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ORIGINAL ARTICLE

Insecticidal potential of Ag-loaded 4A-zeolite and its formulations with *Rosmarinus officinalis* essential oil against rice weevil (*Sitophilus oryzae*) and lesser grain borer (*Rhyzopertha dominica*)

Ahmed M. El-Bakry[1]*, Hanan F. Youssef[2], Nahed F. Abdel-Aziz[1], Elham A. Sammour[1]

[1] Pests and Plant Protection Department, National Research Centre, Dokki, Cairo, Egypt

[2] Ceramics, Refractories and Building Materials Department, National Research Centre, Dokki, Cairo, Egypt

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*Corresponding address:
ah_albakry@hotmail.com

Abstract

The insecticidal efficiency of Ag-loaded 4A-zeolite (Z_{Ag}) and its formulations with *Rosmarinus officinalis* essential oil (RO) was evaluated against *Sitophilus oryzae* (L.) and *Rhyzopertha dominica* (F.). For comparison, different rates of Z_{Ag} (0.25, 0.5, 0.75, and 1 g · kg^{-1} wheat) were used solely and in a combination with LC_{50} concentrations of RO. Mortality was assessed after 7, 14, and 21 days of insect exposure to treated wheat. The progeny production was also evaluated. The use of Z_{Ag} accomplished a complete mortality (100%) on *S. oryzae* and 96.67% on *R. dominica* as well as 100% mortality of progeny against the two insect species after the longest exposing duration (21 days), at the highest rate (1 g · kg^{-1}). On the other hand, the complete mortalities of Z_{Ag} formulations on *S. oryzae* were obtained after 14 d of treatment with F1 formulation (0.605 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}) and after 7 days with the other tested formulations. In addition, the complete mortality on *R. dominica* was obtained only by F8 (0.059 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}) formulation after 14 days of treatment. Concerning the efficiency of the examined formulations on the progeny of *S. oryzae*, F1 (0.605 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}) and F2 (0.605 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag}) formulations recorded 100% mortality. In addition, F3 (0.605 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag}) and F4 (0.605 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}) formulations suppressed the progeny production. Furthermore, the complete mortality of *R. dominica* progeny was obtained with F7 (0.059 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag}) and F8 (0.059 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}) formulations. Z_{Ag}, especially its formulations with *R. officinalis* oil, had potential effects against two stored-product insects. F1 and F8 formulations could be treated efficiently on *S. oryzae* and *R. dominica,* respectively.

Keywords: insects, *Rhyzopertha dominica*, *Rosmarinus officinalis*, *Sitophilus oryzae*, stored products, zeolite

Introduction

Cereals play a very important role as sources of vital nutrients. Cereals are considered to be a dominant source of energy, carbohydrates, protein and fiber. They also contain a number of micronutrients e.g. vitamin E, some B vitamins, some elements like magnesium and zinc (McKevith 2004). Cereals such as wheat and rice are major sources of nutrients for human diets. These grains are highly susceptible to infestation by stored product insects such as the rice weevil [*Sitophilus oryzae* (L.) (Coleoptera: Curculionidae)] and the lesser grain borer [*Rhyzopertha dominica* (F.) (Coleoptera: Bostrichidae)]. *Sitophilus oryzae* is one of the most injurious insect pests on cereals. Infestation by *S. oryzae* larvae and adults leads to loss of cereal weight by about 75% (Dal Bello *et al.* 2001), and poorer grain quality. The weevils also minimize seed germination resulting in lower prices for seed grains (Moino *et al.* 1998). Likewise, *R. dominica* is a devastating insect pest of stored products. Both larvae and adults feed on whole, intact grains causing considerable damage (Jood *et al.* 1996; Rees 2007). These insects are interior feeders resulting in significant physical damage and weight reduction, thereby affecting the quantity and the quality of the grains (Kučerová *et al.* 2003; Rees 2007).

Synthetic insecticides have been regarded as the most effective methods to combat insect pests of stored grains. The random use of these chemicals induced many serious problems, involving insect resistance, toxic residues, and harmful effects on humans and the environment (Tapondjou *et al.* 2005; Abdel-Aziz *et al.* 2018). It is a worldwide necessity for the grain industry to reduce pesticide utilization due to serious complications concerning insecticide deregulation, resistant populations and consumer worries because of insecticide residues. Therefore, safe methods for pest management are urgently needed (Fields 1998; Rajashekar and Shivanandappa 2010).

A viable substitute for residual insecticides of stored product protection is inert dusts (Quarles and Winn 1996). Inert dusts are employed to control stored grain insects (Kljajić *et al.* 2010a; El-Bakry *et al.* 2017; Kavallieratos *et al.* 2018). In contrast to traditional contact insecticides, inert dusts act via their physical properties and therefore, they are commonly slow acting (Maceljski and Korunic 1972). Insect mortality which occurs primarily is a result of desiccation; the water loss is an outcome of cuticle damage.

