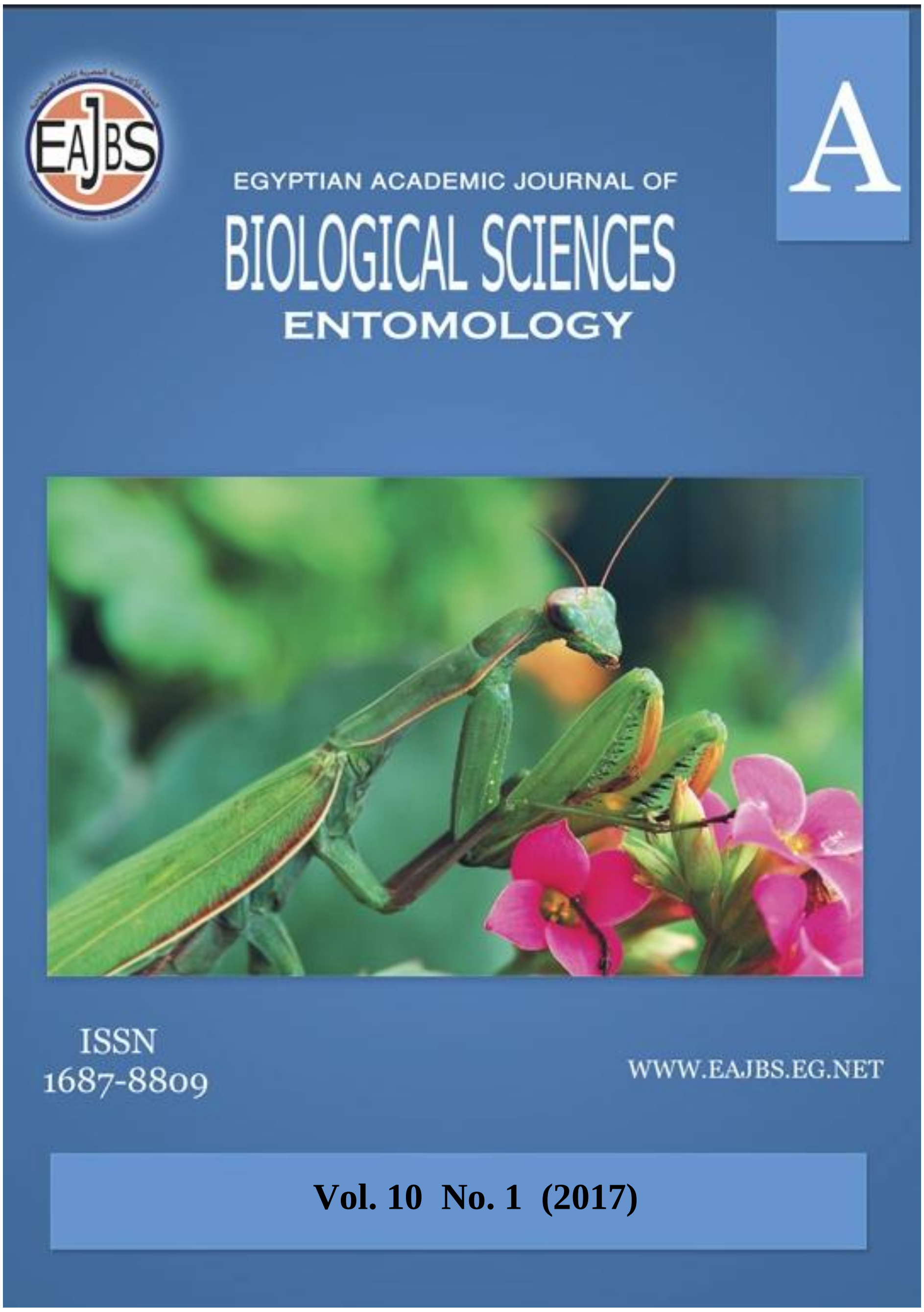

Egyptian Academic Journal of Biological Sciences is the official English language journal of the Egyptian Society for Biological Sciences, Department of Entomology, Faculty of Sciences Ain Shams University.
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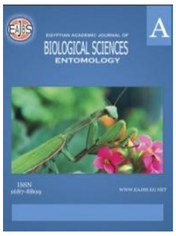
www.eajbs.eg.net

