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Toxicity of some Insecticides with A New Nano Additive against Two Lepidopterous Insect Pests

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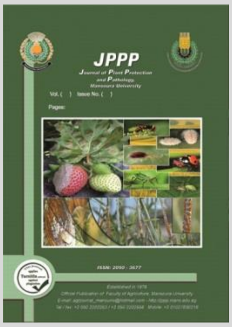

ABSTRACT

Tomato plants are the second important vegetable crop grown in Egypt. Insect pests pose a serious threat in vegetable production both in terms of quality and quantity. Order Lepidoptera is one of the larger orders in insects. The cotton leafworm, *Spodoptera littoralis* (Boisd.) (Lepidoptera: Noctuidae) and the leaf miner, *Tuta absoluta* (Meyrick) (Lepidoptera: Gelechiidae) are the most serious lepidopterous insect attaching the tomato crop. Pesticides are the basis for defending against major biological disasters and important for ensuring national food security. Nano materials motivate the toxicity of pesticides. In this study the pesticide Marsa 24% SC (belongs to Methoxyfenozide) used for controlling *S. littoralis*, while Calazole 2% EC (Emamectin Benzoate) applied on *T. absoluta*. Each pesticide will apply with and without nano cupper complexe salt (1-(2-bromophenyl)-$1\lambda^4$-diazane hexadecyltrimethyl-$1\lambda^4$-azane, bromo trichloro cuprate (II). Results indicated that the addition of nano salt increases the mortality percentage for both pests (22.45, 59.22 to 100 %) and decreases the lethal time (10 to 3 days; 13 to 4 days) comparing with pesticides without nano salt.

Keywords: *Spodoptera littoralis* and *Tuta absoluta*, tomato plant, methoxy fenozide, emamactin benzoate, nano additives.

INTRODUCTION

Tomato, *Lycopersicon esculentum* Mill is a vegetable crop of large importance throughout the world (FAO, 2002). Tomatoes are grown both under plastic covered greenhouses and in open field. One of the most important insect pests that are effecting tomato production is the cotton leafworm, *Spodoptera littoralis* (Boisd.) and the tomato leaf miner, *T. absoluta* (Meyrick). The tomato leaf miner, *Tuta absoluta*. *S.littoralis* is a polyphagous pest of many economically important crops such as tomato, cotton, sweet potato, soybean, etc (Senrung *et al*., 2014).

On leaves, larvae feed only on mesophyll leaving the epidermis intact (OEPP, 2005).

Selective insecticides with modes of action different from those of broad-spectrum neurotoxic insecticides are highly desirable in integrated pest management (IPM) programmes. Marsa 24%SC (Methoxyfenozide) is a carbohydrazide that is hydrazine in which the amino hydrogens have been replaced by 3-methoxy-2-methylbenzoyl, 3,5-dimethylbenzoyl, and tert-butyl groups respectively(Carlson *et al*., 2001). Also, Calazole 2% EC (Emamectin Benzoate) is an insecticide of Syngenta Crop Protection(Fanigliulo and Sacchetti, 2008). These compounds have a strong activity and could be used to control many important Lepidoptera pests and a high selectivity on un target organisms. Methoxyfenozide (RH-2485), tebufenozide (RH-5992) and chromafenozide (ANS-118) are three lepidopteran-specific DBH-type compounds that are currently available on the market as safer insecticides with reduced mammalian toxicity and high efficacy against deleterious caterpillars in agriculture and forestry (Hadi and Guy 2009).

In recent years, the employment of nanotechnology to make new formulations has shown large scope for diminishing the random use of pesticides and to protect environment alternatives. Nano-based pesticides are purposed to delivery suitable amounts of active ingredients by using targeted and planned release mechanisms (Camara *et al*., 2019). Khot *et al*., 2012 investigated the usage of nanomaterials in different sizes in several fields like, environmental science, plant protection, pathogen detection and pesticide residue detection.