Zeolites are hydrated solids with a microporous structure that are used as adsorbents, based on their unique structure of having internal pores of nanoscale sizes. Applying zeolites in seed drying is unique; Rhino Research has investigated their capability and effectiveness in drying seeds, herbs, fruits and vegetables, as well as a material for DNA preservation (Lundahl *et al.* 2013). It is a fact that using zeolites in the seed drying technology secures economic benefits by minimizing weather risks and can help keeping seeds within an appropriate and manageable time frame. The benefits of using zeolites in this field are: 1. It is low cost and is comparable to similar technologies such as silica gel and ovens. 2. 4A-zeolite-drying technology is more effective than other methods such as charcoal, silica, ovens and sun drying.

Silver is one of the most common ions to combine in 4A-zeolite structures for attaining biological activity, basically due to its high stability and broad spectrum against different types of bacteria, viruses, germs, and fungi (Mansor *et al.* 2009; Shameli *et al.* 2010). Ag^+ replaces part of the framework of Na^+ cations via exchange process through impregnation of the solid powder into silver-containing liquid.

The aim of this study was to assess and compare the insecticidal cumulative mortality of silver-loaded 4A-zeolite (Z_{Ag}) as well as its formulations with *R. officinalis* oil (Z_{Ag}+RO) against the adults of *S. oryzae* (L.) and *R. dominica* and their progeny production.

Materials and Methods

Plant materials

Leaves of *R. officinalis* were collected during the flowering stage from the medicinal and aromatic plant farm at the National Research Centre, in El-Nubaria region, Egypt.

Preparation of the essential oils

The collected plant material was washed with tap water, followed by distilled water and dried under shade for 5 days at room temperature (26 ± 1°C). Extraction of the essential oil (EO) was done by hydro-distillation using a Clevenger apparatus for 5 h. The resulting oil was dried over anhydrous sodium sulfate, and kept in dark bottles at 4°C until used for chemical analysis and toxicity experiments.

Gas chromatography-mass spectrometry (GC-MS) analysis

In order to identify the main constituents of the rosemary (*R. officinalis*) essential oil, the extracted EO was diluted with diethyl ether and 1 μl was injected into gas chromatography (Trace GC ULTRA) coupled with ISQ Single Quadruple mass spectrometry. Nonpolar 5% Phenyl methylpolysiloxane capillary column (TG-5MS) (30 m × 0.25 mm ID × 0.25 um) was used. The analysis was carried out under the following conditions: oven temperature programmed from 40°C (3 min) to 280°C for 5°C min^{-1}, then isothermal at 280°C for 5 min. Helium was the carrier gas at a flow rate of 1 ml · min^{-1}. Spectra were obtained in the electronic ionization (EI) mode with 70 eV ionization energy.

Insects

The rice weevil [(*S. oryzae*) (L.) (Coleoptera: Curculionidae)] and the lesser grain borer [(*R. dominica*) (F.) (Coleoptera: Bostrichidae)] colonies were maintained in the laboratory for 4 years without exposure to insecticides. *Sitophilus oryzae* and *R. dominica* cultures were reared on sterilized intact wheat grains in glass containers (1 l). Insect rearing and all experiments were carried out at 26 ± 1°C and 65 ± 5% R.H. Adults used in the experiments were 2 weeks post-emergence of unknown sex.

Preparation of Ag-loaded 4A-zeolite (Z_{Ag})

4A-zeolite synthesis

In this work, 4A-zeolite was prepared following the method of Youssef *et al.* (2008). In a typical synthesis of 4A-zeolite-A (Z) from clay, kaolin rock was calcined at 750°C for 4 h to get an amorphous material, metakaolinite, which is the main precursor for 4A-zeolite-A crystals. Metakaolinite was treated with caustic soda of certain normality to produce a dense gel containing monomer species of both sodium silicate and sodium aluminate. The final step of 4A-zeolite processing was the hydrothermal treatment of the fresh gel at 80°C for 2 h. The produced powder was collected and washed with distilled water several times to eliminate the excess alkali and dried overnight in an electric oven at 80°C.

Loading of silver into 4A-zeolite pores

Silver nitrate (BDH chemicals – England) was used as the Ag source; cation exchange is the mechanism by which silver exchanges sodium in the pores of 4A-zeolite. In a typical process, 5.0 g of 4A-zeolite powder was immersed in 100 ml of 0.1 M $AgNO_3$ solution at 70°C for 6 h under magnetic stirring. The solid product was washed well with 250 ml deionized water and dried at 100°C for 24 h. The wt% concentration of silver (for 0.1 initial concentration of $AgNO_3$) to be exchanged onto the 4A-zeolite, determined by atomic absorption spectra (Savant AA, GBC, Australia) was 0.162%/1.0 g 4A-zeolite.