Citation: *Egypt. Acad. J. Biolog. Sci. (A. Entomology) Vol. 10(1)pp: 9- 16 (2017)*

Egypt. Acad. J. Biolog. Sci., 10(1): 9–16 (2017)

Egyptian Academic Journal of Biological Sciences
A. Entomology

ISSN 1687- 8809
www.eajbs.eg.net



The Effect of Silica Nano-particles on Some Biological Aspects of *Callosobruchus Maculatus*

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ARTICLE INFO
Article History
Received:17/12/2016
Accepted: 18/1/2017

Keywords:
Biological parameters
Callosobruchus maculatus
hydrophilic nano-silica

ABSTRACT

This study aimed to evaluate the efficiency of hydrophilic silica nano-particles at 500 ppm concentration compared with recommended chemical insecticide "Malathion" against *Callosobruchus maculatus* Fab. (Coleoptera: Chrysomelidae) under laboratory stored conditions. *C. maculatus* is a major pest of cowpeas in Egypt. Hydrophilic silica-nano-particles showed that the number of *C. maculatus*, mortality were 99 ± 1.2, 96 ± 3.2, 100 ± 0.0 and 100 ± 0.0 % six, four, two months and zero time post treatment; respectively, reduced to 5 ± 4.2, 12 ± 6.2 , 24 ± 3.2 and 63 ± 1.2 in case of using Malathion. Biological parameters revealed decrease of egg number and seed damage % with hydrophilic silica nano-particles. This investigation recommends Silica nano-particles as an effective matter in control *C. maculatus* under laboratory condition with low damage in cowpea seeds. Also, we need more study on the effect of using different degrees of temperature during using silica nanoparticles on pest suppression.

INTRODUCTION

Cowpea, Vigna unguiculata (L.) Walpers is an important legume crops in Egypt and in many African regions Coudert, (1984); Greenhalgh, (2000), because it provides protein, vitamins, amino acids, and minerals Odah, (1995). It is very well known that cowpea plant highly acceptable to insects thus produces low crop yields Latunde-Dada, (1990). Seed yield loss in cowpea during storage due to bruchids (seed beetles) considered as serious problem Rees, (2004). *Callosobruchus maculatus* Fab. (Coleoptera: Chrysomelidae), is a major pest of economically important leguminous grains especially cowpeas Appleby & Credland, (2003) and (2004). Adults typically lay their eggs on the surface of pods or dehisced seeds in the field before or around the time of harvest Caswell, (1968); Germain *et al.,* (1987). The pest causes maximum damage during February to August Anton *et al.* (1997); Tuda *et al.* (2005).

These eggs are later brought unnoticed into seed stores, where the protected environment results in rapid insect development and population growth. The ability of C. *maculatus* to multiply fast under storage conditions Adugna (2006). Nano-particles associated with their atomic strength possess distinct physical, biological and chemical properties Leiderer and Dekorsy, (2008). They can be arranged or assembled into ordered layers Ulrichs *et al.,* (2006). Thus nanotechnology deals exhibit different physical strength, magnetic properties chemical reactivity and electrical conductance Nykypanchuk *et al.,* (2008).

Nanotechnology, a promising field expected to give technical innovations in the future.

