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ALUMINUM AND ZINC OXIDES NANOPARTICLES AS A NEW METHODS FOR CONTROLLING THE RED FLOUR BEETLES, *Tribolium castaneum* (HERBEST) COMPARED TO MALATHION INSECTICIDE.

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ABSTRACT

Among the red flour beetles, *Tribolium castaneum* (Herbest) is a cosmopolitan and serious pest of cereal grains and their products. Undoubtedly, the excessive use of pesticides and chemical compounds led to a lot of diseases to humans, animals and the environment, in addition to high costs. In the present study two nanoparticles, Aluminum oxide (Al_2O_3) and Zinc oxide (ZnO) were used as stored product insect protectants compared to malathion as standard reference. Results obtained cleared showed that malathion had the highest adverse effect on the all parameters studied of *T. castaneum* adults viz, mortality , offspring and weight loss percentage. Data obtained indicated that the increasing of concentration and exposure period caused increasing in mortality (%) and decreasing in weight loss (%).Also results accentuated that the two nanoparticles (Al_2O_3 and ZnO) significantly inhibited the number of progeny and weight loss (%) and the concentration of 2 g/kg wheat grain had the highest effect based on the LC_{50} values ZnO was had the most effect compared to Al_2O_3 nanoparticles.

Finally, although malation was the premier, the present study suggest to use Al_2O_3 and ZnO nanoparticles in integrated pest management programs as alternative to chemical insecticides where they are considered safe for humans if compared with synthetic insecticide.

INTRODUCTION

Post-harvesting grain crops are exposed to many insect pests that cause loss in quantity in addition to low quality. Among the red flour beetles, *Tribolium castaneum* (Herbst) is a cosmopolitan and serious pest of cereal grains and their products. Adult beetle and larva feed on stored food stuffs viz. dry fruits, pulses, bran, coat, germ, grain dust and prepared cereal foods. (Atwal, 1976; Hamed and Khattak, 1985; Khattak *et al.*, 1999; Dars *et al.,* 2001). This insect is unable to feed on intact grains, however, it does considerable loss to grains damaged by other insects and flour and other products (Li and Arbogast, 1991). In case of serious infestation, the flour turns yellowish and mouldy, has a pungent, disagreeable odour and becomes unfit for human consumption (Atwal, 1976).

This loss in weight and quality could be prevented either by use of pesticides or by non-chemical methods. Chemical methods involve the use of synthetic insecticides in most parts of the world.

Reacting to the disadvantages of using traditional chemical pesticides was the need to use modern methods of combat such as nanotechnology.

Nanotechnology, the process to generate, manipulate, and deploy nanomaterials, represents an area holding significant promise for the agricultural scenario (Baruah and Dutta, 2009; Navrotsky, 2000; Kuzma, 2007). Nanotechnology employs nanoparticles (NPs) having one or more dimensions in the order of 100 nm or less (Auffan *et al.,* 2009). Other authors refer to NPs as colloidal particulate systems with size ranging between 10 and 1000 nm. Nanomaterials hold great promise regarding their application in plant protection and nutrition due to their size-dependent qualities, high surface-to-volume ratio and unique optical properties. A wide variety of materials are used to make NPs, such as metal oxides, ceramics, silicates, magnetic materials, semiconductor quantum dots (QDs),lipids, polymers, dendrimers and emulsions (Niemeyer and Doz, 2001; Oskam, 2006; Puoci *et al*., 2008).

The aim of this study was to investigate the entomotoxicity of Aluminum oxide (Al2O3) and Zinc Oxide (ZnO) nanoparticles compared to malathion against *T. castaneum* (Herbest) under laboratory conditions.

MATERIALS AND METHODS

Synthesis of Aluminum oxide (Al_2O_3) nanoparticles

Chemical routes for production of these materials Include sol–gel, hydrothermal processing and control precipitation of boehmite obtained from aluminum salts, alkoxides and metallic Powders. Gamma alumina nanoparticles was prepared by sol gel method using aluminium nitrate precursor and ammonium carbonate route possess spherical nano-sized particle (Ruihong et al., 2006 and Hochepied et al., 2003). User-sized experiments were 10 ± 2 nm..

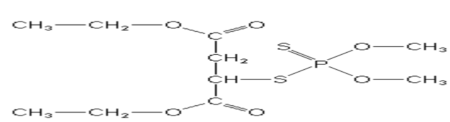
Synthesis of Zinc Oxide (ZnO) nanoparticles

ZnO nanoparticles has been prepared as reported by (Beek *et al*.,2005) through the hydrolysis and condensation of zinc acetate dehydrate by potassium hydroxide in alcoholic medium at low temperature condition. The ZnO nanoparticles settled at the bottom and the excess mother liquor was removed and the precipitate was washed with methanol. The precipitate was then dispersed in a mixture of methanol and of chloroform (Seow *et al*., 2009). User-sized experiments were 20±5 nm.

Both compounds were prepared in Nanotech Egypt Company Limited, Cairo, Egypt.(pure 99.99%) and their use in the form of powders concentration 2 , 1 , 0.5 , 0.25 and 0.125 g/Kg crush.

Chemical insecticide:

Malathion



Common name: Malathion

Chemical name: O,O dimethyl-S-(1,2 dicarboxyethyl) Ethylophosporodithioate

Formula: $C_{10}H_{19}O_6PS_2$

Dust (1%) concentration 0.1 , 0.08 , 0.06 and 0.04 g/Kg to compared with both nanoparticles .

Multiplication of *Tribolium castaneum* for the experiment:

The insect's culture was established to supply adequate number of the insects of similar age for the experiments. Sufficient quantities of crushed grains were firstly sieved to remove stone, dust and insects. The crushed grains were then sterilized by freezing for 24:48 h at -18 to 22°C. All crushed grains were maintained in an incubator at a constant temperature of 29 ± 1 °C and 65 ± 5% R.H. for two weeks to obtain equilibration moisture content with this R.H. (Ezz, 1976). Newly emerged of *Tribolium castaneum* adults were introduced into buckets containing the disinfested crushed wheat. Ten days after introduction, adults were removed from each bucket and the containers were observed beginning from 30 days after the insect's introduction for emergence of offspring.

Lethality effect:

Different concentrations of nanoparticles and malathion were admixed with crushed grains to determine their effects. Concentrations of 2,1, 0.5, 0.25 and 0.125 gm. /kg. for nanoparticles and 0.04, 0.06 , 0.08 and 0.1 g/kg of malathion. Each of prepared concentration was added to twenty gm crushed grains infested with 20 newly emerged adults (1-2 weeks – old) of *Tribolium castaneum*. In jars (250 ml) three replicates done for each treatment and the control. All replicates were kept at 27 ± 1 °C and 65 ± 5 % R.H. for all treatments and the control.

Effect on biology, damage and grain weight loss:

The crushed grains were treated with the same concentrations used with the toxic effect method mentioned above. After 15 days of treatment the insects were removed, after 60 days of exposure the emerged insect adults were recorded and the percent of reduction, and grain weight loss were estimated.

Data analysis:

Analysis of variance (ANOVA) procedures in SAS (2008) were used to detect differences between treatment means.

RESULTS AND DISCUSSION

Looking into data obtained in Table (1) show that malathion significantly increased mortality and reduced the number of progeny and weight loss when the concentration increased compared to control. Mortality percentage ranged frm 41.7 to 98.3 after two weeks post treatment at the all tested concentrations of malathion, also the number of progeny reached to 5, 32, 72 and 95 at concentrations of 0.1, 0.08, 0.06 and 0.04 g/kg. , respectively.

Moreover, the percent weight loss decreased from 6.9 to 2.1 % at 0.04 and 0.1 g/kg, respectively.

Table (1): Effect of malathion on mortality, emergency, reduction percentage and weight loss percentages of *T.castaneum* adults.

Con. w/w	% Adult Mortality after		Mean no. f emerged adults	% Reduction of adults	% Weight loss
	1 week	2 weeks			
0.04	41.7	60.0	95	48.1 d	6.9 b
0.06	53.3	73.3	72	63.1 c	4.7 c
0.08	66.7	91.7	32	83.6 b	3.3 d
0.1	81.7	98.3	5	97.4 a	2.1 e
Untreated			195		34

Data illustrated in Table (2), indicated that accumulative mortality (%) of *T. castaneum* increased gradually by increase the period of exposure and scored a higher mortality reached to 30.66±0.33 and 68.66±0.88 individuals after 6 and 15 days for treated with Al_2O_3 nanoparticles at concentration of 2 gm./kg, respectively.

Also the results in Table (2) revealed that the reduction percentages of progeny was increased with the increased of concentration. The highly reduction was observed with concentration of 2 g/Kg for Aluminum oxide (Al_2O_3) nanoparticles (69.06%) for *T.castaneum*. Quite the contrary, the increased of concentration reduced the of number of progeny and weight loss percentage, where recorded that lowest effect on progeny at concentration 2 g/Kg (60.33) individual and also less in weight percentage (4.9 %) at similar concentration.

Table (2): Percent mortality (Mean ± SE) of *T.castaneum* adults treated with Aluminum oxide (Al_2O_3) nanoparticles under store conditions.

Con. (gm./Kg)	Adult mortality % after		No. of emerged after 60 days	% Reduction	% Weight loss
	6 days	15 days			
0.125	7.66±0.33	19.33±0.33	100.34±0.33	48.54	10.4
0.25	10.66±0.33	27.66±0.33	93.66±0.88	54.97	9.3
0.5	18.33±0.33	40.33±0.33	89.33±0.33	54.19	8.7
1	21.33±0.88	51.33±0.33	81.66±0.88	58.12	7.2
2	30.66±0.33	68.66±0.88	60.33±0.33	69.06	4.9

Data illustrated in Table (3), cleared that accumulative mortality (%) of *T. castaneum* increased gradually by increased the period of exposure and the number of mortality scored a higher mortality reached to 34.66±0.33and 69.66±0.33 individuals after 6 and 15 days for treated with ZnO nanoparticles at concentration of 2 gm./kg, respectively.

From Tables (2 and 3) clear to ZnO was more influential than SiO_2 at the all concentrations exposed periods.

Table (3): Percent mortality (Mean ± SE) of *T.castaneum* adults treated with Zinc Oxide (ZnO) nanoparticles under store conditions.

Con. (gm./Kg)	Adult mortality % after		No. of emerged after 60 days	% Reduction	% Weight loss
	6 days	15 days			
0.125	9.66±0.33	20.33±0.33	90.33±0.33	53.67	8.9
0.25	12.66±1.45	29.33±0.66	81.33±0.88	58.29	7.3
0.5	20.33±0.33	42.33±1.21	69.00±0.33	64.51	6.5
1	26.00±1.01	55.33±0.33	59.66±0.33	69.41	4.8
2	34.66±0.33	69.66±0.33	49.33±0.33	74.70	4.3

Also the results in Table (3) revealed that the reduction percentages of progeny were increased with the increase of concentration. The highly reduction was illustrated with concentration of 2 g/Kg for Zinc Oxide (ZnO) nanoparticles (74.70%). Yet, the increased concentration reduced the weight loss percentage from 8.9 at 0.125 g/kg to 4.3% at 2 g/kg crushed wheat.

The LC50 values for Al_2O_3 and ZnO nanoparticles on adults of *T.castaneum* are shown in Table 4. According to these values, adults of *T.castaneum* were more sensitive to ZnO than Al_2O_3 nanoparticles. However, there was not any significant difference between LC50 of ZnO and Al_2O_3 nanoparticles. These results indicated that LC50 decreased with increasing in exposure periods.

Table (4): LC_{50} (g/Kg Seed weight) values of with Aluminum oxide (Al_2O_3) and Zinc Oxide (ZnO) nanoparticles against *T.castaneum* adults after different period:

Day	LC50	Confidence limits		Slope ± SE	Chi square (X2)	P value
		Lower	Upper			
Aluminum oxide (Al_2O_3) nanoparticles						
6	6.04	3.42	17.69	1.17±0.19	4.16	0.24
15	0.82	0.64	1.11	1.11±0.14	0.54	0.91
Zinc Oxide (ZnO) nanoparticles						
6	6.23	3.42	19.61	1.09±0.18	3.02	0.39
15	0.73	0.57	0.96	1.12±0.14	0.13	0.99

It is known that malathion formulation comprise adjuvant materials beside the active ingredient while nanoparticles have no any additive materials where it act only by their natural properties. So, the present study suggests that the distinction of malathion effect may due to the adjuvants. However, the safety of studied nanoparticles on human and its environment make it the best for the control of stored product insects if compared with malathion which cause severe hazards on human and the environment. Also nanoparticles have longer residual activity than malathion which gradually loss its activity, in contrast the activity of nanoparticles increases with the increase of exposure period .in addition to nanoparticles are more persistent than malathion where the act by their natural properties.

Previous researches confirmed that metal nanoparticles are effective against plants pathogens, insects and pests. Hence, nanoparticles can be used in the preparation of new formulations like pesticides, insecticides and insect repellants (Barik *et al*., 2008 ; Gaibhiye *et al.,* 2009 ; Owolade *et al.,* 2008 and Abo Arab *et al*., 2014)

Amorphous nanosilica is obtained from various natural sources like the shell wall of phytoplankton, epidermis of vegetables, burnt pretreated rice hulls and straw at thermoelectric plants and volcanic soil. Amorphous nanosilica displayed promising potential as a biopesticide (Barik *et al*., 2008). The silica NPs were physio-sorbed by the cuticular lipids disrupting the protective barrier and thereby causing death of insects purely by physical means (Barik *et al*., 2008). Use of amorphous silica as a nanobiopesticide is considered safe for humans by World Health Organization (WHO). Debnath *et al.* (2011) observed higher insect mortality from treatment with silica nanoparticles (15–30 nm) than with bulk silica (100–400 nm). The similar efficacy of nanoparticles with different coatings (i.e., with no coating or with hydrophobic, hydrophilic, or lipophilic coatings) indicated a mechanical mode of action that could be enhanced for smaller particles. A second study, however, indicated that silica nanoparticles coated with 3-mercaptopropyltriethoxysilane were more efficient than those coated with hexamethyl disilazane (Debnath et al., 2012), and in this case the effect was not related to size since the former nanoparticles (29–37 nm) were larger than the latter (15–20 nm).Furthermore, surface charged modified hydrophobic silica NPs (3–5 nm) were successfully used to control a range of agricultural insect pests and animal ecto-parasites of veterinary importance (Ulrichs *et al.,* 2006). It was successfully applied as a thin film on seeds to decrease fungal growth and boost cereal germination (Robinson, 2010). Nano-silica may be useful against stored grain, household pests, animal parasites, fungal organisms, worms,etc.

Nano Al_2O_3 and amorphous nano SiO_2 were found to be highly effective and nano ZnO was moderately effective against *Sitophilus oryzae*. But nano Al_2O_3 has deleterious effects on seeds, whereas non crystalline nano SiO_2 has no such adverse effect on rice seeds. Here we present the first report showing that nanocides, especially nano SiO_2 can be effectively used to control insect pests (Leiderer and Dekorsy, 2008). Yang *et al.,* (2009) demonstrated the insecticidal activity of polyethylene glycol-coated nanoparticles loaded with garlic essential oil against adult *T. castaneum* insect found in stored products. It has been observed that the control efficacy against adult *T. castaneum* was about 80 %, presumably due to the slow and persistent release of the active components from the nanoparticles. Goswami *et al*. (2010) studied the applications of different kind of nanoparticles viz. silver nanoparticles (SNP), aluminium oxide (ANP), zinc oxide and titanium dioxide in the control of rice weevil , *Sitophilus oryzae*. In their study they performed bioassay, in which they prepared solid and liquid formulations of the above-mentioned nanoparticles; later, they applied these formulations on rice and kept in a plastic box with 20 adults of *S. oryzae* and observed the effects for 7 days. It was reported that hydrophilic SNP was most effective on the first day. On day 2, more than 90 % mortality was obtained with SNP and ANP. After 7 days of exposure, 95 and 86 % mortality were reported with hydrophilic and hydrophobic SNP and nearly 70 % of the insects were killed when the rice was treated with lipophilic SNP. However, 65 % mortality was observed in case of ZNP (Goswami *et al*.2010).

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أستخدام دقائق اكاسيد الالمونيوم والزنك كطريقه جديده فى مكافحة خنفساء الدقيق الصدئية مقارنة بمبيد الملاثيون

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تعتبر خنفساء الدقيق الصدئيه واحده من أوسع الحشرات انتشارا فى العالم وافه خطيره للحبوب النجيليه ومنتجاتها مما ادى الاستخدام المكثف من المبيدات والمركبات الكيماويه بلا شك الى مجموعه من الامراض للانسان والحيوان والبيئه بالاضافه الى التكاليف العاليه . واستخدمت فى هذه الداسه نوعان من دقائق النانو هما اكسيدى الالمونيوم والزنك كواقيات ضد حشرات المواد المخزونه مقارنه بالملاثيون كمبيد كيماوى حشرى , واظهرت النتائج المتحصل عليها ان مبيد الملاثيون كان صاحب التاثير الضار الاعلى على جميع المقاييس المدروسه وكذا النسبه المئويه للفقد فى الحبوب .

أظهرت النتائج المتحصل عليها زياده فى نسبة الموت وخفض الفقد فى الوزن وذلك مع زيادة التركيز وكذا مع زيادة فترة التعريض للدقائق المستخدمه . ايضا النتائج المتحصل عليها اكدت ان اكسيدى الالمونيوم والزنك فى صوره النانو ادت الى تثبيط معنوى لاعداد الخلفه الناتجه وكذا تقليل الخفض فى الوزن وأن تركيز ٢ جرام / كجم حبوب قمح كان هو الاشد تاثيرا وذلك على اساس التركيز القاتل لـ ٥٠% من الحشرات المعامله .

كما اوضحت النتائج ان اكسيد الزنك كان هو الاشد تاثيرا مقارنه باكسد الالمونيوم . واخيرا بالرغم من تفوق الملاثيون فى هذه الدراسه الا ان الدراسه تقترح استخدام اكسيدى الالمونيوم والزنك فى صورة نانو فى برامج المكافحه المتكامله للافات كبدائل للمبيدات الكيماويه حيث تعتبر امنه للانسان اذا ما قورنت بالمبيدات المصنعه