Bioassay

Efficiency of *Rosmarinus officinalis* oil

The toxicity of *R. officinalis* essential oil against each of the *S. oryzae* and *R. dominica* adults was determined by direct contact assay (Broussalis *et al.* 1999). A series of concentrations of *R. officinalis* oil were prepared in acetone. One ml of each concentration was mixed with 50 g of wheat in 200 ml plastic vessels. The same procedure was applied to untreated wheat. The solvent was allowed to evaporate, then, 20 adults of each insect species were separately introduced into each vessel. Four replicates of both treated and untreated wheat were used. The mortality of treatments and control were recorded after 12, 24, 48 and 72 h of treatment. High mortality was achieved after 48 h of treatment; consequently, the number of dead insects was counted after 48 h of treatment and mortality percentages were estimated. LC_{50} values of *R. officinalis* on *S. oryzae* and *R. dominica* were calculated as described by Finney (1971).

The efficiency of Ag-loaded 4A-zeolite

The test was carried out under laboratory conditions. Ag-loaded 4A-zeolite (Z_{Ag}) was applied at rates of 0.25, 0.50, 0.75 and 1.00 g · kg^{-1} of wheat. For each tested insect species and dust rate applied, 1 kg lots of whole-grain wheat were used. Lots of 1 kg of untreated wheat served as the control. After applying the Z_{Ag} powder, the vessel contents were hand mixed and then mixed in a rotary mixer for 10 min. The same procedure was applied to the control samples. The next day, for each exposure period (7, 14 and 21 days), four samples (50 g each) of treated wheat were placed in 200 ml plastic vessels, and 20 adults of *S. oryzae* and *R. dominica* were introduced separately into each vessel. The same procedure was applied to untreated wheat. The cumulative mortality was determined after 7, 14, and 21 days of contact with treated wheat. The effects of dusts on insect progeny production were evaluated as follows: after 21 days, wheat was sieved to remove all insects (dead and alive), and then the wheat containers were covered with cotton cloth and fixed with rubber bands. Progeny production was determined by counting live insects in treated and control wheat grains sieved after 8 and 10 weeks for *S. oryzae* and *R. dominica,* respectively.

The efficiency of Ag-loaded 4A-zeolite formulations

The LC_{50} concentrations of *R. officinalis* oil (0.605 and 0.059 g · kg^{-1} of wheat) on *S. oryzae* and *R. dominica*, respectively and Ag-loaded 4A-zeolite concentrations of 0.25, 0.50, 0.75 and 1.00 g · kg^{-1} of wheat were mixed individually by adding 1 ml acetone. After evaporation of the solvent, the two tested insects were treated by each formulation as previously mentioned. The cumulative mortality was determined after 7, 14, and 21 days of contact with treated wheat. Moreover, the effects of the formulations on insect progeny production were investigated.

The formulations of Ag-loaded 4A-zeolite (Z_{Ag}) were:

– F1 (0.605 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag});
– F2 (0.605 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag});
– F3 (0.605 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag});
– F4 (0.605 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag});
– F5 (0.059 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag});
– F6 (0.059 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag});
– F7 (0.059 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag});
– F8 (0.059 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}).

Data analysis

The mortality of each concentration of the tested essential oil was calculated after 48 h as the mean of four replicates. The mortality was subjected to probit analysis (Finney 1971) to obtain the LC_{50} values, using Minitab 18.1 (Minitab 2017). The values of LC_{50} were considered significantly different if the 95% confidence limits did not overlap. The data of Z_{Ag} and its formulations were analyzed separately for each insect species, using the two-way analysis of variance (ANOVA) procedure with insect mortality as a response variable, and the dose rate or the tested formulations and exposure intervals, as main effects. The mortalities of progeny production were analyzed separately for each insect species, using one-way ANOVA. The significance of mean differences was determined by Fisher least significant difference (LSD) test at $p < 0.05$ (Sokal and Rohlf 1969).

Results

Chemical constituents of *R. officinalis* essential oil

The chemical constituents of *R. officinalis* essential oil are listed in Table 1. The major compounds identified by gas chromatography-mass spectrometry (GC–MS) were 1,8-cineole (26.75%), α-pinene (24.64%), camphor (12.82%), camphene (8.16%), β-pinene (5.13%), borneol (4.54%), α-terpineol (3.63%), caryophyllene (2.36%), cymene (2.08%), β-myrcene (1.77%), 3-octanone (1.66%) and aromadendrene (1.53%).