Nowadays, nanotechnology has being embraced pest control Harper (2010) and has a potential to revolutionize different groups of nano-pesticide overcome like insecticides, fungicides, herbicides Matsumoto *et al.* (2009), Niemeyer and Doz (2001), Leiderer and Dekorsy, (2008). However, food without insecticide residues, worker safety, insect resistant, and deregistration of current synthetic insecticides are several reasons to search for alternatives Prakash & Rao, (1997). Currently, there are many chemicals that are toxic to stored-grain pests, including insecticides such as organophosphates, pyrethroids and fumigants such as methyl bromide and phosphine Park *et al.,* (2003) and Kljajic and Peric, (2006). These chemicals are effective for pest control but have several problems to users Okonkwo and Okoye, (1996). Nano-silica against different insect species showed up to complete mortality Debnath *et al.,* (2010). Nano-pesticides and nano encapsulated pesticides are expected to reduce the volume of application and slow down the fast release kinetics. Niemeyer and Doz (2001), Leiderer and Dekorsy, (2008). Mode of action occur destruction of the natural water barrier, the waxy layer of the cuticle Leiderer and Dekorsy, (2008). Nanotechnology gives major impulses to technical innovations in the future Leiderer and Dekorsy, (2008) Subramanyam and Roesli (2000). The chemistry of silica provides the functionalization opportunity for a variety of surface Banerjee and Santra, (2009). This investigation focused on the effect of hydrophilic silica nano-particles as a possible alternative in controlling *C. maculatus* and their effectiveness under stored conditions. Finding new safe nanocide will have a significant impact on the development and implementation of effective, long term and Sustainable control method against *C. maculatus* especially or other bruchids species.

MATERIALS AND METHODS

Insects rearing: *C. maculatus* was collected from infested cowpea obtained from reared culture at Plant Protection Institute, Dokki, Egypt in glass jars under laboratory conditions of 30°C±1°C, 75±5% relative humidity (RH) in continuous darkness. Winston and Bates (1960), 2-3 day old were used for the experiments.

Nano-particles: Hydrophilic silica nano-particles was prepared following the method described described by Zang and Pinnavaia (2010) via nano Tech Company 6th October City Egypt, funded by Faculty of Agriculture Cairo University.

Malathion: Common name: Malathion. Via Shora company for agricultural products. Chemical name: O, O dimethyl - S - (1, 2 dicarboxyethyl) Ethylophosphorodithioate. Formula: $C_{10}H_{19}O_6PS_2$.

Bioassay: The effect of the tested Hydrophilic silica nano-particles was tested as a cumulative mortality during (1, 2, 3, and 4th day post treatment) at four periods post treatments zero time, two, four and six months. Glass petri dishes (12 cm in diameter) were used in bioassay experiment on *C. maculatus*. Fifty grams of cow pea was placed in each plate. Cow pea seeds were treated either with 500 ppm hydrophilic silica nano-particles or 1gm/kg. Malathion as a recommended pesticide Salem *et al.* (2015). Then, the plates were shaken manually Subramanyam and Roesli (2000). In one additional set, no nano-particles were mixed with cowpea, and this set served as control. The plates were examined daily till 4th day where10 unsexed adults were introduced into each plate. All bioassays were performed at 29 ± 1 ºC, 65 ± 5 % R.H.

Biological aspects: persistent effect was studied, hydrophilic silica nano-particles 500 ppm and Malation 1gm/kg. at zero time, two, four and six months Following exposing to treatment, two pairs of newly emerged cowpea (2-3 day old) were placed in a jar and were observed for egg lying till adult emergence Abd El-Aziz, (2000) besides Weight loss and seeds damage were recorded.

Data analysis: The data were analyzed using two-way ANOVA; software version R 2.8.1, Means were separated by using the Tukey-Kramer test, at P=0.05.

RESULTS AND DISCUSSION

Results showed that used silica nano-particles at 500 ppm, caused mortality 99 ± 1.2, 96 ± 3.2, 100 ± 0.0 and 100 ± 0.0 % in the fourth day (six, four, two months post treatment and zero time ; respectively, reduced to 86 ± 1.3, 89 ± 1.3, 87 ± 1.2 and 91 ± 3.2 % for the third day and to 57 ± 0.0, 69 ± 0.0, 72 ± 0.0 and 77 ± 4.2 for the second day and gave its minimum % of mortality one day after where it was 22 ± 1.4, 27 ± 1.5, 26 ± 1.2 and 29 ± 1.2 while the mortality % decreased gradually with post treatment extension in periods with no significant difference between results in the first, second, third or fourth day post investigation in tested periods Table (1) and Fig. (1).

