



Comparative toxic effects of *Eucalyptus globulus* L. (Myrtales: Myrtaceae) and its green synthesized zinc oxide nanoparticles (ZnONPs) against *Rhyzopertha dominica* (F.) (Coleoptera: Bostrichidae)

Muhammad Amir Siddique¹ · Mansoor ul Hasan¹ · Muhammad Sagheer¹ · Shahbaz Talib Sahi²

Received: 7 April 2021 / Accepted: 1 November 2021 / Published online: 12 November 2021
© African Association of Insect Scientists 2021

Abstract

Rhyzopertha dominica (F.) (Coleoptera: Bostrichidae) causes quantitative and qualitative losses to stored cereals. The excessive use of synthetic residual insecticides led to the development of resistance. These pesticides have adverse effect on the environment. Green synthesized nanoparticles can be a good replacement of synthetic insecticides. Nanoparticles of ZnO prepared using the extract of *Eucalyptus globulus* L. (Myrtale: Myrtaceae) were never evaluated against *R. dominica*. Therefore, the present study was planned to evaluate the insecticidal potential of leaf extract of *E. globulus* and green synthesized zinc oxide nanoparticles (ZnONPs) against adults of *R. dominica*. Green synthesized ZnONPs were prepared using leaves extract of *E. globulus* as a simple, non-toxic and ecofriendly green material. Characterization of nanoparticles was carried out using UV- visible spectroscopy, Particle Size Analysis (PSA) and Scanning Electron Microscope (SEM) analysis. Insecticide bioassays were conducted using six concentrations (300, 600, 900, 1200, 1500, and 1800 ppm) of *E. globulus* extract. Similarly six dose rates (100, 200, 300, 400, 500 and 600 ppm) of green synthesized ZnONPs were evaluated after four exposure periods (3, 7, 11 and 15 days). The insect mortality due to *E. globulus* leaf extract was 62.5% against 1800 ppm dose rate while 80.5% mortality of insect was observed against 600 ppm dose rate of ZnONPs after 15 days exposure period. The LC₅₀ for leaf extract of *E. globulus* and green synthesized ZnONPs were 1043.06 and 202.11 ppm respectively. Post treatment growth inhibition of *R. dominica* was 75.7% and 87.0% against extract and ZnONPs of *E. globulus* after 30 days. These results indicate that *E. globulus* leaf extract and green synthesized ZnONPs are effective against *R. dominica* and can be used as an eco-friendly approach for stored product pest management.

Keywords Toxicity · *E. globulus* · Phytofabricated zinc oxide nanoparticles · Lesser grain borer

Introduction

A number of insects cause infestation to stored cereals and their products (Stejskal et al. 2015). These insects are responsible for 10 to 20 percent damage to stored wheat (Khan et al. 2010). Post-harvest losses in stored cereals are up to 9% in developed countries while in developing countries these are 20% (Phillips and Thorne 2010).

Worldwide, *Rhyzopertha dominica* is the major primary insect pest of stored cereals and food commodities that

has the ability to cause quantitative and qualitative losses (Mason and McDonough 2012). It is the common cosmopolitan pest of food storages (Haines 1991) that can move down to a depth of 12 m into the grain mass, which is deeper as compare to other grain beetles (Flinn et al. 2010).

Currently, the main strategy to control stored product insect pests in warehouses is the phosphine fumigation along with the use of residual insecticides for surface treatment as grain protectants (White and Leesch 1996; Yasir et al. 2021). Unfortunately, these insecticides cause contamination of food with toxic pesticide residues (Shojaaddini et al. 2008; Debnath et al. 2011). Moreover, the development of pesticide resistance in stored product pests is the major issue in stored product pest management (Lorini et al. 2006). Keeping in view the pest resistance and pesticide residues, it seems that chemical control is an approach that has limitations for sustainable pest management. Therefore, in recent

✉ Muhammad Amir Siddique
amiragri10@gmail.com

¹ Department of Entomology, University of Agriculture, Faisalabad, Pakistan

² Department of Plant Pathology, University of Agriculture, Faisalabad, Pakistan

decades, researchers are working on alternative strategies e.g. application of plant extracts, inert dusts (diatomaceous earth), microbial biopesticides and nanoparticles for sustainable pest management (NPs) (Chanbang et al. 2007; Liu et al. 2008; Debnath et al. 2011; Shafiqhi et al. 2014; Ziaee and Ganji 2016).

Plant products are cheaper biopesticides (Mishra et al. 2012) that are potentially suitable for integrated management of stored product insect pests (Saxena 1989; Schmutterer 1992). Eucalyptus extract contains bioactive compounds that have antifungal, antibacterial, antioxidative, fumigant and insecticide activities (Batish et al. 2008; Martins et al. 2013; Sebei et al. 2015, Rossi and Palacios 2015). The leaf powder of *E. globulus* has insecticidal bioactivity against *Callosobruchus maculatus* (F.) (Coleoptera: Chrysomelidae) a pest of gram seeds by reducing the insect oviposition, progeny emergence and grain infestation rates (Rahman and Talukder 2006).

Nanomaterials have great potential for their application in plant protection and nutrition due to their size-dependent qualities, high surface to volume ratio and unique optical properties (Oskam 2006; Puoci et al. 2008). In recent years, nanotechnology has emerged as a brilliant approach to develop more efficient products for pest control (Rouhani et al. 2012). In general, nanotechnology can be defined as manipulation of materials at the atomic level by a combination of engineering, chemical, and biological approaches (Cauerhff and Castro 2013). According to British Standards Institution nanotechnology is the manipulation and control of matter on the nanoscale dimension by using scientific knowledge of various industrial and biomedical applications (PAS 71:2011).

This technology is helpful for employing nanosized particles and nanoformulations of pesticides for sustainable management of insect pests (Khot et al. 2012). Nanoparticles are being used in many fields of agricultural biotechnology (Rahman et al. 2009) and have the potential to be used as insecticides (Leider and Dekorsy 2008). Silver nanoparticles have widely been used (Ki et al. 2007; Arjunan et al. 2012; Marimuthu et al. 2011) along with aluminum nanoparticles (Stadler et al. 2010, 2012) and nanosilica (Debnath et al. 2011; Barik et al. 2012) for the management of indoor and outdoor pests across the world. Surface-functionalized silica nanoparticles are good substitute to conventional pesticides and showed very effective results against *Sitophilus oryzae* (L.) (Coleoptera: Curculinidae) (Debnath et al. 2011).