Contact toxicity of the tested essential oil

The insecticidal activity of *R. officinalis* essential oil against both *S. oryzae* and *R. dominica* using direct contact assay is shown in Table 2. LC_{50} values ($g \cdot kg^{-1}$), 95% confidence limits ($g \cdot kg^{-1}$) and slopes of regression lines of the tested oil were recorded. *Rosmarinus officinalis* oil was more efficient against *R. dominica* than *S. oryzae,* where the LC_{50} values were 0.059 and 0.605 $g \cdot kg^{-1}$, respectively.

Ag-loaded 4A-zeolite preparation

Figure 1 shows the X-ray diffraction pattern for the prepared 4A-zeolite-A and its silver loaded form (Z_{Ag}). It is clear that some reduction occurred in the Ag-loaded zeolite, seen as shorter peak intensities. This is attributed to the long immersion (2 h) of the zeolite powder in the aggressive acidic solution of $AgCl_3$ under magnetic stirring in the Ag-loading step into zeolite pores.

Figure 2 shows the internal microstructures using SEM and the chemical analysis of the prepared Z_{Ag}, using Energy Dispersive X-ray spectroscopy (EDX). In Figure 2A, the characteristic cubic morphology of 4A-zeolite was intensively scattered in the whole scanned area, indicating a very good crystallization of the zeolite from kaolin. Figure 2B shows the chemical analysis of zeolite powder, containing the silver ingredient. The amount of silver introduced into zeolite pores and cavity was found to be 0.162 mg/1.0 g zeolite.

Table 1. Main constituents (%) of *Rosmarinus officinalis* essential oil extracted from Egyptian medicinal plants

Compounds	RT [min]	Percentage
α-thujene	7.92	0.24
α-pinene	10.59	24.64
Camphene	11.09	8.16
β-pinene	12.56	5.13
3-octanone	13.08	1.66
β-myrcene	13.13	1.77
1-Phellandrene	13.19	0.38
α-Terpenene	13.68	0.36
Cymene	14.06	2.08
1,8-Cineole	14.39	26.75
γ-Terpinene	15.35	0.93
α-Terpinolene	16.49	0.33
Linalool	16.97	0.54
Trans-Pinocarveol	18.5	0.24
Camphor	18.71	12.82
Borneol	19.5	4.54
Terpinen-4-ol	19.5	0.96
α-Terpineol	20.38	3.63
Verbenone	21.15	0.15
Thymol	23.23	0.16
Caryophyllene	28.32	2.36
Aromadendrene	28.93	1.53
Humulene	29.41	0.31
γ-Cadidene	29.73	0.13
Cadalene	33.43	0.09
Abietatriene	41.79	0.11

RT – retention time

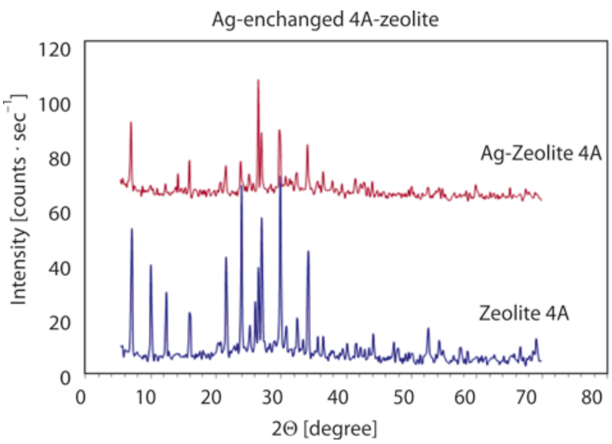

Fig. 1. X-ray diffraction of 4A-zeolite and its silver-modified form, prepared by microwaves from Egyptian kaolin

Table 2. Contact toxicity of *Rosmarinus officinalis* towards *Sitophilus oryzae* and *Rhyzopertha dominica*

Insects	LC_{50}* [g · kg^{-1}]	95% Confidence limits [g · kg^{-1}]		Slope ± SE	Intercept ± SE	Chi Square [χ^2]
		lower limit	upper limit			
Sitofilus oryzae	0.605	0.575	0.6318	9.45 ± 0.46	–26.28 ± 1.30	58.26
Rhyzopertha dominica	0.059	0.050	0.068	2.48 ± 0.12	–4.41 ± 0.23	74.47

