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Efficacy of Some Nanoparticles against the Adults of Red Flour Beetle *Triboliumcastaneum* (Herbst) under Laboratory Conditions

Maha S.Khalil[1], Safaa M.Halawa[1], M.M.Azab[1], Sh. Abouelkassem[2]and Amany R.Morsy[1]
(1) Department of Plant Protection, Faculty of Agriculture, Benha University, Egypt.
(2) Department of Plant Protection, Faculty of Agriculture, Alazhar University, Asiut,Egypt.

Abstract

Stored grain insect pests cause high deterioration to grains and seeds in storage, such as weight loss, less germination and reduced nutrition values of grains. In the present study,theefficacyof threenano-particlesnano-malathion, organic nano-silica and inorganic nano-silicawereevaluated by mixing with grains under laboratory conditions against the adults of*Triboliumcastaneum*. (Herbst) (Coleoptera: Tenebrionidae).The results showed that nano-malathion had the highest adverse effect on all parameters after 14 days of treatment. The median lethalconcentrations (LC_{50s}) of organic nano-silica and inorganic nano-silica on adults*of T. castaneum* were2.76 and 0.90% after10 days of treatment, respectively. The lethal concentration (LC_{50}) of nano-malathion was 34×10^{-5}%while the (LC_{50}) of conventional malathion was 0.10% after 3 days of treatment.Inorganic nano silica showed significant inhibitor on the number of *T. castaneum* adult progeny at the lower concentration.

Key words: Malathion, Nano-malathion, Nano-silica,*Triboliumcastaneum*, The median lethal concentration.

Introduction

The red flour beetle, *Triboliumcastaneum* (Herbst,1797) (Coleoptera: Tenebrionidae)) is an important worldwide pest of stored products, it's major secondary pest of stored grainbased products, including maize, rice and wheat, particularly in the tropic regions **(Howe 1965; Gonzalez *et al.* 2013; Sabbour, 2014 and Wagan*et al.* 2016)**. This pest can cause considerable damage to stored grains and completely destroy kernels. Moreover, the product quality is affected by presence of eggs and dead insects, and holes on the grains **(Lu and He 2010)**. The efficient control of stored grain pests has long been the aim of entomologists throughout the world. Synthetic chemical pesticides have been used for many years to control stored grain pests **(Salem *et al.* 2007).**Malathion is the most commonly used, and is a choice in the stored grain in different countries because of its high potency to a wide range of pests and its relatively low toxicity in mammalian **(Flehi-Slim *et al.* 2015; Rezg*et al.* 2010; Wang *et al.*2014)**. Nanotechnology has been considered one of the main technologies of the 21st century. This technology involves design, synthesis, characterization and application of particles or systems with dimensions less than 100 nanometer **(Hoyt and Mason 2008)**.Also, nanoparticles a new generation of environmental remediation technologies that could provide cost-effective solution to some of the most challenging environmental clean-up problems **(Chinnamuthu and MurugesaBoop-Palhi 2009)** and help us to produce new pesticides, insecticides and insect repellent **(Owolade*etal.* 2008).** Also, researchers believe that nanotechnology will revolutionize agriculture including pest management in the near future **(Bhattacharyya *et al.* 2010).**Silica nanoparticles (SNPs) have been evaluated against the cotton leafworm *Spodopteralittoralis***(El-bendary and El-Helaly 2013)**.

Yang *et al.* (2009) expressed that nano-particles loaded with garlicessential oils is efficacious against *Triboliumcastaneum*(Herbst).**Vani and Brindhaa(2013)** used Silica nanoparticles (SNPs)to control stored grain pests *Corcyra cephalonica*.**El-Samahy*et al.* (2014)**studied(SNPs)againstthe lesser grain borer beetle *Rhyzoperthadominica* and the red flour beetle *Triboliumcastaneum*. **Gamal (2018)** tested twonano-particles, silica oxide (SiO_2) and aluminium oxide (Al_2O_3) were used asstored product insect protectants in comparison with malathion as standardreference, by mixing with grains against *Sitophilusoryzae*.The present work was carried out to evaluate the efficacy of three nanoparticles nano-malathion, organic nano-silica and inorganic nano-silica insecticide against the red flour beetle *Triboliumcastaneum*under laboratory conditions.

