Nano-particles: A recent approach for controlling stored grain insect pests

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ABSTRACT

Stored grain insect pests cause high risks to grains and seeds in storage, such as weight loss, less germination and reduced nutrition values of grains. The use of chemical insecticides has become undesirable as they cause a lot of diseases to humans and animals, in addition to their high costs. In the present study, two nano-particles, silica oxide (SiO$_2$) and aluminium oxide (Al$_2$O$_3$), were used as stored product insect protectants in comparison with malathion as standard reference, by mixing with grains against Sitophilus oryzae. The results obtained clearly showed that malathion had the highest adverse effect on all parameters studied of S. oryzae adults. The results obtained indicated that mortality(%) increased and weight loss(%) decreased with increase in concentration and exposure period. Also, the results showed that the two nano-particles (SiO$_2$ and Al$_2$O$_3$) significantly inhibited the number of progeny of S. oryzae adults. In addition, the data showed that SiO$_2$ had the most effect as compared with Al$_2$O$_3$ nano-particles. SiO$_2$ and Al$_2$O$_3$ nano-particles gave good result in this study. Finally although malathion was outstanding, the present study suggest the use of (SiO$_2$ and Al$_2$O$_3$) nano-particles for protecting stored grains as alternative to chemical insecticides because they are relatively safe for human as compared with malathion. Further research is needed in order to obtain information regarding the practical effectiveness and lack of side effects of nanoparticles in protecting stored products.

Key words: Nano-particles, Sitophilus oryzae, wheat, grains.

INTRODUCTION

Insects are one of the basic problems of stored grains all over the world due to the quantitative losses, they cause (Fileds, 2006). 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). This loss in quantity and quality could be prevented either by use of pesticides or by non-chemical methods. Chemical methods involve the use of synthetic insecticides. Reacting to the disadvantages of using traditional chemical pesticides was the need to use a new methods of combat, such as nanotechnology. Nanoparticles represent 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).

Nanoparticles help to produce new pesticides, insecticides and insect repellent (Owolade et al., 2008). Also, researchers believe that nanotechnology will revolutionize agriculture including pest management in the near future (Bhattacharyya et al., 2010). Although there have been numerous studies on the toxic effects of nanoparticles on bacteria, fungi and animal pathogens (Feng et al., 2000; Samuel and Guggennbichler, 2004 and Reddy et al., 2007). Nanotechnology employs nanoparticles having one or more dimensions in the order of 100 nm or less (Auffan et al., 2009). Other researchers 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
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properties (Oskam, 2006; Puoci et al., 2008). Young et al. (2009) expressed that nanoparticles loaded with garlic essential oils is efficacious against Tribolium castaneum (Herbst). Stadler et al. (2010) showed that nano-alumina could be successfully used to control stored grain pests.

The rice weevil, Sitophilus oryzae (L.), and Rhizopertha dominica are major pests of stored grain in Egypt, and have spread worldwide by commerce. Both adults and larvae feed on grains. They attack wheat, corn, oats, rye, barley and cereal. They cause extensive losses in the quality and quantity of commercial products, as well as deterioration of seed viability worldwide (Madrid et al., 1990).

The aim of this study was to investigate the entomotoxicity of silica nanoparticles (SiO$_2$) and aluminum oxide nanoparticles (Al$_2$O$_3$) in comparison with malathion against S. oryzae under laboratory conditions.

MATERIALS AND METHODS

Insect used

The original strains of insect used were obtained from the Department of Stored Product Pests, Plant Protection Research Institute, Sakha Agriculture Research Station. The insect species were tested and their life cycles were identified according to the method described by Badawy and Doraeham (1991).

For the rice weevil, *S. oryzae* (L.) (Coleoptera: Curculionidae), the adults were reared on wheat grains under laboratory conditions of 28+1°C, 70.0+5.0% R.H. The insects were emplaced in glass jars (500 gm); 200 gm wheat grains and 300-400 adult insects. Adults were left for two weeks in order to lay egg in the jars and were then removed. The new adults emergence were collected for use in the tests by sieving the culture.

Insecticides

**Malathion**

Common name: Malathion

Chemical name: O,O dimethyl 1-5 (1,2 dicarboxyethyl) ethylphos-phorodithioate.

Formula: C$_{10}$H$_{15}$O$_8$PS$_2$

The applied formulation: odorless malathion (dust 1% w/w)

Source: Kafr El-Zayat pesticides and chemical co., Egypt.