Table 1: Mean mortality % among *C. maculatus* adults exposed to Malathion 1gm/kg. and nano-silica hydrophilic 500 ppm at three periods post investigation.

Different experimental periods post treatment		**Death % among treated and untreated adults**			
		First day	Second day	Third day	Fourth day
Zero time	**Control**	0 ± 0.0	3 ± 2.3	0 ± 0.0	1 ± 2.2
	Malathion	55 ± 1.1	61 ± 4.6	61 ± 1.1	63 ± 1.2
	Nano-silica	29 ± 1.2	77 ± 4.2	91 ± 3.2	100 ± 0.0
Two months later	**Control**	0 ± 0.0	0 ± 00	4 ± 1.7	0 ± 0.0
	Malathion	22 ± 1.3	23 ± 2.5	23 ± 6.2	24 ± 3.2
	Nano-silica	26 ± 1.2	72 ± 0.0	87 ± 1.2	100 ± 0.0
Four months later	**Control**	0 ± 0.0	1 ± 2.1	0 ± 0.0	0 ± 0.0
	Malathion	11 ± 1.1	11 ± 1.2	12 ± 1.4	12 ± 6.2
	Nano silica	27 ± 1.5	69 ± 0.0	89 ± 1.3	96 ± 3.2
Six months later	**Control**	0 ± 0.0	0 ± 0.0	0 ± 0.0	4 ± 5.3
	Malathion	3 ± 1.2	4 ± 0.2	4 ± 1.7	5 ± 4.2
	Nano-silica	22 ± 1.4	57 ± 0.0	86 ± 1.3	99 ± 1.2
P		0.0001	0.0001	0.0001	0.0001
F		23.62	24.66	211.46	324.34
LSD		7.22	7.99	8.33	8.67

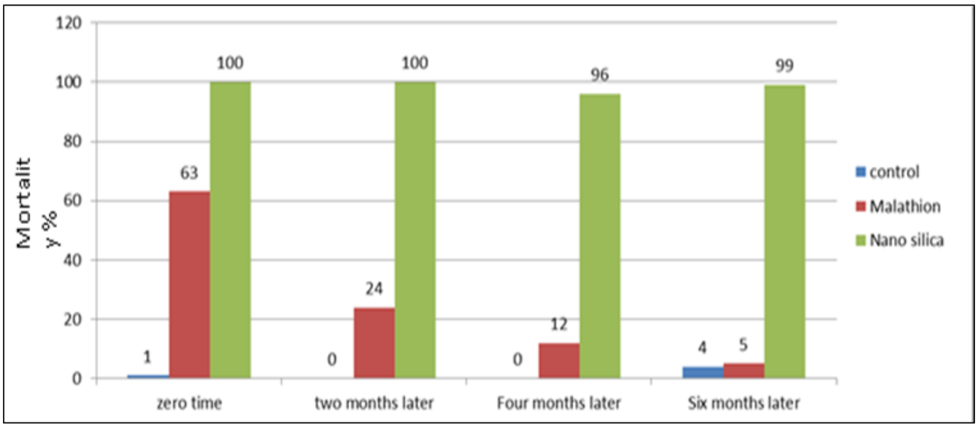

Fig. 1: Mean mortality % among *C. maculatus* adults exposed to Malathion 1gm/kg. and nano-silica hydrophilic 500 ppm six months post investigation.

Egg number increased gradually with period extension at either Malathion or hydrophilic silica nano-particles but more rapidly in case of pesticide, the same relation was found in egg number/ seed. Figs. (2, 3) and Table (2).