Different strategies are employed for the synthesis of nanoparticles. The traditional physicochemical methods have environmental concerns due to toxic compounds formed as byproducts. Physical methods require high temperature and pressure whereas chemical and biological methods require room temperature and pressure for reducing and stabilizing

the nanoparticles. Green synthesis method is a fast, economical, simple, environment friendly and reproducible approach to prepare nanoparticles (Mukherjee et al. 2001).

Nowadays, metal oxide nanoparticles are receiving remarkable attention, as they can transform the viable conventional to unconventional materials in various fields of solid state. Metal oxide nanoparticles are being basically used as a heterogeneous nanocatalyst in a variety of organic transformations as they contain high surface area than their bulk counterparts (Iravani 2011 and Kavitha et al. 2013). Nanopesticides (NPs) seem to be environment friendly (Jiang et al. 2010). Nanoparticles can be helpful in application of pesticides at reduced dose rate (Perez de Luque and Rubiales 2009) or can boost the effectiveness of insecticidal formulations (Liu et al. 2008; González et al. 2014; Patil et al. 2016).

Thus nanotechnology will reform agriculture including management of different insect pests of stored grains in near future. Green synthesized ZnO-NPs have not been used against *R. dominica* for their biocidal and growth inhibitory potential. Therefore, the current study was planned to evaluate the insecticidal potential of *E. globulus* leaf extract and green synthesized ZnO-NPs against *R. dominica*.

Materials and methods

Insect culture

Heterogeneous population of *R. dominica* was collected from grain market and farmer storages located in district Faisalabad, Punjab, Pakistan. These insects were reared on sterilized wheat grains in plastic jars placed in cooled incubator maintained at optimum growth conditions (30 ± 2 °C and $65\pm 5\%$ R.H.) to get the F₁ population of uniform age that was used for further bioassay studies.

Preparation of plant extracts

Leaves of *E. globulus* were collected, washed with water and dried in shade. Dried leaves were converted into fine powder using an electric grinder. The rotary shaker was used to prepare the extract from leaf powder. In a flask, 50 g of leaf powder was taken in 200 ml acetone. The mixture containing flask was placed on rotary shaker at 220 rpm for 72 h. After that the extract was filtered out using the filter paper (whatsman No.1). To get the fine material, the extract was also centrifuged for 20 min. The coarse particles were settled down and fine plant extract was separated into beaker. The filtrate was placed in a rotary evaporator to get the pure extract. The pure extract was stored in a refrigerator at 4 °C before their use for bioassay studies.

Synthesis of ZnO- NPs

For the synthesis of ZnO-nanoparticles, 50 ml plant extract was taken in 100 ml beaker and boiled at 70–80 °C. Then, 4gm of Zinc nitrate hexahydrate was added slowly into the hot plant extract, which will be converted into reddish brown colored solution. This reaction mixture was heated at 70–80 °C with magnetic stirring. As the reaction progressed, the color of the solution slowly changed from reddish brown to pale yellow indicating the formation of ZnO-NPs. The heating process remained continue until the formation of reddish-orange colored paste. The paste was transferred to ceramic crucible followed by heating at 400 °C for 2 h. The obtained pale white colored powder was used for further studies (Aminuzzaman et al. 2018).

Characterization of the synthesized nanoparticles

UV–Vis spectroscopy analysis was done for characterization of green synthesized ZnO-NPs at room temperature using UV spectrophotometer. The optical absorbance of bio-reduction metal oxide ions in the solution was measured in the range of wavelengths 300–800 nm. The results were recorded and the absorption curve was created. UV-Vis spectroscopy is generally known to study size and shape controlled particles in aqueous suspensions. The average particle size was determined by Particle Size Analysis.

The Scanning Electron Microscope analysis was done from Lahore University of Management Sciences (LUMS). The surface morphology, size, shape and structure of the green synthesized nanoparticles were investigated by Scanning Electron Microscopy (SEM).

Bioassays

Bioassay to evaluate the toxicity of different concentrations of plant extracts

For the determination of toxicity of plant extract, experiment was carried out in petri dishes having size 9cm diameter and whatsmann filter paper No.1 was used for bioassay. Different concentrations (300, 600, 900, 1200, 1500 and 1800 ppm) of *E. globulus* leaf extract were sprayed on filter papers which were allowed to dry at room temperature for 10 min. The filter papers treated with acetone alone were used as control. Thirty adults of *R. dominica* were released in each petri dish. Five wheat grains were placed in each petri dish as food to avoid starvation of insects. After that petri dishes were covered by the lid using adhering tape. All petri dishes were kept in incubator at 30±2 °C and 65±5% R.H. Experimental design was

factorial under CRD. Whole experiment was repeated four times. Mortality of beetles was observed after 3,7,11 and 15 days of application of phytochemicals.

Bioassay to evaluate the toxicity of green synthesized nanoparticles

To evaluate the insecticidal bioactivity of green-synthesized nanoparticles, six concentrations (100, 200, 300, 400, 500 and 600 ppm) of ZnO-NPs were applied on filter papers, after drying these were placed in petridishes. In control treatment, the filter-papers were treated with acetone only. Thirty adults of *R. dominica* were released in each petri dish. Five wheat grains were placed in each petri dish as food to avoid the chances of insect starvation during exposure period. The petri dishes were covered by lid using adhering tape. All petri dishes were kept in incubator at 30±2 °C and 65±5 R.H. Factorial CRD design was followed for the experiment. The experiment was repeated four times. Mortality data of treated insects were observed after 3,7,11 and 15 days of treatment.