Nanoparticles

**Synthesis of aluminium oxide (Al$_2$O$_3$)**

The chemical routes for production of these materials include Sol-gel hydrothermal processing and control precipitation of boehmite obtained from aluminum salts, alkoxides and metallic powder. Gamma alumina nanoparticles were prepared by Sol-gel method using aluminum nitrate precursor. Ammonium carbonate route posses spherical nano-sized particle (Ruихong et al., 2006 and Hochepied et al., 2003). User sized experiments was 10+2 nm

Supplier: Nano-tech. Egypt for photo-electronics.

Appearance color: White

Appearance (form): powder.

Solubility: Dispersed in ethanol or water

Avg. Szie (TEM): 10+2 nm

Shape (TEM): Spherical like shape.

**Silica nanoparticles (SiO$_2$):**

Supplier: Nano Tech. Egypt for photo-electronics.

Appearance color: white

Appearance form :powder

Solubility: Dispersion into water or ethanol

Avg. Size (TEM): 40 nm

**Synthesis of silica nanoparticle**

A sequential method has been used, for the first time to prepare monodisperse and uniform-size silica nanoparticles using ultrasonication by sol-gel process. The silica particles were obtained by hydrolysis of tetraethyl orthosilicate (TEOS) in ethanol medium. Rao et al. (2005) and van Helden et al. (1981) reported a pioneering method for the synthesis of spherical and monodisperse silica nanoparticles from aqueous alcohol solutions of silicon alkoxides in the presence of ammonia as a catalyst. Thus different sizes of silica nanoparticles were prepared ranging from 50 nm to 10 µm with a narrow size distribution. The size of particles depends on the type of silicon alkoxide, and the alcohol user sized experiments was 40 nm.

Preparation of grains for experiment

Enough quantities of wheat grains were firstly sieved to remove stone, dusts and insects. The grains were then sterilized by heating at 70°C for one hour, and the wheat grains were left to cool and reabsorb moisture. The sterilized grains were used in this test.

Treating wheat grains against *Sitophilus oryzae*

**Toxic effect**

Different concentration of nanoparticles and malathion were mixed with wheat grains to determine their effect on *S. oryzae*, that is, concentrations 0.1, 0.3, 0.5, 1.0 and 1.5%
w/w gm/kg of nanoparticles and 0.04, 0.06, 0.08 and 0.1% w/w gm/kg of malathion of each prepared concentration was added to twenty gm of treatment wheat grains infested with 20 newly emerged adults (1-2 weeks old) of S. oryzae. Experiments were applied in jars (250 ml) with three replicates for each treatment and the untreated control. All replicates were kept at 28±1°C and 70±5 R.H. for all treatment and control. Mortality percentage was recorded after one and two weeks post-treatment. All obtained results were corrected for natural mortality using Abbott's formula (1925) as follow:

\[
\text{\% correct mortality} = \frac{\text{Mortality \% treated} - \text{Mortality \% of control}}{100 - \text{Mortality \% of control}} \times 100
\]

And was statistically computed as described by Litchfield and Wilcoxon (1949) LC\textsubscript{50}, confidence limit and slope value were calculated after one and two weeks post treatment.

### Biological effect of nanoparticles and malathion

The wheat grains were treated with same concentrations used with the toxic effect methods mentioned above. After two weeks post-treatment, the insect, S. oryzae, was removed. The emerged adults insects were recorded and the percentage reduction was calculated using the following equation:

\[
\text{\% Reduction} = \frac{\text{NEC} - \text{NET}}{\text{NEC}} \times 100
\]

NEC = Number of adult emerging in control.
NET = Number of adult emerging in treatment

### Weight loss %

The weight loss of wheat grains against S. oryzae and R. dominica were determined three months post-treatment by sieving the dusts and insects from the wheat grains. The weight loss of wheat grains was calculated as dry weight loss according to the following equation of Harris and Lindblad (1978).

\[
\text{\% loss} = \frac{\text{Initial dry weight of grains} - \text{dry grains wheat after 3 mont hs}}{\text{Initial dry weight of grains}} \times 100
\]