Materials and methods

Insect used:

The red flour beetle *T.castaneum* (Herbst) (Tenebrionidae, Coleoptera) was used in this study. Tests were performed in the stored product pests Laboratory at the Plant Protection Department, Faculty of Agriculture, BenhaUniversity. The insects were reared in glass jars (approx. 500 ml) containing semi-artificial diet (crushed wheat mixed with yeast (5% w/w). All cultures and experiments were held at 28 ± 2 °C and 65±5 RH with 16 hours light and 8 hours dark. The glass jars were covered with muslin.

Tested Materials:

1-Malathion

Common name: Malathion
Chemical name: O, O dimethyl 1-5 (1, 2dicarboxyelhyl) ethylphos-phorodithioate.
Formula: $C_{10}H_{19}O_6PS_2$
The applied formulation: 57 % EC
Source: Brought from El-Nasr Chemical Industry Co., Egypt

2-Nano-malathion

The applied formulation: 10 % EC
Source: purchased from Nano Way C., Elmaadi, Egypt

3-Silica (SiO_2): and organic nano-silica (nano-SiO_2):

Appearance color: white
Appearance form: powder
Solubility: Dispersion into water or ethanol
Source: purchased from Nano Way C., Elmaadi, Egypt
Avg. Size (TEM): 100 nm

Toxicity test:

Different concentrations of tested materials were mixed with crushed wheat grains to determine their effect on adults of*T.castaneum*. These concentrations were 0.1, 0.05, 0.025, 0.0125, 0.006 and 0.003%(w/w)in the case of malathionand 5×10^{-4}, 2.5×10^{-4}, 1.6×10^{-4}, $1.25\times10^{-4}$and 1×10^{-4}% (w/w) for nano-malathion.Also,different concentrations of organic nano-silica and inorganic nano-silicawere 3, 2.5, 2, 1.5, 1 and 0.5%(w/w)each prepared concentration was added to 10g of treatment crushed wheat grains infested with 30 newly emerged adults (1-2 weeks old) of *T.castaneum*. Experiments were applied injars (500 ml) with three replicates for each treatment and the untreatedcontrol. All replicates were kept at 28+1ºC and65-70 RHfor all treatment and control. Mortality percentages were recorded at 1, 2, 3, 5, 7, 10 and 14 days after treatment. Adults of *Triboliumcastaneum*were removed from the jars after 14 days holdings periods. The insect progeny was inspected after 60 days post-treatment and the reduction in the progeny was calculated according to the following equation:

Reduction % = (No. of adults in control - No. of adults in treatment / No. of adults in control) ×100

Results and discussions

Toxic effect of nano-malathion at different concentrations on the mortality percentage and the reduction in progeny of *T. castaneum* adults is summarized in **Table (1).**The mortalitypercentage increased with increasing concentration and exposure time. The results showed that nano-malathion at the highest concentration of5% exhibitedhighestmortality of100%. Reduction percentages of progenywere increased with increasing concentration. The high reduction was observed with concentration of 5% for nano-malathion 100%.

Data set up in**Table (2)** indicated that the conventionalmalathioncaused high mortality and reduced the number of progeny when the concentration increased compared to control. These data are in agreement with **Ali *et al.* (2007)**and**Abd-El-Salam*et al.* (2015)**, who found that malathion had the highest activity against the all parameters studied of *T. castaneum* adultsmortality, offspring and weight loss percentage.

The LC_{50} values for malathionandnano-malathion on adults of *T. castaneum*are shown in **Table (3).**The calculated lethal concentrations were34×10^{-5} and0.10% for nano-malathion and malathion, respectively. According to these values,nano-malathion was more potent c.a. 300 fold than that ofmalathion against the adults of *T. castaneum*. These results indicated that nano-malathion particles has a promising agent could be used against stored insect in the future.