Growth inhibitory effect of plant extracts and green synthesized nanoparticles

Seven lots of 200 gm of sterilized wheat grains were taken in plastic containers. Grains were spread in the trays in a thin layer for uniform application of the test products. One lot of wheat grains was treated with 300 ppm of *E. globulus* leaf extract with the help of hand sprayer. 5ml of solution was used to treat the grains. Similarly other 5 lots were treated with 600, 900, 1200, 1500 and 1800 ppm of plant extract separately. One lot of grains was treated with acetone and considered as control. From each treated lot, 50-gram sample was taken in small plastic jars (11 cm height × 6.5 cm width) which served as experimental unit. Thirty adults of *Rhyzopertha dominica* were released in each jar. Jars were covered with muslin cloth and placed in the incubator at 30± 2 °C and 65±5 R.H. Factorial CRD design was followed for the experiment. Similar procedure was followed to evaluate the growth inhibitory effect of green synthesized ZnO-NPs using six dose rates (100, 200, 300, 400, 500 and 600 ppm). Each experiment was repeated four times. Data regarding population build up were recorded after 30 days.

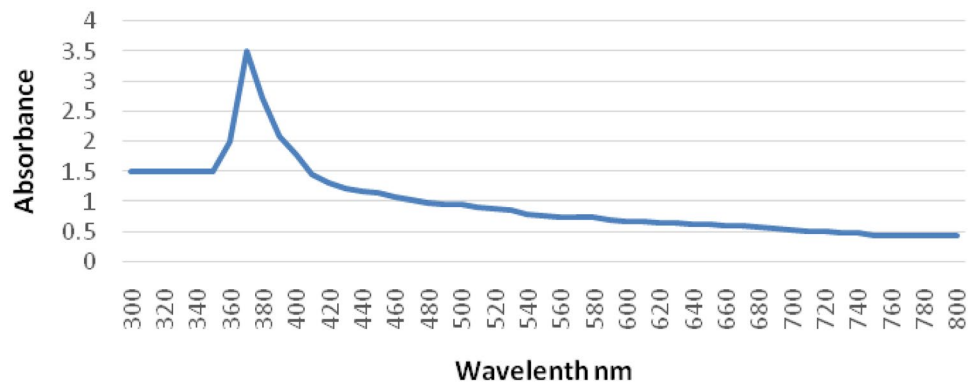
Statistical analysis

Mortalities were corrected by using Abbott's formula (Abbott 1925).

$$\text{Corrected Mortality} = \frac{\text{Observed mortality} - \text{Control mortality}}{100 - \text{Control mortality}} \times 100$$

The mortality data were analyzed statistically using Statistix 8.1 Analytical software (2003) for analysis of variance

Fig. 1 UV–visible spectroscopy of green synthesized ZnO-NPs



(ANOVA) to determine the variation among concentrations and exposure periods. Means of significant treatments were computed using the Tukey-(HSD) test at $\alpha=0.05$. LC_{50} was calculated using the Probit analysis (Finney 1971).

Growth inhibition of F₁ progeny of *R. dominica* was calculated by using following formula (Yasir et al. 2019).

$$\% \text{ inhibition of F}_1 \text{ progeny} = (1 - t/c) \times 100$$

Where t = the total number of insects developed in treated commodity

c = the total number of insects developed in control treatment

Results

The size reduction of zinc ions into ZnONPs were observed as the color changed from reddish brown to pale yellow indicating the formation of ZnO-NPs. The diluted solution of synthesized zinc oxide nanoparticles was analyzed by UV-Vis spectrophotometer to check the maximum absorption of

ZnONPs. The maximum peak with wavelength 370 nm was recorded (Fig. 1). It indicates that maximum given peak of ZnONPs displayed excitation absorption (at 370 nm) due to their large excitation binding energy and sharp band, it means that zinc ions were efficiently reduced by the plant extract.

The average particle size of green synthesized nanoparticles is 186.7 nm (Table 1). The results given in Fig. 2 represent the size distribution curve of ZnO-NPs in which the particle distribution is more uniform with a narrow range.

Scanning Electron Images (SEM) of green synthesized ZnO-NP (magnified $\times 10000$ – 300000) given in Fig. 3 show that ZnO-NPs are approximately spherical, flower and walnut shaped. The results also represent that these nanoparticles are crystalline in structure.

Toxicity of *E. globulus* leaf extract and green synthesized ZnO-nanoparticle

The mortality data in response of six dose rates of plant extract and ZnO-NPs were recorded after 3, 7, 11 and 15 days of treatment application. The analysis of variance (ANOVA) shows that all concentrations ($df = 5$,

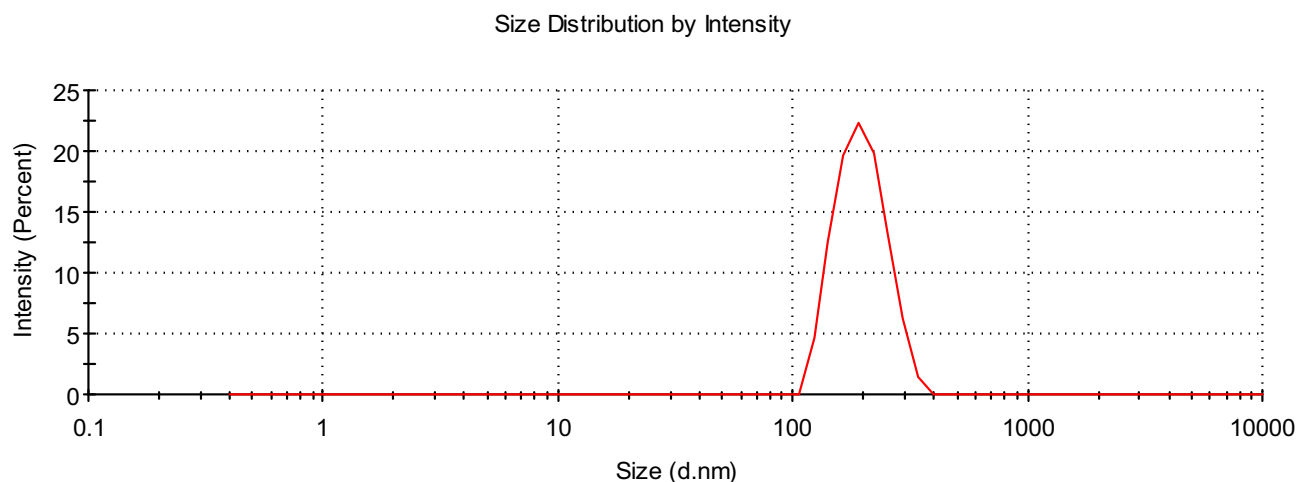
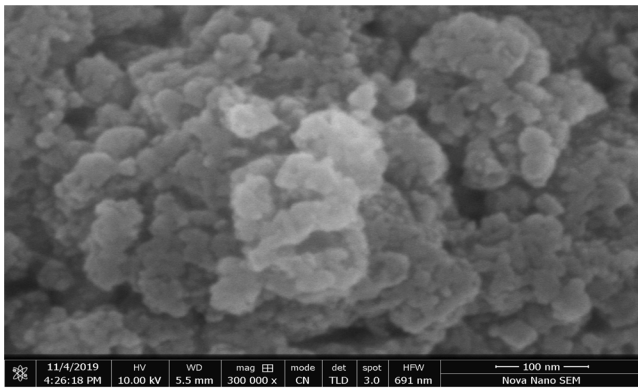
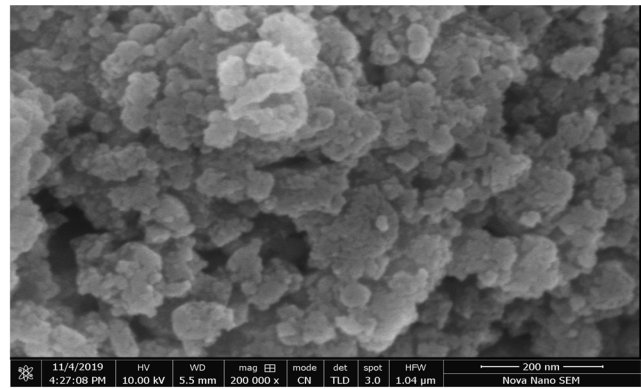