### Germination tests

The germination tests were accomplished on wheat grains of each treatments according to Qi and Burkholder (1981) with slight modification. Sixty seeds after 3 months post-treatment were divided into three replicates, placed on Petri dishes containing cotton layers (instead of filter paper), soaked with tap water and covered with paper. Grain germination percentages were recorded four days after treatment of wheat grains with water after three months post-treatment according to the following equation:

\[
\text{\% germination} = \frac{\text{No. of seeds germination}}{\text{Total No. of seeds used (60)}} \times 100
\]

### RESULTS

#### Toxicity of malathion, silica and aluminum nanoparticles against S. oryzae

Results obtained (Table 1) showed the tested malathion and nano-particles materials (silica and aluminum) and the mortality percentages of S. oryzae weevil after treatment. Malathion had the most effective treatment against S. oryzae, followed by silica and aluminum nanoparticles with LC\textsubscript{50} (0.04 and 0.03), (0.61 and 0.39) and (0.86 and 0.62), respectively after one and two weeks. The LC\textsubscript{50} values of the tested materials were positively correlated with the time of exposure under all treatments.

The data in Table 2 showed the differences in the mortality percentages of S. oryzae among treatments, as one and two weeks post-treatment, reduction of emerged adults and the loss weight of wheat grains. The mortality percentage increased with increasing concentration and exposure time. The results showed that malathion had the highest concentration of 0.1% gm/kg and highest

### Table 1: Toxicity of different tested materials on S. oryzae at indicated weeks.

<table>
<thead>
<tr>
<th>Total materials</th>
<th>One week</th>
<th>Two weeks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LC\textsubscript{50} (g/kg)</td>
<td>Confidence limits</td>
</tr>
<tr>
<td></td>
<td>Upper</td>
<td>Lower</td>
</tr>
<tr>
<td>Malathion</td>
<td>0.046</td>
<td>0.051 0.038</td>
</tr>
<tr>
<td>Silica nano SiO\textsubscript{2}</td>
<td>0.37</td>
<td>0.49 0.26</td>
</tr>
<tr>
<td>Aluminum nano Al\textsubscript{2}O\textsubscript{3}</td>
<td>0.42</td>
<td>0.57 0.33</td>
</tr>
</tbody>
</table>
mortality of 98.3%. Reduction percentages of progeny were increased with increasing concentration. The high reduction was observed with concentration of 0.1 g/kg for malathion, 100%. Yet increase in concentration reduced the loss weight percentage from 5.1% at 0.04 g/kg to 0.7% at 0.1 g/kg wheat grains for malathion as compared with control, 29.00%.

Also, the results in Table 3 indicated that accumulative mortality percentages of *S. oryzae* increased gradually by increase in exposure time, and the number of mortality was higher as it reached 40.0 to 65.0% after one and two weeks of treatment with silica oxide nanoparticles at the concentration of 1.5 g/kg, respectively. Also, results obtained showed that the silica oxide nanoparticles significantly inhibited the number of progeny and weight loss of wheat grains against *S. oryzae*. The highly reduction in F1 progeny was observed with concentration of 1.5 g/kg for silica oxide nanoparticles (78.4%). In addition, the increased concentration reduced the weight loss percentage from 12.2 at 0.1 g/kg to 2.3 at 1.5 g/kg wheat grains as compared with control 29.0%.

The data in Table 4 showed that the differences in the mortality percentages of *S. oryzae* among treatments, as recorded one and two weeks, increased gradually by increasing the concentration and exposure time of aluminum oxide (*Al₂O₃*) nanoparticles. The number of mortality was higher as it reached 36.6 to 61.7 for individuals after one and two weeks at concentration of 1.5 g/kg, respectively. The results obtained showed that the *Al₂O₃* nanoparticles significantly inhibited the number of progeny and weight loss of wheat against *S. oryzae*. The high reduction in progeny was observed with concentration of 1.5 mg/kg (73.4%). In addition, the increase in concentration reduced weight loss percentage from 13.6 to 3.1% at 0.1 to 1.5 g/kg, respectively as compared with the control (29.00%).

The data in Table 5 demonstrated the effect of malathion, silica oxide nanoparticles and aluminum oxide nanoparticles on the wheat germination percentage after three months post-treatment. Malathion had no effect on the germination of wheat grains after three months post-treatment. A slight effect in germination of wheat grains with the silica oxide (*SiO₂*) and aluminum oxide (*Al₂O₃*) nanoparticles was observed as compared with control. Aluminum oxide nanoparticles was the highest treatment that reduced the germination percentage of
Table 5: Effect of malathion, silica oxide (SiO$_2$) and aluminum oxide (Al$_2$O$_3$) nanoparticles on germination.