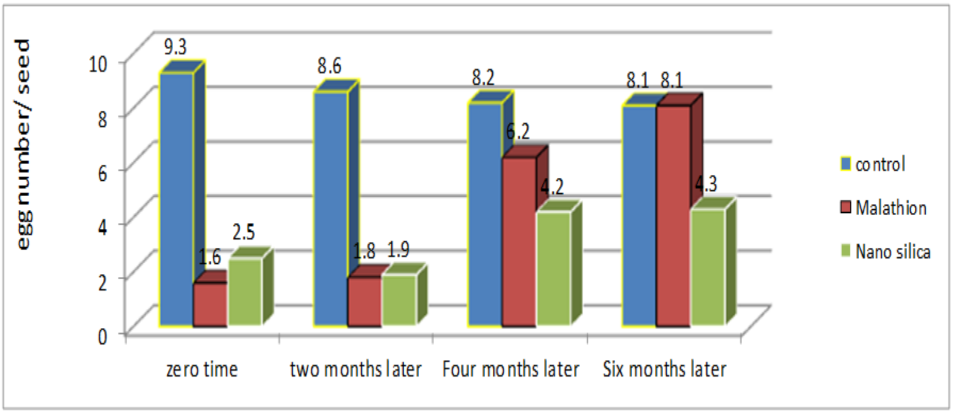

Fig. 2: Egg number/seed among *C. maculatus* adults and weight loss to Malathion 1gm/kg. and nano-silica hydrophilic 500 ppm at three periods post investigation.

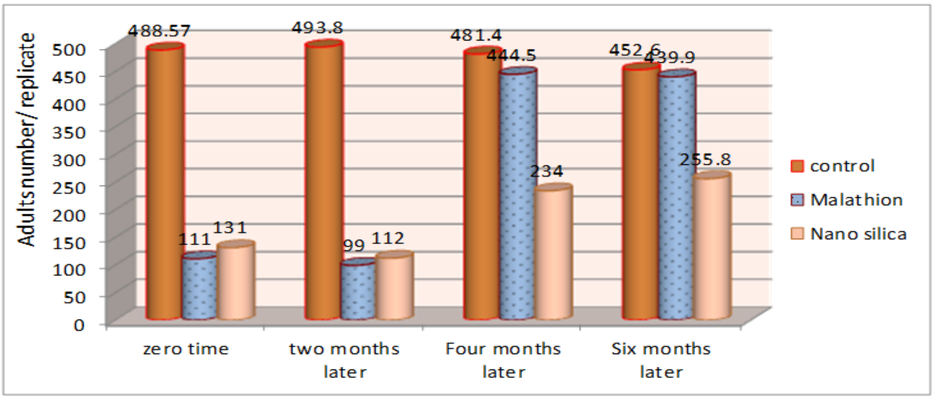

Fig. 3: Adult's number / replicate among *C. maculatus* adults and weight loss to Malathion 1gm/kg and nano-silica hydrophilic 500 ppm at three periods post investigation.

Table 2: Egg number/seed and Adults/replicate *C. maculatus* adults and weight loss % and damaged seeds % among cowpea seeds exposed to Malathion 1gm/kg. and nano-silica hydrophilic 500 ppm at three periods post investigation.

Different experimental periods post treatment		**Tested parameters**			
		Egg number/seed	Adults / replicate	weight loss %	damaged seeds %
Zero time	**Control**	9.3± 0.5	488.5 ± 25.7	44.82 ± 3.5	100 ± 0.0
	Malathion	1.6 ±0.6	111 ± 14.3	6.5 ± 1.0	34.6 ± 2.5
	Nano-silica	2.5 ± 0.5	131 ± 35.1	6.3 ± 0.5	25.7 ± 1.0
Two monthlater	**Control**	8.6 ± 2.2	493.8 ± 45.9	55.5 ± 3.4	100 ± 0.0
	Malathion	1.8 ± 0.7	99 ± 22.5	11.3 ± 3.2	45.3 ± 3.7
	Nano-silica	1.9 ± 1.3	112 ± 11.9	12.6 ± 1.7	22.4 ± 0.0
Four montlater	**Control**	8.2 ± 1.1	481.4 ± 19.9	49.7 ± 0.6	100 ± 0.0
	Malathion	6.2 ± 3.1	444.5 ± 23.5	39.5 ± 2.5	32.1 ± 1.2
	Nano-silica	4.2 ± 1.3	234 ± 21.7	23.45 ± 4.3	26 ± 3.2
Six months later	**Control**	8.1 ± 3.7	452.6 ±13.1	48.9 ± 0.6	100 ± 0.0
	Malathion	8.1 ± 2.5	439.9 ± 29.6	43.8 ± 1.1	52.7 ± 3.2
	Nano-silica	4.3 ± 1.9	255.8 ± 0.0	22.3 ± 2.3	29 ± 1.6
P		0.0001	0.0001	0.0001	0.0001
F		111.34	66.79	53.22	62.11
LSD		3.6	76.44	8.11	12.3

