initial concentration of nano was also lower than synthetic in soil, photodegradation also may have major role in the degradation process, which are shown in results obtained in tables (8 and 9).Thus this may explain that the degradation rate of nano was higher than synthetic form.

Nanoscience has greatly contributed to major achievements in various fields. A better alternative to synthetic pesticide is nano pesticide [26]. Nano pesticides will often undergo changes in their degree of dispersion over time, depending on the concentration of the nanopesticide and different environmental factors [27]. Transportation in air of nano pesticides varies than that of a synthetic pesticide the pesticide molecules transfer from soil and plant surfaces to the air byvolatilization, whereas for a nano pesticide the release of particles is likely to be important.The uptake pathway of a nano pesticide into organisms is also different from that of a conventional pesticide.For conventional pesticides the octanol/water partition coefficient (K_{ow}) is an important characteristic and also dissipation, uptake, and distribution behavior is independent of the concentration. For nano pesticides many parameters as uptake, distribution within organisms depend highly on the concentration and many important factors include pH, pore size distribution, ionic strength, dissolved organic carbon concentration, and clay content affect the release of the pesticide and consequently the persistence.

4. Conclusions

Field trials were conducted for (Actara 25% WG (thiamethoxam), Oshin 20% SG (dinotefuran), Mospilan 20% SP (acetamiprid) and Evisect 75% WG (thiocyclam hydrogen oxalate)) against aphid adults and whitefly nymphs during 2018 and 2019 seasons. Mospilan was the most effective insecticide during the first and the second seasons on aphids and dinotefuran was the most effective on whitefly for both seasons too. Thus, they were chosen to be transformed into nano-form to measure the efficacy of the four insecticides and to specify the rate of application for nano-form according to the $LC_{50.}$ Third season with field trials was conducted to evaluate Oshin 20% SG (dinotefuran), Mospilan 20% SP (acetamiprid) and the nano form of the same insecticides against aphids and whitefly. Nano-mospilan and nano-oshin proved to be superior of all treatments against aphids and followed by mospilan then oshin. As for whitefly nano-oshin was superior followed by oshin then nano-mospilan and mospilan. Converting insecticides into nano-form may solve many problems in controlling several pests due to efficacy and low quantities of usage and will be one of the promising solutions in the future.

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