*concentrations resulting in 50% mortality after 48 h of treatment

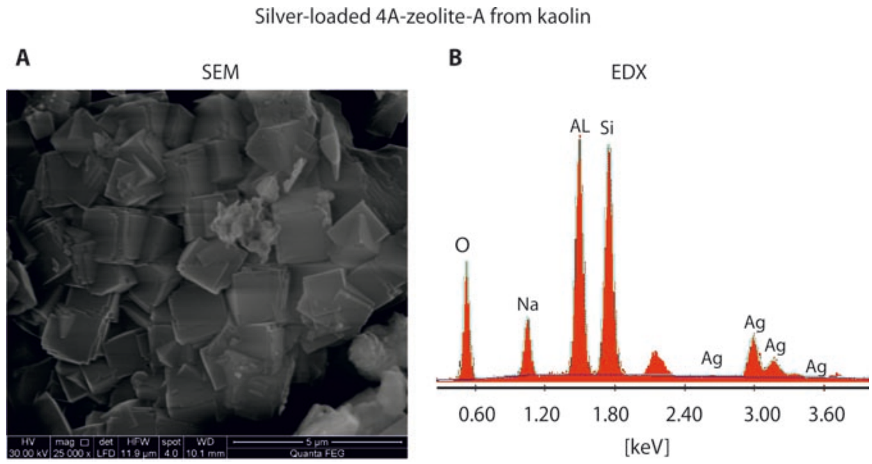

Fig. 2. A – scanning electron microscope (SEM) and B – microchemical analysis (EDX) for the prepared silver-loaded 4A-zeolite

Effectiveness of Ag-loaded 4A-zeolite

Data in Table 3 revealed the efficiency of Ag-loaded 4A-zeolite (Z_{Ag}) against *S. oryzae* and *R. dominica.* The mortality of *S. oryzae* did not exceed 41.67% after 7 days of contact to wheat treated with Z_{Ag} at the highest application rate (1.0 g · kg^{-1}), while it did not transcend 23.33% on *R. dominica* after the same period. After 14 days of contact with the highest application rate, mortality reached 95% for *S. oryzae,* while mortality of *R. dominica* was notably lower, merely

Table 3. Mortality of *Sitophilus oryzae* and *Rhyzopertha dominica* after 7, 14, and 21 days of exposure to wheat treated with Ag-loaded 4A-zeolite

Treatments	Rate [g · kg^{-1}]	Average cumulative mortality (%) ± SE		
		7 days	14 days	21 days
Sitophilus oryzae				
Control	0.00	10.00 ± 2.8 ef	10.00 ± 2.8 ef	10.00 ± 2.8 ef
Z_{Ag}	0.25	6.66 ± 1.6 f	46.67 ± 1.6 c	71.67 ± 1.6 b
	0.50	20.00 ± 2.8 de	91.67 ± 4.4 a	100.00 ± 0.0 a
	0.75	28.33 ± 3.3 d	91.67 ± 6.0 a	98.33 ± 1.6 a
	1.00	41.67 ± 8.8 c	95.00 ± 2.8 a	100.00 ± 0.0 a
Rhyzopertha dominica				
Control	0.00	3.33 ± 3.3 g	6.67 ± 6.6 g	10.00 ± 5.7 fg
Z_{Ag}	0.25	13.33 ± 3.3 fg	40.00 ± 5.7 e	63.33 ± 6.6 cd
	0.50	13.33 ± 3.3 fg	50.00 ± 5.7 de	76.67 ± 3.3 bc
	0.75	16.67 ± 6.6 fg	56.66 ± 3.3 d	90.00 ± 0.0 ab
	1.00	23.33 ± 6.6 f	63.33 ± 8.8 cd	96.67 ± 3.3 a

Means that share the same letter within a row or column (interaction between the main effects of rates and exposure time) are not significantly different at $p < 0.05$

63.33%. After 21 days of contact with the highest application rate, the mortality of *S. oryzae* reached 100%, in addition mortality of *R. dominica* recorded a satisfying result with 96.67% mortality. In general, *S. oryzae* was more susceptible to Z_{Ag} than *R. dominica.*

Mortality of progeny of *S. oryzae* and *R. dominica* exposed to Z_{Ag} was recorded in Table 4. Although all applied concentrations could not suppress the progeny production of the two tested insects, the highest application rate achieved 100% fatalities against the insect species. In addition, the mortalities resulting from the application rates of 0.5 and 0.75 g · kg^{-1} on *S. oryzae* were around 93%, while these two concentrations recorded 76.92 and 83.38% mortality, respectively, on *R. dominica.*

The effectiveness of Ag-loaded 4A-zeolite formulations

The mortalities of the two exposed insect species to Z_{Ag} formulations were elucidated in Table 5. The mortality of *S. oryzae* treated with F2 (0.605 g · kg^{-1} RO + + 0.5 g · kg^{-1} Z_{Ag}); F3 (0.605 g · kg^{-1} RO + 0.75 g · kg^{-1}

Table 4. Mortality of progeny of *Sitophilus oryzae* and *Rhyzopertha dominica* treated with Ag-loaded 4A-zeolite