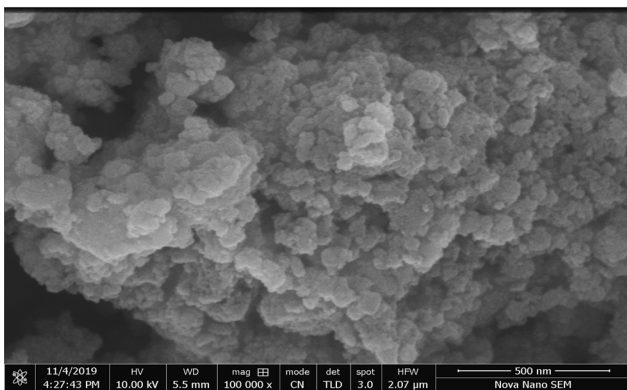
Fig. 2 Particle size distribution curve for ZnO-nanoparticles



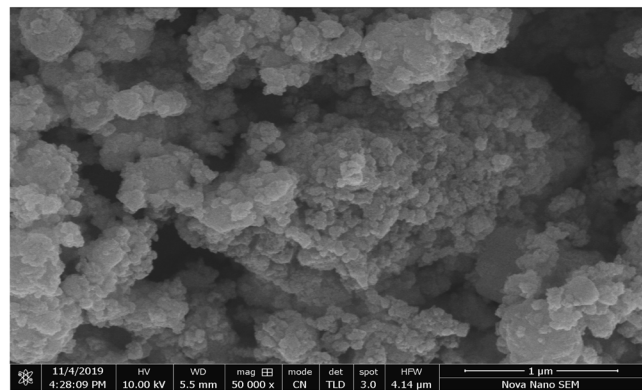
(a) SEM images ZnO NPs 100 nm



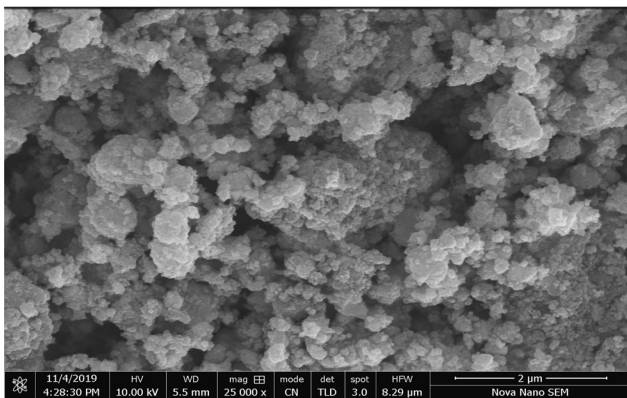
(b) SEM images ZnO NPs 200 nm



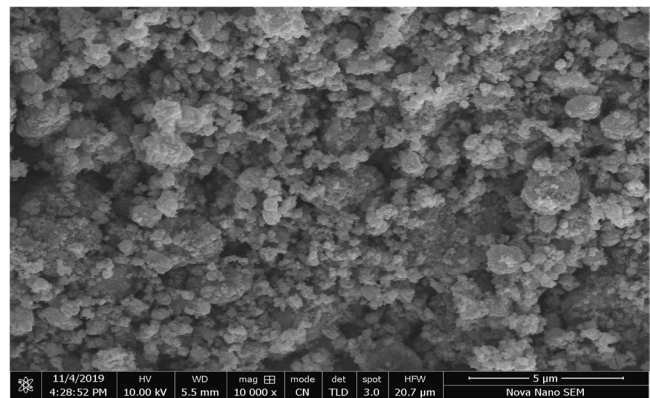
(c) SEM images ZnO NPs 500 nm



(d) SEM images ZnO NPs 1 μm



(e) SEM images ZnO NPs 2 μm



(f) SEM images ZnO NPs 5 μm

Fig. 3 (a–f) Scanning Electron Microscope (SEM) images of green synthesized ZnO NPs

$F = 445.90$, $P = 0.0000$) and exposure periods ($df = 3$, $F = 173.13$, $P = 0.0000$) had significant effect on mortality while their interaction effect ($df = 15$, $F = 2.04$, $P = 0.239$) was not significant. The highest mortality (62.5%) of *R. dominica* was observed at 1800 ppm dose rate of *E.*

globulus leaf extract after 15 days of exposure time while the minimum mortality was (10.8%) after 3 days. Highest mortality values 48.3, 54.3, 58.9 and 62.5% with 1800 ppm were observed after 3, 7, 11 and 15 days respectively. The results regarding mean mortality were found to

Table 1 Particle size analysis of green-synthesized ZnO-NPs

		Size (d.nm)	%age intensity	St Dev (d.nm)
Z-Average ^a (d.nm): 186.7	Peak-1	199.2	100.00	48.04
^b PdI: 0.081	Peak-2	0.0	0.0	0.00
Intercept: 0.915	Peak-3	0.0	0.0	0.00

^ad.nm = diameter in nanometer, ^bPdI = Polydispersity index

be dose and exposure time dependent (Table 2). The highest LC₅₀ (1982.11 ppm) was recorded after 3 days while lowest LC₅₀ was 1043.06 ppm after 15 days. The results show that as the exposure period increased the LC₅₀ value decreased (Table 3).