<table>
<thead>
<tr>
<th>Tested materials</th>
<th>Conc. (gm/kg)</th>
<th>% After 3 months post-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>95.0 b</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>92.0 c</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>92.0 c</td>
</tr>
<tr>
<td>Silica nano (SiO$_2$)</td>
<td>0.5</td>
<td>86.0 d</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>80.0 e</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>76.0 e</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>92.0 c</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>90.0 c</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>91.0 c</td>
</tr>
<tr>
<td>Aluminum nano (Al$_2$O$_3$)</td>
<td>0.5</td>
<td>88.0 cd</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>86.0 f</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>69.0 g</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>100.0 a</td>
</tr>
<tr>
<td>Malathion</td>
<td>0.06</td>
<td>100.0 a</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>99.0 a</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>100.0 a</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td>100.0 a</td>
</tr>
</tbody>
</table>

DISCUSSION

Malathion had the highest effect, followed by silica oxide (SiO$_2$) and aluminum oxide (Al$_2$O$_3$) nanoparticles. The tested nanoparticles are promising and require some improvement in their physical properties. It is known that malathion formulation comprise adjuvant materials beside the active ingredient, while nanoparticles do not have any additive materials, where they act only by their natural properties. As such, the present study suggests that the distinction of malation effect may be due to the adjuvants. However, the safety of the studied nanoparticles on human and the environment make them the best for the control of stored product insect pests when compared with malathion, but they cause severe hazards on human health and the environment. Previous researches confirmed that metal nanoparticles are effective against plant pathogens, insects and pests. Hence, nanoparticles can be used in the preparation of new formulations like pesticides, insecticides and insect repellents (Barik et al., 2008; Gaibhiye et al., 2009; Abo-Arab et al., 2014). The significant mortality for both nanoparticles at all concentrations tested in the present study is similar to results of those recommended for commercially available insecticidal dusts (Arthur, 2000; 2002; Athanassiou et al., 2003, 2004; Vayias and Athanassiou, 2004). Stadler et al. (2010) applied successfully nanoparticles against two stored pests. The obtained mortality percentage at concentration of 1 g/kg (95.33 ± 0.33) for Al$_2$O$_3$ nano-particles is in accordance with the findings of Goswami et al. (2010). It has been revealed that the control efficacy against adult Tribolium castaneum was about 80%, presumably due to the slow and persistent release of the active components from the nano-particles (Leiderer and DeKorsy, 2008). They found that nano Al$_2$O$_3$ and amorphous nano SiO$_2$ were highly effective and nano ZnO was moderately effective against S. oryzae. Thus nano Al$_2$O$_3$ had deleterious effects on seeds, whereas non-crystalline nano-SiO$_2$ had no adverse effect on rice seeds. The present study is the first to report that nanocides, especially nano SiO$_2$ can be effective used to control insect pests. Also, Salem 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 ZnO nano-particles. In addition, they indicated that Al$_2$O$_3$ had higher effect than ZnO against T. castaneum. Ebeling and Wagner (1959) proposed that insecticidal efficacy of the dust become enhanced if the particles are finally divided. Damage occurs to the insect protective wax coat on the cuticle, by sorption and abrasion. Debnth 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 by conventional milling process unlike sprayable formulations of conventional pesticides, leaving residues on the stored grain. Therefore, silica and aluminum oxides nano-particles have a good potential to be used as grain protecting agent and alternatives to chemical insecticides.
if applied with proper safety measures. Also, one way to minimize the adverse effects of inert dusts is to use a minimum amount that is still effective on insects and choose a product that is effective at lower rates.

CONCLUSION

The insecticidal activity of silica and aluminum oxides nano-particles against S. oryzae indicate the potential use of this nanoparticles as a natural source of insecticidal materials. Insecticidal activity was confirmed in nanoparticles, although the results showed that silica and aluminum nano-particles varied in their effectiveness against S. oryzae. Malathion had the highest effect, followed by SiO$_2$ and Al$_2$O$_3$ nanoparticles. The ability of using SiO$_2$ and Al$_2$O$_3$ nano-particles as alternatives to the chemical control of S. oryzae (stored grain insect pests) is possible. This approach can help reduce the estimation 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 and its non-target toxicity, and to determine the potential of other nano-structured materials as pest control options for insects.

REFERENCES


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