Treatments	Rate [g · kg^{-1}]	Average no. of progeny ± SE	Average no. of dead insects ± SE	% Mortality ± SE
Sitophilus oryzae				
Control	0.00	210.89 ± 5.8	10.44 ± 0.4	4.95 ± 0.1 d
Z_{Ag}	0.25	63.11 ± 2.1	48.89 ± 2.5	77.47 ± 1.3 c
	0.50	46.22 ± 6.2	43.11 ± 6.1	93.27 ± 1.0 b
	0.75	22.89 ± 1.6	21.33 ± 1.6	93.18 ± 1.1 b
	1.00	15.33 ± 0.7	15.33 ± 0.7	100.00 ± 0.0 a
Rhyzopertha dominica				
Control	0.00	40.00 ± 4.0	4.00 ± 2.3	10.00 ± 5.3 c
Z_{Ag}	0.25	30.67 ± 1.3	16.00 ± 0.0	52.17 ± 2.3 b
	0.50	17.33 ± 2.6	13.33 ± 3.5	76.92 ± 12.3 ab
	0.75	8.00 ± 2.3	6.67 ± 1.3	83.38 ± 11.1 a
	1.00	8.00 ± 1.3	8.00 ± 1.3	100.00 ± 0.0 a

Means within a column followed by the same letter are not significantly different at $p < 0.05$

Table 5. Mortality of *Sitophilus oryzae* and *Rhyzopertha dominica* after 7, 14, and 21 days of exposure to wheat treated with Ag-loaded 4A-zeolite formulations

Formulations	Average cumulative mortality (%) ± SE		
	7 days	14 days	21 days
Sitophilus oryzae			
Control	0.0 ± 0.0 c	6.67 ± 3.3 b	10 ± 0.0 b
F1*	96.67 ± 3.3 a	100 ± 0.0 a	100 ± 0.0 a
F2	100 ± 0.0 a	100 ± 0.0 a	100 ± 0.0 a
F3	100 ± 0.0 a	100 ± 0.0 a	100 ± 0.0 a
F4	100 ± 0.0 a	100 ± 0.0 a	100 ± 0.0 a
Rhyzopertha dominica			
Control	0.0 ± 0.0 e	0.0 ± 0.0 e	0.0 ± 0.0 e
F5	76.67 ± 3.3 d	83.33 ± 6.6 cd	93.33 ± 3.3 abc
F6	80.00 ± 5.7 d	86.67 ± 3.3 bcd	93.33 ± 3.3 abc
F7	83.33 ± 3.3 cd	93.33 ± 6.6 abc	96.66 ± 3.3 ab
F8	93.33 ± 3.3 abc	100.00 ± 0.0 a	100.00 ± 0.0 a

*F1 = (0.605 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}); F2 = (0.605 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag}); F3= (0.605 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag}); F4 = (0.605 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}); F5 = (0.059 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}); F6 = (0.059 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag}); F7 = (0.059 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag}); F8 = (0.059 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}); Means that share the same letter within a row or column (interaction between the main effects of formulations and exposure time) are not significantly different at $p < 0.05$

Z_{Ag}) and F4 (0.605 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}) formulations recorded 100% mortality after 7 days of contact with the treated wheat. Moreover, F1 (0.605 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}) formulation achieved 96.67% mortality after the same period, while the mortality of *S. oryzae* treated with Z_{Ag} reached 100% only after 21 days from contact with the highest application rate (1.0 g · kg^{-1}).

Concerning the efficiency of the tested formulations, F5 (0.059 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}); F6 (0.059 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag}); F7 (0.059 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag}) and F8 (0.059 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}) contra *R. dominica,* data revealed that the mortality ranged from 76.67 to 93.33% after 7 days compared with only 13.33 to 23.33% of wheat exposed to Z_{Ag}. After 14 and 21 days of contact to wheat treated with the previous formulations (F5, F6, F7 and F8), the mortality ranged from 83.33 to 100% and 93.33 to 100%, respectively, compared with wheat treated with Z_{Ag}, where, the mortality ranged from 40 to 63.33% and 63.33 to 96.67%, respectively.

Data in Table 6 demonstrated the progeny mortality of *S. oryzae* and *R. dominica* treated with Z_{Ag} formulations. The average no. of progeny declined progressively to 1.33 of *S. oryzae* treated with F1 and F2 formulations and the mortality of these two formulations were 100%. In addition, F3 and F4 formulations suppressed the progeny production. Similarly, the average no. of *R. dominica* progeny treated with Ag-loaded 4A-zeolite formulations ranged from 3 to 9 compared with 8 to 30 of the same compound without formulations. Furthermore, F7 and F8 formulations recorded 100% mortality of *R. dominica* progeny.