In case of ZnO-NP, the analysis of variance (ANOVA) of mortality data of *R. dominica* treated with different concentrations after different exposure times show that all concentrations (df = 5, F = 470.93, P = 0.0000) and exposure periods (df = 3, F = 245.35, P = 0.0000) had significant effect on mortality. Similarly their interaction effect (df = 15, F = 3.05, P = 0.0008) was also significant. The maximum mortality (80.5%) of *R. dominica* was observed at 600 ppm dose rate of green-synthesized ZnONPs after 15 days of exposure time. While the minimum mortality (17.5%) was observed at 100 ppm dose rate of ZnO-NPs after 3 days of exposure time. In case of different exposure periods, the highest mortality values 55, 66.1, 73.2 and 80.5% were observed against 600 ppm after 3, 7, 11 and 15 days respectively. The results showing mean mortality were found to be dose and exposure time dependent (Table 4). The LC₅₀ values decreased from 564.77 ppm to 202.11 ppm as the exposure time increased which indicates the efficacy of the green-synthesized ZnONPs increased with the increase of exposure period (Table 5).

Table 2 Percentage corrected mortality (Mean ± SE) of *Rhyzopertha dominica* adults caused by different concentrations of *Eucalyptus globulus* leaf extract at different exposure periods

Concentrations (ppm)	Exposure times (days)			
	3	7	11	15
300	10.8 ± 0.83d	20.7 ± 1.99c	22.3 ± 0.89d	26.8 ± 1.03e
600	23.3 ± 1.36c	25.0 ± 1.65c	35.7 ± 1.45c	38.4 ± 1.70d
900	27.5 ± 1.59c	34.5 ± 1.41b	39.3 ± 1.45c	45.5 ± 0.89c
1200	35.8 ± 0.83b	37.9 ± 1.41b	45.5 ± 0.89b	52.7 ± 0.89b
1500	44.2 ± 0.83a	49.1 ± 0.86a	55.4 ± 1.03a	57.1 ± 1.45ab
1800	48.3 ± 0.96a	54.3 ± 1.65a	58.9 ± 1.03a	62.5 ± 1.03a

Means (within the same column) with same letters are not significantly different

Means of significant treatments were computed using the Tukey-(HSD) test at $\alpha = 0.05$

n (number of replications) = 4

Growth inhibitory effect of *Eucalyptus globulus* leaf extract and ZnO-NPs

In another experiment, the effect of *E. globulus* leaf extract and green synthesized ZnO-NPs on growth inhibition of F₁ progeny of *R. dominica* developed on diet treated with different concentrations was observed after 30 days exposure time. The growth inhibition (%) increased with the increase in dose rate of bio-insecticides at the same duration. In case of *E. globulus* leaf extract 75.7% growth inhibition was observed at 1800 ppm dose rate, while 35.6% inhibition at 300 ppm dose rate. In case of ZnO-NPs the highest growth inhibition was 87.0% of F₁ progeny of *R. dominica* with 600 ppm dose rate while lowest inhibition was 55.7% at 100 ppm was observed (Table 6).

Discussion

In this study ZnO-NPs were synthesized using *E. globulus* leaf extract as reducing agent by green synthesis method and characterized by UV Vis-Spectroscopy, Particle Size Analysis (PSA) and Scanning Electron Microscope (SEM). Our results regarding characterization of ZnO-NPs with UV Vis-spectroscopy analysis absorption at wavelength 370 nm are supported by Aminuzzaman et al. 2018 who found the absorption peak at wavelength of 375 nm of ZnO-NPs. According to our results regarding particle size of ZnO-NPs, the average size of green synthesized ZnO-NPs was found 180.7 nm and these are also in accordance with Alam et al.

Table 3 Toxicity of *Eucalyptus globulus* leaf extract against adults of *Rhyzopertha dominica*

Exposure time (days)	^a LC ₅₀ (ppm)	^b Fiducial limits	^c χ^2	S.E	Slope
3	1982.11	1178.94 – 3332.45	1.0	0.11	1.51
7	1769.06	938.79 – 3333.64	0.9	0.14	1.20
11	1285.50	700.80 – 2358.03	1.00	0.13	1.23
15	1043.06	557.52 – 1951.44	1.00	0.14	1.19

^aLC₅₀ = Lethal concentration that kills 50% of the exposed insects.

^bFiducial limits = Lower and Upper limits. ^c χ^2 = Chi-square values.

^ddf = degree of freedom

n (number of replications) = 4, $\alpha = 0.05$

Table 4 Mean Mortality (%) of *Rhyzopertha dominica* caused by different concentrations of green-synthesized ZnONPs using *Eucalyptus globulus* leaf extract at different exposure periods

Concentrations (ppm)	Exposure times (days)			
	3	7	11	15
100	17.5 ± 0.83f	23.2 ± 1.03d	28.57 ± 1.45e	37.0 ± 1.51e
200	24.2 ± 1.59e	26.8 ± 1.78d	33.03 ± 0.89e	49.1 ± 1.77d
300	32.5 ± 1.59d	41.9 ± 1.71c	47.32 ± 1.70d	53.7 ± 1.85 cd
400	39.2 ± 1.59c	52.7 ± 1.71b	58.93 ± 1.78c	61.1 ± 1.85c
500	49.2 ± 0.83b	58.0 ± 1.71b	66.1 ± 1.03b	71.3 ± 1.77b
600	55.0 ± 0.96a	66.1 ± 1.03a	73.2 ± 1.03a	80.5 ± 1.77a