Table 1. Toxicity of nano-malathion mortality and reduction in progeny of *Triboliumcastaneum* adults at indicated days

Concentration %(w/w)	Accumulative Adult mortality (%) after indicated days							Mean No. of the progeny after 60 days	Reduction in progeny%
	1	2	3	5	7	10	14		
5×10^{-4}	**46.7**	**67.8**	**82.2**	**91.1**	**100**	**-**	**-**	**-**	**100**
2.5×10^{-4}	**42.2**	**54.4**	**65.6**	**78.9**	**85.6**	**94.4**	**97.8**	**13**	**97**
1.6×10^{-4}	**35.6**	**46.7**	**55.6**	**70**	**75.6**	**81.1**	**88.9**	**41**	**90.6**
1.25×10^{-4}	**32.2**	**43.3**	**51.1**	**64.4**	**72.2**	**76.7**	**82.2**	**89**	**79.5**
1×10^{-4}	**28.9**	**37.8**	**45.6**	**61.1**	**66.7**	**67.8**	**75.6**	**124**	**71.5**
Control	**0**	**0**	**0**	**1.1**	**2.2**	**2.2**	**3.3**	**435**	**-**

Table 2. Toxicity of malathion and reduction in progeny of *Triboliumcastaneum* adultsat indicated days

Concentration %(w/w)	Accumulative Adult mortality (%) after indicated days							Mean No. of the progeny after 60 days	Reduction in progeny%
	1	**2**	**3**	**5**	**7**	**10**	**14**		
0.1	**66.7**	**81.1**	**92.2**	**100**	**-**	**-**	**-**	**-**	**100**
0.05	**38.9**	**61.1**	**71.1**	**81.1**	**92.2**	**100**	**-**	**9**	**97.9**
0.025	**35.6**	**55.6**	**60.0**	**65.6**	**74.4**	**82.2**	**87.8**	**51**	**88.3**
0.0125	**27.8**	**47.8**	**51.1**	**58.9**	**65.6**	**75.6**	**80.0**	**93**	**78.6**
0.006	**17.8**	**32.2**	**42.2**	**50.0**	**58.9**	**70.0**	**71.1**	**115**	**73.6**
0.003	**12.2**	**26.7**	**36.7**	**42.2**	**52.2**	**63.3**	**65.6**	**194**	**55.4**
Control	**0**	**0**	**0**	**1.1**	**2.2**	**2.2**	**3.3**	**435**	**-**

Table 3. Comparison of the LC_{50}(w/w) % between nano-malathion and malathion on *Triboliumcastaneum* adults after three days exposure time.

Pesticides	Lethal concentration % (w/w) LC_{50}	LC_{90}	LC_{95}	Slope ± SE
nano-malathion	**34×10^{-5}** **(6×10^{-6} – 175×10^{-4})**	**0.0145** **(0.0028– 0.074)**	**0.080** **(0.016– 0.416)**	**0.50 ± 0.36**
Malathion	**0.010** **(0.003– 0.031)**	**0.575** **(0.189– 1.751)**	**1.805** **(0.593–5.495)**	**0.732 ± 0.24**

The efficiency of both organic nano- silica and inorganic nano-silica were assessed against *T.castaneum*adults under laboratory conditions of 28 ±1°C and 65±5% RH. The results of the effect of organic nano-silica on adult mortality and reduction in progeny *Triboliumcastaneum*are presented in **Table (4)**. Mortality percentage was increased with increase both concentration and prolonged exposure time at all treated treatment.As mortality increased by increasing concentrations and time of exposure to reach 62.2, 60, 58.9, 53.3, 43.3 and 23.3% at concentrations 3, 2.5, 2, 1.5, 1 and 0.5% after 14days, respectively for *T. castaneum*. Reduction in progeny was varied between 92.9 to 65.01%at various tested concentrations of organic nano-silica.These data was in agreement with **El-Samahy*et al.* (2015)** who estimated the efficiency of silica nano particles as mortality percent on stored wheat insects*S. oryzae* and*T. castaneum* under laboratory conditions. The SiNPs mixture showed high protective effect for wheat grains against tested insects by using high concentrations.