Discussion

The main constituents of the essential oil extracted from *R. officinalis* were similar to those of Santoyo *et al.* (2005); Badreddine *et al.* (2015) and Abdelgaleil *et al.* (2016). The concentrations of the main compounds were significantly and/or slightly different. The variations in the chemical components of essential oils can be attributed to various environmental and genetic differences (Perry *et al.* 1999; El-Bakry *et al.* 2016). The results of the experiments displayed above indicated that the examined oil possessed contact insecticidal properties against the adults of *S. oryzae* and *R. dominica*. Laznik *et al.* (2012) and Khani *et al.* (2017) reported that *R. officinalis* had a toxic effect on *S. oryzae*. In addition Kalinović *et al.* (2003) mentioned that *R. officinalis* oil caused complete mortality of *R. dominica* at 0.02 ml · g^{-1} after 48 h of treatment.

Storage insects express varying degrees of susceptibility toward inert dusts due to morphological, physiological and ecological differences between insect species. Insects with thinner and gentler wax coats are more sensitive to inert dusts. Zeolites are microporous crystalline aluminosilicates stemming from the reaction of volcanic rocks, ash strata and alkaline underground water (Eroglu 2015). Natural zeolites (alkaline aluminum silicates), depending on their physical characteristics, are the most comparable to diatomaceous earth. Therefore they can be categorized in the same group as dusts which contain natural silicates (Subramanyam and Roesli 2000). Earlier entomological and agricultural research investigated the potential

Table 6. Mortality of progeny of *Sitophilus oryzae* and *Rhyzopertha dominica* treated with Ag-loaded 4A-zeolite formulations

Formulations	Average no. of progeny ± SE	Average no. of dead insects ± SE	% Mortality ± SE
Sitophilus oryzae			
Control	216.00 ± 12.8	2.67 ± 2.6	1.24 ± 1.1 b
F1*	1.33 ± 1.3	1.33 ± 1.3	100.00 ± 0.0 a
F2	1.33 ± 1.3	1.33 ± 1.3	100.00 ± 0.0 a
F3	0.00 ± 0.0	0.00 ± 0.0	100.00 ± 0.0 a
F4	0.00 ± 0.0	0.00 ± 0.0	100.00 ± 0.0 a
Rhyzopertha dominica			
Control	46.00 ± 8.5	3.00 ± 1.7	6.52 ± 4.9 c
F5	9.00 ± 0.0	4.50 ± 1.2	50.00 ± 13.3 b
F6	7.50 ± 0.3	4.50 ± 0.3	60.00 ± 6.2 b
F7	7.00 ± 0.5	7.00 ± 0.5	100.00 ± 0.0 a
F8	3.00 ± 2.9	3.00 ± 2.9	100.00 ± 0.0 a

*F1 = (0.605 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}); F2 = (0.605 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag}); F3= (0.605 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag}); F4 = (0.605 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}); F5 = (0.059 g · kg^{-1} RO + 0.25 g · kg^{-1} Z_{Ag}); F6 = (0.059 g · kg^{-1} RO + 0.5 g · kg^{-1} Z_{Ag}); F7 = (0.059 g · kg^{-1} RO + 0.75 g · kg^{-1} Z_{Ag}); F8 = (0.059 g · kg^{-1} RO + 1 g · kg^{-1} Z_{Ag}); Means within a column followed by the same letter are not significantly different at $p < 0.05$

of zeolite formulations on *R. dominica* and *S. oryzae* (Kljajić *et al.* 2010a; Andrić *et al.* 2012; Subramanyam *et al.* 2015).

The current research indicated that *S. oryzae* was more sensitive to Z_{Ag} or its formulations than *R. dominica*. Our findings confirmed those of Kljajić *et al.* (2010a) and Kljajić *et al.* (2011). The results also showed that the efficiency of Z_{Ag} on the tested insects was poor after 7 days with the highest application rate. Andrić *et al.* (2012) stated that the mortality of *S. oryzae* treated with natural zeolite was very low and ranged from 2 to 35% 7 days after exposure. Kljajić *et al.* (2010b) reported that the exposure period of 7 d was insufficient for any significant effects to be achieved with natural zeolite. Our results were in agreement with Kljajić *et al.* (2010a) and El-Bakry *et al.* (2017) who stated that the efficiency of inert dusts increases with an augmented time of exposure. Kljajić *et al.* (2011) reported that natural zeolite, like other inert dusts, acts more slowly against stored product insects than synthetic insecticides, hence, most dusts achieve high efficiency 14 or 21 days after application.