Weight loss show near % at all experimented periods where it gave 44.82, 55.5, 49.7 and 48.9 % with zero time, two, four and six months post treatment; respectively where decreased to 6.5, 11.3, 39.5 and 43 % with Malathion, the percentage decreased significantly with hydrophilic silica nano-particles where it gave 6.3, 12.6, 23.4 and 22.3 % at the same previous tested periods. Fig. (4) and Table (2).

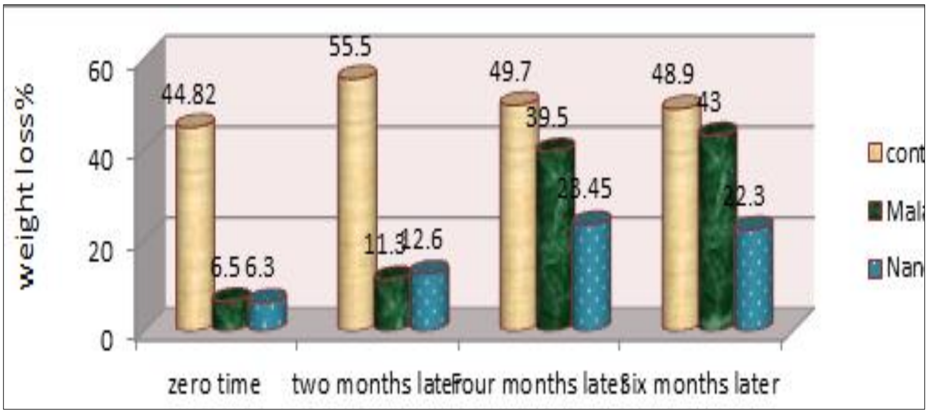

Fig. 4: weight loss % among cowpea seeds exposed to Malathion 1gm/kg. and nano-silica hydrophilic 500 ppm at three periods post investigation.

All control seeds treatment were completely damaged with 100 % at all tested periods (Fig. 5) where the damage increased to 34.6, 45.3, 32.1 and 52.7 % with Malathion and reached its lowest levels 25.7, 22.4, 16 and 29 % with hydrophilic silica nano-particles treatment. (Fig. 5 and Table 2).

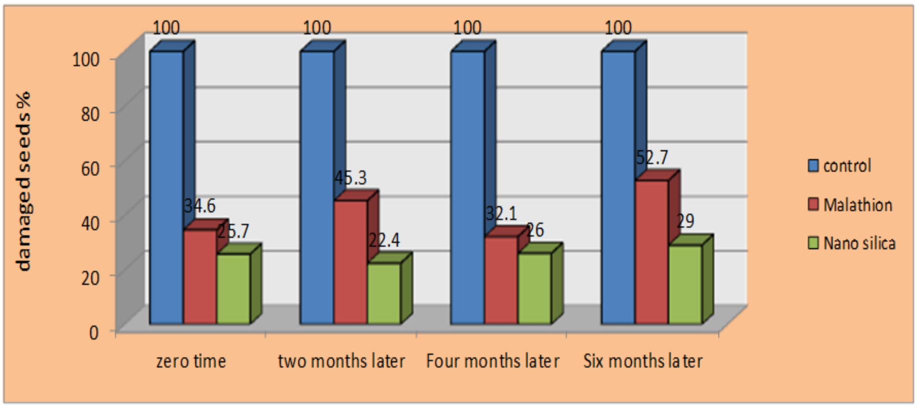

Fig. 5: Damaged seeds % among cowpea seeds exposed to Malathion 1gm/kg. and nano-silica hydrophilic 500 ppm at three periods post investigation.