Means (within the same column) with same letters are not significantly different

Means of significant treatments were computed using the Tukey-(HSD) test at $\alpha=0.05$

n (number of replications) = 4, $\alpha=0.05$

2019 who reported the average size of green-synthesized Fe₂O₃NPs in range of 56-350 nm. Similarly Scanning Electron Microscope results of ours study are in good agreement of findings of Pal et al. 2018 who reported that green synthesized ZnONPs are spherical and crystalline in nature. Phenols the major phytochemical components (Santos et al. 2011; Campos et al. 2002) are present in extract of *E. globulus*. In addition, phytochemicals e.g. flavonoids, glycosides, tannins, saponins, terpenoids and reducing sugars, involved in the bio-reduction of metal ions (Godghate and Sawant 2014) are also present in *E. globulus* leaf extract. The polyphenols such as quercetin-glucuronide, epicatechin, (Santos et al. 2012) and flavonoids (Sheny et al. 2012; Raghunandan et al. 2009) present in *E. globulus* facilitate in transforming the shape of nanoparticles.

In the present study, the toxic effect of *E. globulus* leaf extract and green synthesized ZnO-NPs was evaluated against lesser grain borer. Plant extract had insecticidal effect on adults of *R. dominica*. Both eco-friendly biopesticides showed effective results but green synthesized ZnONPs showed more efficacy than *E. globulus* leaf extract. According to results of our experiments, mortality of lesser grain borer increase with the increase in concentration of plant extract. Similarly with the increase of exposure period mortality of test insects also increased. Our results

Table 5 Toxicity of green-synthesized ZnONPs using *Eucalyptus globulus* leaf extract against adults of *Rhyzopertha dominica*

Exposure time (days)	^a LC ₅₀ (ppm)	^b Fiducial limits	^c χ^2	S.E	Slope
3	564.77	322.91- 987.77	0.99	0.12	1.37
7	371.38	227.33- 606.71	0.97	0.11	1.53
11	285.22	177.05- 459.46	0.97	0.11	1.58
15	202.11	118.09- 345.88	0.99	0.12	1.41

^aLC₅₀=Lethal concentration that kills 50% of the exposed insects.

^bFiducial limits=Lower and Upper limits. ^c χ^2 =Chi-square values.

^ddf=degree of freedom

n (number of replications) = 4, $\alpha=0.05$

also revealed that as LC₅₀ value decreased mortality of the insects increased which showed the efficacy of test products. The results of this study are supported by Malaikozhundan et al. (2017) who explained the insecticidal toxicity of *Bt*-ZnO nanoparticles against *Callosobruchus maculatus* and found that these nanoparticles were much effective in the control of *C. maculatus*. Wazid et al. (2018) also investigated the insecticidal effect of zinc oxide nanoparticles against *C. maculatus* at different concentrations and recorded that as the concentrations and post treatment exposure time increased, the mortality also increased. Malaikozhundan and Vinodhini (2018) tested *Pongamia pinnata* coated zinc oxide nanoparticles against *C. maculatus* and results showed that due to Pp-ZnO NPs there was reduction in reproduction rate and hatchability of *C. maculatus*. Furthermore, 100% mortality of *C. maculatus* was observed due to Pp-ZnO NPs

Table 6 Growth inhibition (Mean ± SE) of F₁ progeny of *Rhyzopertha dominica* caused by different concentrations of *Eucalyptus globulus* leaf extracts and green synthesized ZnO-NPs after 30 days

Test Product	Concentrations (ppm)	Growth inhibition (%)
<i>E. globulus</i> leaf extract	300	35.6 ± 1.76e
	600	39.8 ± 1.56de
	900	44.5 ± 1.75d
	1200	53.9 ± 1.48c
	1500	64.9 ± 1.61b
Green synthesized ZnO-NPs	1800	75.7 ± 1.36a
	100	55.7 ± 1.50d
	200	63.5 ± 1.92c
	300	69.4 ± 1.72c
	400	76.0 ± 1.21b
	500	82.5 ± 0.77ab
600	87.0 ± 1.40a	

Means (within the same column) having similar letters are not significantly different. = 100*(1-t/c), where t is the number of adults in treated grains, and c is the number of adults in control

n (number of replications) = 4, $\alpha=0.05$

at dose 25 µg /mL. Stadler et al. (2012) successfully applied nano alumina and found 100% mortality of *S. oryzae*. Effectiveness of green zinc oxide nanoparticles may be attributed due to damage to protective wax coat on the cuticle of insects, both by sorption and abrasion so that the insects begin to lose water and die due to desiccation (Arumugam et al. 2015). The nanotechnology is greatly helpful for ecofriendly sustainable pest management, as nanoparticles show different electrical conductance, physical strength, biochemical activity, and magnetic properties (Nykypanchuk et al. 2008). Plant extracts can be proficiently employed for the synthesis of silver and gold nanoparticles as good reducing agents. With the use of plant extracts, the shape and size can easily be controlled. These types of nanoparticles produced using plants have been applied in a variety of applications for human benefit (Kumar and Yadav 2009).

In present study, the growth inhibitory effect of both *E. globulus* leaf extract and green synthesized ZnO nanoparticles on the F₁ progeny of *R. dominica* was also observed after 30 days. The results showed that both *E. globulus* leaf extract and green synthesized ZnO-NPs had notable effect but green synthesized ZnO-NPs were more efficient. The results of current study are supported by Doaa and Nilly (2015) who used silica nanoparticles against three main stored grain insect pests *S. oryzae*, *R. dominica* and *C. maculatus* and results were complete reduction in F₁ progeny obtained for all the three pest. Salem et al. (2015) used aluminium oxide and zinc oxide nanoparticles against *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae) and obtained good results regarding mortality and growth inhibition.

Conclusion

The present study showed good toxicity of *E. globulus* leaf extract and green synthesized zinc oxide nanoparticles (ZnO-NPs) against *R. dominica*. Green synthesized ZnO-NPs showed more toxicity than *E. globulus* leaf extract. Moreover, green synthesized ZnO-NPs has reduced the progeny development of the treated insects showing good growth inhibitory effect. Thus, green synthesized ZnO-NPs can be an alternative of conventional insecticides and can be used for ecofriendly sustainable management of stored product pests.