Adjuvants such as surfactants progress pesticide efficiency by double mechanisms. surfactants raise the foliar uptake of pesticides. Thus, the choice of the adjuvant in an agrochemical formulation is definitive (Castro *et al.*, 2013). K.A. Krogh *et al.* (2003) wrote a review about effects of adjuvants(surfactants) in pesticides and environmental properties. Adjuvants have a wide range of substances (solvents and surfactants). Alcohol ethoxylates (AEOs) and alkylamine ethoxylates (ANEOs) are nonionic surfactants (pesticide adjuvants), (Krogh *et al.*, 2003). Brecke and. Unruh, 2003 studied the Spray Additives.

Spray additives are enhance performance and handling of pesticides. Additives are classified according to their use . Additives include surfactants, spreaders, crop oils, stickers, and antifoaming agents.

The objective of this study to determine the efficiency of some insecticides with new nano additive against S. littoralis and T. absoluta.

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MATERIALS AND METHODS

Rearing of insects:

Rearing of *S. littoralis*:

A laboratory colony of cotton leafworm (S. littoralis) was reared in the Plant Protection Research Institute (PPRI), Mansoura, Egypt. Larval stages instars were dailyfeeded on castor leaves in laboratory under constant conditions of 27±2°C, photoperiod of 14 h light and 10 h dark and 65±5% R.H.

Rearing of *T. absoluta:*

The leaves of tomato including *T. absoluta* were collected form the unsprayed farm of Agriculture College, Mansoura University (Dakahlia, Egypt). The larvae were reared for two generations before the beginning of the tests on leaves of unsprayed tomato which were provided daily, in laboratory under constant conditions of 25±2°C, photoperiod of 14 h light and 10 h dark and 70±10 % R.H (Bajonero and Parra, 2017).

Treatments:

- Marsa 24% SC (Methoxyfenozide).
- Calazole 2%EC (Emamectin Benzoate).
- Nano surfactant additive: 1-(2-bromophenyl)-1λ^4-diazane hexadecyl- trimethyl-1λ^4-azane, bromo trichlorocuprate (II) salt.

Preparation of nano additive "1-(2-bromophenyl)-1λ^4-diazane hexadecyltrimethyl-1λ^4-azane, bromo trichloro cuprate(II) salt :

Solid state reactions of (0.01mole) cupper chloride (II) with 0.02mole of 1-(2-bromophenyl)-1λ^4-diazane was grinded in the mortar with 0.01mole of CTAB and 0.01mole cupper chloride (II) for 2hour until all components mixed well. The prepared complex was 1-(2-bromophenyl)-1λ^4-diazane hexadecyl trimethyl-1λ^4-azane, bromo trichloro cuprate(II) salt with a (chemical Formula: $(C_{25}H_{50}Br_2Cl_3CuN_3)^{2-}$ and molecular Weight: 722.40).

Method of application:

(1) Leaf dipping method:

The 2nd larval instar larvae were used to determine the toxicity action of the materials (Marsa 24% SC and Marsa 24%SC with additive). Tomato leaf discs were cut and dipped into the treatments for 20 seconds, then left for air dryness, 10 larvae for each replicate were released to each leaf disc placed. Five concentrations and three replicates were used to estimate each concentration-mortality line. The concentrations used were 20-50-100-300-500 ppm. The same number of leaf discs per treatment was dipped into dis. water as an untreated check. Before and after treatment, larvae were maintained under laboratory conditions (constant temperature 25 ±2 °C and 70± 5 % R.H. after 24 h of treatment). The percentage of mortality was recorded after 72 h. The data were corrected relatively to control mortality (Abbott, 1925). LC_{50} value was determined using probit analysis statistical method of (Finney, 1971). Lethal time, also, was calculated after 24, 48,120,240and 320h.