It is often more crucial in meaningful circumstances of cereal storage to suppress progeny production than to focus on gaining direct fatal impacts against parent insects (Kljajić *et al.* 2010a). Our results elucidated that Z_{Ag} gave 77–100%, 52.17–100% progeny mortality against *S. oryzae* and *R. dominica,* respectively, depending on the application rate. On the other hand, Kljajić *et al.* (2010b) found that none of the same applied rates of natural zeolite caused complete progeny reduction, whether on *S. oryzae* or *R. dominica*. Similar results were obtained by Andrić *et al.* (2012) who found that progeny reduction resulted from natural zeolite and modified natural zeolite at application rates 0.5, 0.75 and 1 $g \cdot kg^{-1}$ ranged from 47.5–81.8% on *S. oryzae.* From these previous studies, it could be concluded that the process of loading silver into 4A-zeolite increased the efficiency of progeny reduction. Our results were confirmed by Campolo *et al.* (2014). They investigated the impact of kaolin and diatomaceous earth treated alone and in formulations with *Citrus sinensis* against *R. dominica.* Data revealed that *C. sinensis* induced a synergistic effect against *R. dominica* when combined with kaolin. Also, an antagonistic effect exists when mixing the tested essential oil with diatomaceous earth.

As mentioned before inert dusts have a slow action, so there was a need to overcome this drawback. The current research demonstrated that Z_{Ag} formulations caused 100% mortality after 7 days from treatment against *S. oryzae* and 76.67–93.33% against *R. dominica.* Complete mortality resulted from F8 formulation (0.059 $g \cdot kg^{-1}$ RO + 1 $g \cdot kg^{-1}$ Z_{Ag}) after 14 days of insect contact with treated wheat. The previous studies reported that Minazel and Minazel plus commercial zeolite formulations caused 24–86% and 10–25% mortality against *S. oryzae* and *R. dominica,* respectively, after 7 days of treatment (Kljajić *et al.* 2010a). Moreover, neither of them recorded complete mortality against *R. dominica* even after 21 days of contact with applied wheat at the highest application rate of 0.75 $g \cdot kg^{-1}$. Rumbos *et al.* (2016) evaluated the insecticidal potential of three commercially zeolite formulations against adults of *S. oryzae.* The results indicated that the mortality 21 days after treatment at 1 $g \cdot kg^{-1}$ ranged from 23.9–43.9%. The present data showed that all Z_{Ag} formulations induced 100% mortality on progeny of *S. oryzae*. Moreover, two formulations (F3 and F4) suppressed progeny production. In addition, F7 and F8 formulations achieved complete progeny mortality against *R. dominica.*

Zeolites can partially remove the epicuticle of insects via abrasion by solid non-sorptive particles or through adsorption of the epicuticular layer to sorptive particles resulting in the destruction of the epicuticle. Both operations cause dehydration and result in death by dryness (Glenn *et al.* 2001). The increased efficiency of Ag-loaded 4A-zeolite (Z_{Ag}) compared with the commercial zeolite formulations of the previous studies might be due to Ag. Athanassiou *et al.* (2018) mentioned that the mechanism of action of silver nanoparticles based on the absorption of epicuticle lipids by capillarity, triggered death by water loss from the insect's body.

Milenkovic *et al.* (2017) reported that Ag-natural zeolite had a bactericidal effect which was attributed to released Ag(I) ions. Furthermore, Eroglu (2015) stated that natural zeolite is considered to be a safe food additive. A few studies have mentioned that natural zeolite acts as an anticancer therapeutic agent (Pavelić *et al.* 2001; Tomečková *et al.* 2012). Natural zeolite is employed for medical purposes in animals and humans (Andronikashvili *et al.* 2009). In contrast, Pavelić *et al.* (2017) reported that the *in vivo* results of natural zeolite on rats were not proper for oral animal, hence humans, as a result of releasing Al into the blood and organs.

Conclusions

The current research revealed that Z_{Ag} particularly its formulations had potent toxicity on *S. oryzae* and *R. dominica. S. oryzae* was more responsive to Z_{Ag} or its formulations than *R. dominica.* The examined compounds might be salutary for managing the tested insects in storage bins and silos. The process of loading Ag into natural zeolite increased the efficiency on both the insects and progeny, compared with commercial zeolite formulations, which have been mentioned in previous studies. In order to overcome the slow action of Z_{Ag}, it was formulated with *R. officinalis* oil. The formulation compounds are emphasized as a supreme grain protectant against the two insect species since they overcame the insignificant effects of first 7 days of exposure, especially F1 formulation that contained the lowest rate of Z_{Ag} on *S. oryzae*, and F8 against *R. dominica,* which contained the highest rate of Z_{Ag}. Further studies should be conducted to evaluate other improved formulations based on the same materials against other stored product insects, along with toxicological studies to ensure the safety of the tested compounds for human health. However, Z_{Ag} and its formulations look like a promising alternative to synthetic insecticides.

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