Table 4. Efficiency of organic nano- silica against *T. castaneum*adults under laboratory conditions

Concentration %(w/w)	Accumulative Adult mortality (%) after indicated days							Mean No. of the progeny after 60 days	Reduction in progeny %
	1	**2**	**3**	**5**	**7**	**10**	**14**		
3	**15.6**	**27.8**	**35.6**	**41.1**	**52.2**	**57.8**	**62.2**	**20**	**92.9**
2.5	**11.1**	**25.6**	**28.9**	**33.3**	**40**	**50**	**60**	**31**	**89.04**
2	**8.9**	**23.3**	**27.8**	**34.4**	**38.9**	**46.7**	**58.9**	**43**	**84.8**
1.5	**7.8**	**10**	**12.2**	**23.3**	**30**	**36.7**	**53.3**	**54**	**80.9**
1	**5.6**	**8.9**	**11.1**	**16.6**	**23.3**	**28.9**	**43.3**	**68**	**75.9**
0.5	**4.4**	**6.7**	**7.8**	**11.1**	**12.2**	**18.9**	**23.3**	**99**	**65.01**
Control	**1.1**	**1.1**	**2.2**	**2.2**	**2.2**	**3.3**	**3.3**	**283**	**-**

Table 5. Efficiency of inorganic nano-silica against *T. castaneum*adults under laboratory conditions

Concentration (w/w)%	**Accumulative Adult mortality (%) after indicated days**							**Mean No. of the progeny after 60 days**	**Reduction in progeny %**
	1	**2**	**3**	**5**	**7**	**10**	**14**		
3	**24.4**	**55.6**	**66.7**	**78.9**	**85.6**	**88.9**	**100**	**0**	**100**
2.5	**18.9**	**34.4**	**45.6**	**54.4**	**68.9**	**80**	**87.8**	**0**	**100**
2	**15.6**	**32.2**	**37.8**	**48.9**	**61.1**	**65.6**	**77.8**	**18**	**93.6**
1.5	**12.2**	**30**	**35.6**	**53.3**	**56.7**	**61.1**	**65.6**	**29**	**89.7**
1	**10**	**28.3**	**22.2**	**43.3**	**51.7**	**55**	**61.7**	**53**	**81.3**
0.5	**7.8**	**14.4**	**21.1**	**26.7**	**36.7**	**43.3**	**48.9**	**61**	**78.4**
Control	**1.1**	**1.1**	**2.2**	**2.2**	**2.2**	**3.3**	**3.3**	**283**	**-**

The results in **Tables (4 and 5)** indicated thatthe efficiency of both organic nano-silica and inorganic nano-silica against *T. castaneum*adults under laboratory conditions of 28 ±1°C and 65±5% RHaccumulative mortality percentages of *T. castaneum*increased gradually by increasing the exposure time. And the mortality percentage after treatment with organic nano- silica particles at the concentration 3% was higher as it reached 15.6 to 62.2% after one day and 14days, respectively. Also, results showed that the organic nano-silica particles inhibited the number of progeny against *T. castaneum*. The highly reduction in F1 progeny was observed with concentration of 3% for organic nano-silica particles (92.9%). The data in **Table (5)** showed that the differences in the mortality percentages of *T. castaneum*among treatments, as recorded one day and 14days, increased gradually by increasing the concentration and exposure time of inorganic nano-silica particles. The number of mortality was higher as it reached 24.4 to 100% after one day and 14 days at concentration of 3%, respectively. The results revealed that the inorganic nano-silica particles inhibited the numberof progeny against *T. castaneum*. Completely reduction in progeny was recorded with concentration of 3%.

Table 6. Comparison of the LC$_{50}$ (w/w) % between organic nano- silica and inorganic nano- silica on *Triboliumcastaneum*adultsafter ten days exposure time.

Materials	**Lethal concentration% (w/w)**			**Slope ± SE**
	LC$_{50}$	**LC$_{90}$**	**LC$_{95}$**	
Organic nano silica	**2.76 (1.58 – 4.81)**	**23.69 (13.60 – 41.29)**	**43.58 (25.01 – 75.94)**	**1.37± 0.12**
Inorganic nano silica	**0.90 (0.55 – 1.482)**	**6.26 (3.81 – 10.27)**	**10.84 (6.61 – 17.79)**	**1.55± 0.11**

Data in **Table (6)**revealed that the values of the calculated lethal concentrations were less in inorganic nano-silica than that of organic nano- silica which LC$_{50}$ and LC$_{90}$ values were 0.90, 6.26and 2.76, 23.69% for inorganic nano silicaand organic nano silica, respectively.