(2) Spray method:

The 3rd larval instar larvae of the *T. absoluta* were used for application. Six concentrations of (Calazole 2% EC and Calazole 2%EC with additive) were used as well as three replicates for each concentration. 10 individuals of larvae for each replicate were applied to estimate the mortality line. Different concentrations were sprayed directly on the leaves contains the larvae. The concentrations used were 0.3, 0.7, 1.5, 3,6 and 9 ppm. The same number of leaf discs per treatment was dipped into dis. water as an untreated check. The percentage of mortality was recorded after three days and the data were corrected relatively to control mortality (Abbott, 1925). LC_{50} value was determined using probit analysis statistical method of (Finney, 1971). Lethal time, also, was calculated after 1, 3,5,10and 13 day(d).

Equation: Sun, 1950 (to determine LC_{50} index)

Toxicity index for LC_{50} =

$$\frac{LC_{50} \text{ of the most effective compound}}{LC_{50} \text{ of the least effective compound}} \times 100$$

RESULTS AND DISCUSSION

(1) Toxicity Effect:

Efficiency of the tested materials on larvae of *S. littoralis* and *T. absoluta* :

Data presented in Table (1) assured that, when Marsa 24% without nano additive applied on *S. littoralis*, mortality rate was more little than Marsa 24% SC with nano additive so, LC_{50} (29.16 ppm) and LC_{90} (428.56 ppm) of Marsa 24% SC with nano additive were lower than Marsa 24%SC without nano additive which recorded LC_{50} (129.87 ppm) and LC_{90} (329.68 ppm). Toxicity index was 100% for Marsa 24% SC with nano additive but Marsa 24%SC without nano additive which was 22.45%.

Also, in the same table, data showed that, when the insecticide Calazole 2%EC sprayed on the larvae, mortality was high with LC_{50} 1.40 ppm and LC_{90} 9.07 ppm and toxicity index 59.22% while Calazole 2%EC with nan additive was more effective than Calazole 2%EC only with LC_{50} 0.83 ppm and LC_{90} 4.04 ppm and toxicity index 100%.

Table 1. The insecticidal activity of Marsa 24% SC, Calazole 2%EC and their mixture solutions with nano synthetic surfactant against *S.littoralis* and *T. absoluta* after 72 hour from treatments.

Pests	Treatment pesticide (After 72h)	pH value	LC_{50} (ppm)	LC_{90} (ppm)	Slope	Toxicity index (Ti)
S. littoralis	Marsa 24% SC	8.89	129.87	428.56	2.472	22.45 %
	Marsa 24% SC + additive	6.08	29.16	329.68	1.217	100%
T. absoluta	Calazole 2%EC	7.34	1.40	9.07	1.582	59.22
	Calazole 2%EC + additive	5.98	0.83	4.04	1.867	100%

The obtained results were in agreement with Bingna *et al.* (2018) who proved that the increase in pesticide-loading improve the dispersibility and stability of active ingredients, and promote target ability. Also, Nakagawa (2005); Dhadialla and Ross (2007) illustrated that Methoxyfenozide (RH-2485) had high efficacy against deleterious caterpillars in agriculture and forestry. This compound had been the subject of intensive investigations not only as pest control agents but also as tools for research such as their use as ligands for gene switch. Shivalingaswamy *et al*. (2008) showed the effectiveness of emamaectin benzoate 5 SG against brinjal shoot and fruit borer, *Leucinodes orbonalis*, diamondback moth of cabbage, *Plutella xylostella* and the okra fruit borer, *Earias vittella.* This result agreed with the obtained results. The ability of the additive compounds to ionise effected on adsorption behaviour at relevant pH (Krogh *et al.*, 2003). The ionizable functional groups in nano additives (such as pyrimidines, amines, carboxylates, phosphates, and sulfonates) are respond to pH changes Tao *et al.* (2019). Also, the presence of pathogens or agricultural pests are effected by variation pH in soils and plant leaves Choudhary *et al.* (2017). Therefore, nano carrier systems able to release active agents in response to pH changes.