Nano-materials including polymeric nano-particles, iron oxide nano-particles, gold nano-particles, and silver ions have been exploited as pesticides. Al-Samarrai (2012) pest management (Bhattacharyya *et al.,* (2010) larvicidal Jayaseelan *et al*., (2011) Helicoverpa armigera control Vinutha *et al.,* (2013). Our team tested three types of nano-silica El-bendary and El-Helaly (2016), 500 ppm silica hydrophilic found to be the best concentration used which agreed with our previous report when we applied SNP against Spodoptera littoralis on tomato plants El-bendary and El-Helaly (2013) nano-silica has wide range of applications at several branches of science as industries Iler (1979) Naturally occurring silica is considered to be safe for human consumption. International Agency for the Research of Cancer has already approved the use of amorphous silica as safe Stathers (2004). The application of higher dose of nano-silica was very effective as direct application which agreed with Ulrichss *et al*. (2006).

Our gained results were in the same trend with Nel *et al.* (2006), Lin *et al*. (2006), Li *et al.,* (2008) Sayes *et al.,* (2005) and Leiderer and Dekorsy, (2008). Consequently, increase of time led to increase in its mortal effect which agrees with Beyersmann (2012). So the present paper recommends nano-material as a probable control method to cow pea important pest.

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ARABIC SUMMERY

تأثير حبيبات السيلكا النانومترية على العمليات البيولوجية لحشرة خنفساء اللوبيا

حلمى محمد البندارى
قسم وقاية النبات - كلية الزراعة - جامعة الفيوم - مصر

أستهدفت هذة الدراسة تقدير الكفاءة والفاعلية الحيوية لجزيئات السيلكا النانوميترية المحبة للماء وذلك عند تركيز ٥٠٠ جزء فى المليون ومقارنتها بالمبيد الموصى بإستخدامة (مسحوق الملاثيون ١%) لمكافحة أفة خنفساء اللوبيا كأحد أهم الأفات التى تصيب الحبوب والمواد المخزونة وتعتبر أفة رئيسية من الأفات التى تصيب حبوب اللوبيا فى مصر، وتمت هذة الدراسة تحت الظروف المعملية والتخزينية.

وقد أوضحت النتائج: الى أن جزيئات السيلكا النانومترية أدت الى إرتفاع نسبة الموت الى ٩٩±١,٢، ٩٦±٢,٣، 100±00، 100±00، وذلك عند بدء المعاملة وبعد المعاملة بشهرين (60 يوم) ثم لمدة أربعة شهور (120 يوم) ولمدة ستة شهور (180 يوم) على التوالى. ومن الملاحظ أن نسب الموت إنخفضت الى 5±4.2، 12±6.2، 24±3.2، 63±1.2 وذلك عند إستخدم مبيد مسحوق الملاثيون 1% والموصى بإستخدامة لمكافحة هذة الأفة مقارنة بحبيبات السيلكا النانومترية عند نفس المدد والفترات الزمنية للمعاملات.

كما أن الدراسات البيولوجية أظهرت إنخفاض فى عدد البيض الذى قامت الحشرة بوضعة على الحبة الواحدة وكذلك أنخفاض نسبة فساد وتلف الحبوب عند أستخدام جزيئات السيلكا النانومترية مقارنة بالمبيد الموصى بإستخدامة.

وهذا البحث يوصى بأهمية إستخدام حبيبات السيليكا النانومترية كأحد البدائل الطبيعية المستخدمة فى مجال مكافحة الأفات وخاصة أفات الحبوب المخزونة ومنها حشرة خنفساء اللوبيا مجال الدراسة. ونوصى بدراسات مستقبلية لدراسة الكفاءة والفاعلية الحيوية لهذة المادة تحت ظروف تخزينية حرارية مختلفة.