These data were similar to **Rouhani *et al.* (2012)** who found that the presence of nano-silica and nano-silver resulted 100 and 75% mortalityfor adults of*Callosobruchusmaculatus* at the highest concentration of 2.5 g kg-1 on day 14, respectively. Also, **Ali *et al.* (2017)** found that the effect of nano-silica on the mortality percentages of *C. Chinese*. when the unsexed adults were exposed to broad bean seeds treated with different concentrations of both tested silica types (0.5, 1.0 and 2.0 g/100 g seeds) for different periods (48, 96, 144 and 192 hrs.), it was found that NPS pronounced more insecticidal activity against the bruchid beetle *C. chinesis*.

The present study is clarified that nano- practical's especially nano-SiO$_2$ can be effective used to control insectpests.Also, **Abd-El-Salam*et al.* (2015)**found that malathion achieved the highest effect on mortality of progeny and weight loss against *T. castaneum* as compared with Al$_2$O$_3$and ZnOnano-particles. In addition, they indicated that Al$_2$O$_3$ had higher effect than ZnOagainst T. *castaneum*. **Ebeling and Wagner (1959)** proposed that insecticidal efficacy of the dust became enhanced if the particles are finally divided. Damage occurs to the insect protective wax coat on the cuticle, by sorption and abrasion. **Debnath*et al.*(2011)** demonstrated that the insect began to lose water due to damage of the water barrier.**Eveling (1971)** found that the insects die due to desiccation. This hypothesis for the physical mode of action makes the case in the use of nanocides stronger and the nanocides can be removed byconventional milling process unlike spray ableformulations of conventional pesticide leaving residues on the stored grain. Therefore, silica and aluminum oxides nano-particles have a good potential to be used as grainprotecting agent and alternatives to conventionalchemical insecticides.

Conclusion

The insecticidal activity of the two types of nano-silica and nano-malathionagainst *T. castaneum*indicated the potential use of these nanoparticles as a new technology for insecticidal materials. Insecticidal activity was confirmed in nano-particles, although the results showed that the two types of nano-silica and nano-malathion varied in their effectiveness against *T. castaneum*nano-malathion had the highest effect, followed by inorganic nano-Sio_2 andorganic nano-Sio_2. The ability of using inorganic nano-Sio_2 and organic nano-Sio_2as alternatives to the chemical control of *T. castaneum*(stored grain insect pests) is possible. This approach can help reduce the amount of insecticides applied and subsequently minimize its hazards to human health and environment. Nanoparticles are promising and require some improvement in their physical properties. Further research is needed to identify its mode of action, its non-target toxicity and to determine the potential of other nano-structured materials as pest control options for insects.

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فاعليه بعض جزيئات النانو ضد خنفساء الدقيق الصدئيه تحت الظروف المعمليه

مها سعيد خليل[1], صفاء محمود حلاوه[1], محمد محمد عزب[1], شريف ابو القاسم احمد[2], امانى رشوان مرسى[1]

(1) قسم وقايه النبات – كليه الزراعه – جامعه بنها

(2) قسم وقايه النبات – كليه زراعه اسيوط – جامعه الازهر

تسبب حشرات الحبوب المخزونه الكثير من المشكلات للحبوب و البذور المخزونه, مثل خساره الوزن, قله انبات البذور وكذلك قله القيمه الغذائيه للحبوب. أجرى هذا البحث بهدف تقييم ثلاثه من جزيئات النانو(نانوملاثيون , نانو سيليكا عضويه و نانو سيليكا غير عضويه) تحت الظروف المعمليه كمبيدات لحشرات الحبوب المخزونه مقارنه بالملاثيون التقليدى , وذلك عن طريق خلطها بالحبوب ضد الحشرة الكاملة لخنفساء الدقيق الصدئيه. وقد اوضحت النتائج ان النانو ملاثيون كان اعلى تاثيرا فى كل المعاملات بعد 14 يوم من المعامله .وكان التركيز اللازم لقتل 50% من التعداد للسيليكا العضويه و الغير عضويه 2.76 و 0.90 % بعد 10 ايام على التوالى. وكان التركيز اللازم لقتل 50% من التعداد فى حاله الملاثيوم التقليدى 0.10% بعد 3 ايام , بينما كانت 34×10^{-5} % فى حاله النانو ملاثيون. وكان للسيليكا غير العضويه تاثير هام فى تقليل عدد الحشرات فى النسل الناتج عند التركيزات المنخفضه منها.