(2) Lethal time(LT):

Results In Table (2), revealed that the lethal time (LT_{50} and LT_{90}) for each material marsa 24%SC and marsa 24%SC with nano additive (for *S. littoralis*); Calazole 2%EC and Calazole 2%EC with additive (for *T. absoluta*).

Data in mentioned table illustrated that, LT_{50} and LT_{90} of marsa 24%SC were 5 and 10 d, respectively while and marsa 24%SC with nano additive recorded less little time (2 and 3 d, respectively) than marsa 24%SC alone without additives for *S. littoralis*.

However, when Calazole 2%EC applied on *T. absoluta* without nano additives, LT_{50} and LT_{90} were 5 and 13 d, respectively. While, Calazole 2%EC with nano additive had less little time (2 and 4 d, respectively) than Calazole 2%EC alone without additives for *T. absoluta*. Bingna *et al.* (2018) used nano materials as pesticides and proved that these materials improve the dispersibility and stability of active ingredients, and promote target ability. Mohamed and Lobna (2012) demonstrated the efficacious of several chemicals such as spinosad, abamectin, emamectin benzoate, triflumuron and diafenthiuron against *T. absoluta* and illustrated that the insecticides would continue to be an integral component of pest management programs due mainly to their effectiveness and simple use.

Table 2. The Reducing Treatment Time Effect by adding *nano synthetic surfactant* to Marsa 24% EC, Calazole 2%EC *solutions* against *S. littoralis* and *T. absoluta*.

Pests	Treatment Time/hour(h)	LT_{50} (d)	LT_{90} (d)	Slope
S. littoralis	Marsa 24% SC (LC_{50}=29.2)	5	10	1.914
	Marsa 24% SC (LC_{50}=29.2) + additive	2	3	1.178
T. absoluta	Calazole 2%EC (LC_{50}=0.83)	5	13	2.143
	Calazole 2%EC (LC_{50}=0.83) + additive	2	4	1.781

CONCLUSIONS

In the last few years, the application of nanotechnology in agriculture has grown exponentially. Under environmental conditions, nano formulations able to maintain the stability of the active ingredient, decrease its spread in the environment, and expand its biological activity. But their applications in agriculture remain limited. The pesticide field also requires continued systematic research for the development of improved environmentally responsive, targeted, controlled-release pesticide formulations. Nano formulation are reduced the premature degradation of pesticides, improve their efficacy, and decrease collateral effects towards non target organisms. The use of smart delivery nano pesticides is highly promising as an effective tool for sustainable agricultural development.

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سمية بعض المبيدات الحشرية مع أضافه مادة نانو جديدة ضد اثنين من الآفات حرشفية الأجنحة

نيره سمير المصري، ايمان عوض شحاته و هاله السيد موافى

معهد بحوث وقاية النباتات- الدقى- الجيزة- جمهورية مصر العربية

نباتات الطماطم هي ثاني محصول نباتي مهم يزرع في مصر. تشكل الآفات الحشرية تهديداً خطيراً في إنتاجها من حيث الجودة والكمية. تعد دودة أوراق القطن وحفار أوراق الطماطم (توتا ابسلوتا) من أخطر الآفات على محصول الطماطم. مبيدات الآفات هي أساس الدفاع ضد الكوارث البيولوجية الكبرى ومهمة لضمان الأمن الغذائي الوطني. المواد النانوية تحفز سمية المبيدات. في هذه الدراسة تم تطبيق المبيد الحشري مارسا 24% علي دودة أوراق القطن و كلازول 2% علي حفار أوراق الطماطم (توتا ابسلوتا). كما تم تطبيق كل مبيد مع وبدون إضافة متراكب ملح نانو النحاس. أشارت النتائج إلى أن إضافة ملح النانو يزيد نسبة الموت لكل من الآفات (من 22.45 ، 59.22 إلى 100٪) ويقلل الوقت المميت (10 إلى 3 أيام ، 13 إلى 4 أيام) مقارنة بالمبيدات الخالية من ملح النانو.