Authors' contributions MAS and MH designed and conducted the experiment and collected the data. MAS, MH, and MS analyzed the data. MAS and MH wrote the manuscript. MAS and STS helped in apprehending the idea of this research, designing the layout of experiment and improving the write-up, format and language of this manuscript. MH and MS reviewed the manuscript, add and improved result section, edited the format of the tables according to the format of the

journal. This final manuscript was ultimately perused, scrutinized and approved for final submission by all authors.

Availability of data and material The data sets used and/or analyzed during the current study are available from the corresponding author on request.

Declarations

Ethics approval The authors agree to all the concerned regulations.

Consent for publication The authors agree to publish this scientific paper in the International Journal of Tropical Insect Science.

Conflict of interest The authors declare that they have no conflict of interest.

References

- Abbott WS (1925) A method of computing the effectiveness of an insecticide. *J Econ Entomol* 18(2):265–267
- Alam T, Khanb RAA, Alic A, Sherc H, Ullahc Z, Alid M (2019) Biogenic synthesis of iron oxide nanoparticles via *Skimmia laureola* and their antibacterial efficacy against bacterial wilt pathogen *Ralstonia solanacearum*. *Mater Sci and Eng C* 98:101–108
- Aminuzzaman M, Ying LP, Goh WS, Watanabe A (2018) Green synthesis of zinc oxide nanoparticles using aqueous extract of *Garcinia mangostana* fruit pericarp and their photocatalytic activity. *Bull Mater Sci* 41(2):1–10
- Arjunan NK, Murugon K, Rejeeth CH, Barnard DR (2012) Green synthesis of silver nanoparticles for the control of mosquito vectors of malaria, filariasis and dengue. *Vector Borne Zoonot Dis* 12:262–268
- Arumugam G, Velayutham V, Shanmugavel S, Sundaram J (2015) Efficacy of nanostructured silica as a stored pulse protector against the infestation of bruchid beetle, *Callosobruchus maculatus* (Coleoptera: Bruchidae). *Appl Nanosci* 6(4):445–450
- Barik TK, Kamaraju R, Gowasmi A (2012) Silica nanoparticles a potential new insecticides for mosquito vector control. *Parasitol Res* 111:1075–1083
- Batish DR, Singh HP, Kohli RK, Kaur S (2008) Eucalyptus Essential oil as a Natural Pesticide. *Forest Ecol Manag* 256(12):2166–2174
- Campos MG, Webby RF, Markham KR (2002) The unique occurrence of the flavone aglycone tricetin in Myrtaceae pollen. *Z Naturforsch C* 57(9–10):944–946
- Cauerhff A, Castro GR (2013) Bionanoparticles a green nanochemistry approach. *Electron J Biotechnol* 16(3):11–11
- Chanbang Y, Arthur FH, Wilde GE, Throne JE (2007) Efficacy of diatomaceous earth and methoprene, alone and in combination, against *Rhyzopertha dominica* (F.) (Coleoptera: Bostrichidae) in rough rice. *J Stored Prod Res* 43(4):396–401
- Debnath N, Das S, Seth D, Chandra R, Bhattacharya SC, Goswami A (2011) Entomotoxic effect of silica nanoparticles against *Sitophilus oryzae* (L.). *J Pest Sci* 84(1):99–105
- Doaa MB, Nilly AH (2015) Entomotoxic effect of Aerosil 200 Nano Particles against three main stored grain insects. *IJAR* 3(8):1371–1376
- Finney DJ (1971) *Probit Analysis*. 3rd ed. Cambridge University Press, Cambridge (ISBN 052108041X. OCLC 174198382)
- Flinn PW, Hagstrum DW, Reed C, Phillips TW (2010) Insect population dynamics in commercial grain elevators. *J Stored Prod Res* 46(1):43–47

- Godghate AG, Sawant RS (2014) Secondary metabolites determinations qualitatively from bark of *Butea monosperma* and *Eucalyptus globulus*. *Int J Sci Environ Technol* 3(2):497–501
- González JOW, Gutiérrez MM, Ferrero AA, Band BF (2014) Essential oils nanoformulations for stored-product pest control-characterization and biological properties. *Chemosphere* 100:130–138
- Haines CP (1991) Insects and Arachnids of tropical stored products: their biology and identification. (A training manual). Natural Resources Institute, Chatham, UK 246
- Iravani S (2011) Green synthesis of metal nanoparticles using plants. *Green Chem* 13:2638–2650
- Jiang I, Zheng F, Leng OF, Xu M, Zhao MJ (2010) Advances in research of nanopesticide. *Guangdong Agri Sci* 5:97–100
- Kavitha KS, Baker S, Rakshith D, Kavitha HU, Yashwantha Rao HC, Harini BP, Satish S (2013) Plants as green source towards synthesis of nanoparticles. *Int Res J Biol Sci* 2(6):66–76
- Khan AIS, Din N, Khattak S, Khalil SK, Lou YHY (2010) Appraisal of Different wheat genotypes against Angoumois grain moth, *Sitotroga cerealella* (Oliv.). *Pakistan J Zool* 42:161–168
- Khot L, Sankaran S, Maja J, Ehsani R, Schuster E (2012) Applications of nanomaterials in agricultural production and crop protection: A review. *Crop Prot* 35:64–70
- Ki HY, Kim JH, Kwon SC, Jeong SH (2007) A study on multifunctional wool textile treated with nanosized silver. *J Mater Sci* 42:8020–8024
- Kumar V, Yadav SK (2009) Plant-mediated synthesis of silver and gold nanoparticles and their applications. *J Chem Technol Biotechnol* 84(2):151–157
- Leider P, Dekorsy T (2008). Interactions of nanoparticles and surfaces. *Tag der m Andlichen Pr Aufung: 25 April. 352- Opus 53877*
- Liu Y, Tong Z, Prud'homme RK (2008) Stabilized polymeric nanoparticles for controlled and efficient release of bifenthrin. *Pest Manag Sci* 64(8):808–812
- Lorini I, Beckel H, Schneider S (2006) Efficacy of spinosad and IGR plus to control the pests *Rhyzopertha dominica* and *Sitophilus zeamais* on stored wheat grain In Proceedings of the 9th IWCSF Campinas, Sao Paulo, Brazil pp. 15–18
- Malaikozhundan B, Vaseeharan B, Vijayakumar S, Thangraj MP (2017) *Bacillus thuringiensis* coated zinc oxide nanoparticle and its biopesticidal effects on the pulse beetle, *Callosobruchus maculatus*. *J Photochem Photobiol* 174:306–314
- Malaikozhundan B, Vinodhini J (2018) Nanopesticidal effects of *Pongamia pinnata* leaf extract coated zinc oxide nanoparticle against the Pulse beetle, *Callosobruchus maculatus*. *Mater Today Commun* 14:106–115
- Marimuthu S, Rahman AA, Rajakumar G, Kumar TS, Kirthi A, Jayaseelan C, Bagavan A, Zahir AA, Elango E, Kamaraj C (2011) Evaluation of green synthesized silver nanoparticles against parasites. *Parasitol Res* 108:1541–1549
- Martins C, Natal-da-Luz T, Sousa JP, Gonçalves MJ, Salgueiro L, Canhoto C (2013) Effects of Essential Oils from *Eucalyptus globulus* leaves on soil organisms involved in leaf degradation. *PLoS One* 8(4):61233
- Mason LJ, McDonough M (2012) Biology, behavior, and ecology of stored grain and legume insects. *Stored Prod Prot* 1(7)
- Mishra BB, Tripathy SP, Tripathi CPM (2012) Repellent effect of leaves essential oils from *Eucalyptus globulus* (Mirtaceae) and *Ocimum basilicum* (Lamiaceae) against two major stored grain insect pests of coleopterans. *Nature and Science* 10(2):50–54
- Mukherjee P, Ahmed A, Mandal D, Senapati S, Sankar SR, Khan MI, Pasricha R, Sastry M (2001) Fungus-mediated synthesis of silver nanoparticles and their immobilization in the Mycelial matrix: A novel biological approach to nanoparticle synthesis. *Nano Lett* 1:515–519
- Nykypanchuk D, Maye MM, Van Der Lelie D, Gang O (2008) DNA-guided crystallization of colloidal nanoparticles. *Nature* 451:549–552
- Oskam G (2006) Metal oxide nanoparticles: synthesis characterization and application. *J Solgel Sci Technol* 37:161–164
- Pal S, Mondal S, Maity J, Mukherjee R (2018) Synthesis and Characterization of ZnO Nanoparticles using *Moringa Oleifera* Leaf Extract: Investigation of Photocatalytic and Antibacterial Activity. *Int J Nanosci Nanotechnol* 14(2):111–119
- PAS 71 (2011) Nanoparticles Vocabulary British Standards Institution London United Kingdom 2011
- Patil CD, Borase HP, Suryawanshi RK, Patil SV (2016) Trypsin inactivation by latex fabricated gold nanoparticles: a new strategy towards insect control. *Enzyme Microb Technol* 92:18–25
- Perez de Luque A, Rubiales D (2009) Nanotechnology for parasitic plant control. *Pest Manag Sci* 65:540–545
- Phillips T, Throne J (2010) Biorational approaches for managing stored-product insect. *Annu Rev Entomol* 55:375–397
- Puoci F, Lemma F, Spizzirri UG, Cirilo G, Curcio M, Picci N (2008) Polymer in agriculture a review. *Am J Agric Biol Sci* 3(1):299–314
- Raghunandan D, Basavaraja S, Mahesh B, Balaji S, Manjunath SY, Venkataraman A (2009) Biosynthesis of stable polyshaped gold nanoparticles from microwave-exposed aqueous extracellular antimalignant guava (*Psidium guajava*) leaf extract. *J Nanobiotechnology* 5(1):34–41
- Rahman A, Seth D, Mukhopadhyaya SK, Brahmachary RL, Ulrichs C, Goswami A (2009) Surface functionalized amorphous nanosilica and microsilica with nanopores as promising tools in biomedicine. *Naturwissenschaften* 96(1):31–38
- Rahman A, Talukder FA (2006) Bioefficacy of some plant derivatives that protect grain against the pulse beetle, *Callosobruchus maculatus*. *J Insect Sci* 6(3):1–10
- Rossi YE, Palacios SM (2015) Insecticidal toxicity of Eucalyptus cinerea essential oil and 1, 8-Cineole against *Musca domestica* and possible uses according to the metabolic response of flies. *Ind Crops Prod* 63:133–137
- Rouhani M, Samith MA, Kalantari S (2012) Insecticidal effect of silica and silver nanoparticles on the cowpea seedbeetle, *Callosobruchus maculatus* F. (Col: Bruchidae). *J Entomol Res.* 4:297–305
- Salem AA, Hamzah AM, Nariman ME (2015) Aluminium and zinc oxide nanoparticles as a new method in controlling the red flour beetle, *Tribolium castaneum* (Herbst) compared to malathion insecticides. *J Plant Prot Path* 1:129–137
- Santos SA, Freire CS, Domingues MRM, Silvestre AJ, Neto CP (2011) Characterization of phenolic components in polar extracts of *Eucalyptus globulus* Labill. bark by high-performance liquid chromatography–mass spectrometry. *J Agric Food Chem* 59(17):9386–9393
- Santos SA, Villaverde JJ, Freire CS, Domingues MRM, Neto CP, Silvestre AJ (2012) Phenolic composition and antioxidant activity of *Eucalyptus grandis*, *E. urograndis* (*E. grandis* × *E. urophylla*) and *E. maidenii* bark extracts. *Ind Crops Prod* 39:120–127
- Saxena RC (1989) Insecticides from neem. In: Arnason JT, Philogene BJR, Morand P (Eds.), *Insecticides of plant origin*. ACS symposium series 387:110–135 Washington DC USA
- Schmutterer H (1992) Control of diamond back moth by application of neem extracts. In: Talekar NS (Ed.) *Diamond back moth and other crucifer pests*. Proceedings second International Workshop, Asian vegetable research and development centre. Taipei Taiwan 325–332
- Sebei K, Sakouhi F, Herchi W, Khouja ML, Boukhchina S (2015) Chemical composition and antibacterial activities of seven eucalyptus species essential oils leaves. *Biol Res* 48(1):1–5

- