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IMPACT OF NANOPARTICLE ZINC OXIDE AND ALUMINUM OXIDE AGAINST RICE WEEVIL *SITOPHILUS ORYZAE* (COLEOPTERA: CURCULIONIDAE) UNDER LABORATORY CONDITIONS

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ABSTRACT

Screening test was conducted to evaluate two nanomaterials namely Aluminum and zinc oxides compared to pirmiphos methyl on *Sitophilus oryzae* adults under laboratory conditions. Results showed that aluminum nanoparticles (Al_2O_3) were highly effective agents compared to zinc nanoparticles (ZnO) which had moderately effect against *Sitophilus oryzae*. Insect mortality (%) increased by increasing the period of exposure and level of concentration. Furthermore, the two materials significantly inhibited the number of progeny. The present study suggests to use Al_2O_3 and ZnO as alternatives to chemical insecticides because they are relatively safe for human compared to pirimiphos-methyl which have many disadvantages to human and to environment.

INTRODUCTION

Wheat grain is one of the most important crops for world's population. Losses in wheat grain storage due to insect pests affect food availability for a large number of people.

The application of insecticides and fumigants to control storage insect has led to many problems including the development of insecticide resistance, health hazards especially to mammals, and the risk of environmental contamination (Cox, 2004).

The rice weevil, *Sitophilus oryzae* (L.) (Coleoptera: Curculionidae) is a major pest of stored grains in Egypt. Both adults and larvae feed on whole grains. They attack corn, rice, oats, sorghum and dried beans. It causes extensive losses in the quality and quantity of commercial products as well as it results in deterioration of seeds (Owolade *et al*., 2008).

Nanotechnology is a promising field of research in the present decade and gives opportunities to give impulse to technological innovation in the future. Nanoparticle materials is the most hopeful technology for plant protection against insect pests, recently nanoparticle have shown promise in many fields of agriculture including pest management (Barik *et al*., 2008 and Rahman *et al*., 2009). At near decades, the green revolution would be accelerate by means of nanotechnology (Bahhattachya *et al*., 2010). Nanoparticle materials newly used as pesticides is expected to reduce the volume of application and slow down the fast release kinetics (Leider and Dekorsy, 2008; Edipol *et al*., 2003, Niemeyer and Doz, 2001 and Prez du Luque, 2009). Mode of action depends on destructions of the natural water barrier in the waxy layer of the insect cuticle. Several studies reported the potential of some nanomaterials as insecticides in insect pest management such as nanosilica (Debnath *et al*., 2011 and Barik *et al*., 2012), silver nanoparticle (Ki *et al*., 2007; Arjunan *et al*., 2012 and Marimuthu *et al*., 2011) and aluminum nanoparticles (Stadler *et al*., 2010b, 2012).

Thus, the objectives of the present study were:

- to evaluate the impact of zinc and aluminum nanoparticles against *Sitophilus oryzae* adults.
- to study the effect of these nanoparticles on the biology of *S. oryzae* in comparison with pirimiphos methyl recommended as chemical insecticide.

MATERIALS AND METHODS

Materials:

Insect used:

The adults of rice weevil, *Sitophilus oryzae* (1-2 week old) used in the current study were obtained from laboratory colony, established and reared on wheat seeds (Sakha 91) under constant laboratory conditions of 28$\pm$1^{o}C nd 70$\pm$5% R.H. New adults were selected for the experiments.

Nanoparticles:

Synthesis of zinc and aluminum nanoparticles:

1. Zinc oxide nanoparticles (ZnO):

Synthesis of ZnO nanoparticles were prepared according to Gunalan *et al*. (2011) by dissolving zinc nitrate in distilled water under constant stirring at room temperature, sodium hydroxide solution was added drop by drop. After complete reaction, solution was allowed to settle and the liquid was discarded. The white precipitate formed was washed thoroughly with double distilled water to remove all ions, and then centrifuged at 3000 rpm for 15 min. The obtained precipitation was dried in a hot air oven at 80^{o}C for six hrs. During drying complete conversion of $Zn(OH)_2$ into ZnO took place.

2. Aluminum oxide nanoparticles (Al_2O_3):

Synthesis of Al_2O_3 nanoparticles was prepared according to Rodica *et al*. (2011) by 0.1 M $AlCl_3$ ethanolic solution and adding ammonium hydroxide drop by drop till the gel was formed. The gel was let to maturate for 30 hr at room temperature and then dried to 100^{o}C for 24 hr. The resulting gel were calcined in a furnace for two hr. (heating rate 20^{o}C/min) at temperature values 1200^{o}C at ending Al_2O_3 nanoparticle was formed. The synthesis of the present nanoparticles was performed in faculty of Science, Kafrelsheikh University and laboratory of Plantation Protection Res. Inst., Agricultural Research Center.

Chemical insecticide

Pirimiphos-methyl 0.25%

Chemical name: O-(2 diethyl-amino-6-methyl-pyrimidin-4-Y1) O,O dimethyl phosphorothioate.

Formulation: Powder.

Product by: Starchem for agricultural chemicals.

Bioassay procedures:

Mixing with feeding medium:

Batches of wheat grains (moisture content 13%) were sterilized at 60^{o}C for one hour. Twenty grams of wheat grains in three replicates were weighed in a 250 mL jar, for treatments and untreated (control). The number of treated insects in each replicate was 20 insects. Four levels of nanomaterials and pirimiphos methyl were prepared and admixed with grains to give the required doses. Jars were mechanically shaken for adequate and fixed time to ensure complete mixing process and then covered with muslin cloth tied with a rubber band. Insect mortalities was calculated 1, 2, 3, 7, 15 days post exposure and corrected by using Abbot's Formula (1925).

Effect on offspring:

To study the effect on offspring, mixing method was used as mentioned before and the dead beetles were removed and the experiment was kept under the same conditions till F_1 progeny adults emerged. Inhibition rate (%IR) was calculated as

$$\%IR = (CN-Tn)\ 100/Cn$$

Where:

Cn : is the number of newly emerged insects in the control.

Tn : is the number of insects in the treated jar (Tapondjou *et al*., 2002).

RESULTS AND DISCUSSION

In the current study, two criteria were used for evaluating the toxic effects of Al_2O_3, ZnO and pirimiphos methyl on *S. oryzae* adults; the first was the contact toxicity (mixing with medium) and the second was the effect on new emergence.

Insecticidal activity:

Data obtained in Table 1 reveal the increase in percent mortality with the increase of concentration and period of exposure where mortality % ranged from 10.1 to 18.3 and 30.4 to 53.3 with 0.1 and 0.8 w/w at 3-15 day post-treatment for aluminum oxide. Similar results to were obtained with zinc oxide where the mortality % ranged between 2 and 46.8% from 3 to 15 days of exposure with the all tested levels of concentration. Pirimiphos methyl as a recommended chemical insecticide had the most effect on *S. oryzae* adults compared to ZnO and Al_2O_3 nanoparticles.

The results presented in Tables 1 and 3 obviously showed that Al_2O_3 was the premier in comparison with ZnO nanoparticles based on LC_{50} which ranged from 0.44-0.1 and 0.47-0.15 w/w at 3 and 15 days post-treatment.

Effect on progeny:

Data shown in Table (2) indicated that all rates of concentrations significantly reduced the number of offspring from 193 in control treatment to 66 adults at the concentration of 0.8% w/w of Al_2O_3. The percent of reduction ranged from 49.7 to 67.8% with the all concentrations tested of the two nanoparticles Al_2O_3 and ZnO. Results cleared that Al_2O_3 had an effect on progeny higher than that of ZnO.

Table (1): Impact of nanoparticle materials and pirimiphos-methyl mixed with the media against *Sitophilus oryzae*.

Treatment	Conc% w/w	Periods of exposure (day)				
		1	2	3	7	15
Aluminum oxide (Al_2O_3)	0.1			10.1	16.6	18.3
	0.2			15.3	28.3	33.3
	0.4			18.3	31.7	36.7
	0.8			30.4	36.0	53.3
Zinc oxide (ZnO)	0.1			2.0	3.3	6.1
	0.2			2.0	6.7	13.0
	0.4			7.5	16.0	34.0
	0.8			11.3	27.3	46.8
Pirimiphos - methyl	0.1	38.3	75.0	99.1	100	
	0.2	56.7	78.3	100		
	0.4	85.0	93.7	100		
	0.8	91.3	98.6	100		

Moreover, pirimiphos methyl achieved the highest effect compared to the tested nanoparticles. The results comprised in this study included the following: the all tested concentrations evoked a moderately effects in respect to the studied parameters. However, the effect on progeny had markedly effect higher than that of contact toxicity.

Table (2): Impact of nanoparticle materials and pirimiphos-methyl on progeny (F_1)

Treatment	Conc. % w/w	No. of progeny	% reduction
Aluminum oxide (Al_2O_3)	0.1	94	51.30
	0.2	89	53.89
	0.4	80	58.55
	0.8	62	67.88
Zinc oxide (ZnO)	0.1	97	49.74
	0.2	91	52.85
	0.4	82	57.51
	0.8	66	85.80
Pirimiphos methyl	0.1	87	54.92
	0.2	67	65.28
	0.4	31	83.93
	0.8	3	98.45
Control		193	

Obtained data showed that pirimiphos-methyl significantly increased mortality and inhibited the number of progeny compared to the two nano-particles tested, which had no effect till 48 h post-treatment. These findings are in agreement with those of Abo Arab *et al*. (2014) who reported that malathion increased mortality and reduced the number of progeny of *S. oryzae* or *S. zeamais* compared to nanoparticles (Al_2O_3-ZnO) and control. Also, data obtained indicated that Al_2O_3 had the higher effect against *S. oryzae* compared to ZnO. These results are in accordance with those of Abo Arab *et al*. (2014) who showed that Al_2O_3 caused the highest deterrent effect on both *S. oryzae* and *S. zeamais* compared to titanium oxide (TiO_2) nanoparticle. Also, Salem *et al*. (2015) reported that malathion achieved the highest effect on mortality progeny and weight loss on *T. castaneum* compared to Al_2O_3 and ZnO nanoparticles. In addition, they indicated that Al_2O_3 had an effect higher than that of ZnO on the tested insect. The current study cleared that the tested materials exhibited variant effect on the tested insect *S. oryzae*. Stdlere *et al*. (2010) successfully applied nanoalumina against two stored grain pests *S. oryzae* and *R. dominica* (F.). Insect mortality could be attributed to the impairment of the digestive tract or to surface enlargement of the integument as a consequence of dehydration or blockage of spiracle and trachea.

Ebeling and Wagner (1959) proposed that insecticidal efficacy of the dust becomes enhanced if the particles are finely divided. Damage occurs to the insect protective wax coat on the cuticle, by sorption and abrasion (Debnath *et al*., 2011)

The insects begin to lose water, as the water barrier is damaged (Ebeling, 1971) and die due to desiccation. This hypothesis for the physical mode of action makes the case for the use of nanocides stronger (Debnath *et al*., 2011). Insects are unlikely to become genetically selected or physiologically resistant to such a mechanism of action. However, insects may develop a behavioral response to these particles and avoid contact (Ebeling, 1971).

The nanocides can be removed by conventional milling process unlike sprayable formulations of conventional pesticides leaving residues on the stored grain. Therefore, aluminum and zinc oxides nanoparticles have a good potential as stored grain as well as seed protecting agent and alternatives to chemical insecticides if applied with proper safety applications. Also, one way to minimize the adverse effects of inert dusts is to use a minimum amount that is still effective on insects and choosing a product that is effective at lower rates.

Table (3): LC_{50} values for aluminum oxide, zinc oxide and pirimiphos methyl against *S. oryzae* at different periods

Nanoparticle	Day	LC_{50}	Confidence limit		Slope value
			Lower	Upper	
Aluminum oxide (Al_2O_3)	1	0.00			
	2	0.00			
	3	0.44	0.22	3.18	0.99
	7	0.26	0.13	4.27	0.79
	15	0.10	0.08	0.19	1.19
Zinc oxide (ZnO)	1	0.00			
	2	0.00			
	3	0.47	0.22	10.71	1.89
	7	0.29	0.28	37.41	1.17
	15	0.15	0.14	41.76	1.97
Pirimiphos methyl	1	0.002	0.002	0.003	2.45
	2	0.0009	0.0003	0.001	1.46
	3				
	7				
	15				

Finally, further studies are needed to find out the detailed mechanisms of action of nanocides and evaluate the studied nano-particles on other species under different conditions.

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الملخص العربى

تأثير صغائر أكسيد الزنك وأكسيد الألومنيوم على حشرة سوسة الأرز تحت الظروف **المعملية**

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استهدفت الدراسة تقييم صغائر النانو لأكسيدى الألومنيوم والزنك مقارنة بمبيد البريميفوس ميثيل وذلك على الحشرة الكاملة لسوسة الأرز تحت الظروف المعملية. أظهرت النتائج المتحصل عليها تفوق أكسيد الألومنيوم على الحشرة موضع الدراسة مقارنة بأكسيد الزنك. كما أوضحت النتائج أن النسبة المئوية للموت زادت بزيادة فترة التعرض والتركيز. وبالإضافة إلى ذلك كان للمواد المختبرة تأثير معنوى فى خفض ذرية الجيل الأول للحشرة. وتقترح الدراسة استخدام مركبى صغائر الزنك كبدائل للمبيدات الكيماوية حيث تتمتع بأمان نسبى على البيئة مقارنة بالبريميفوس ميثيل.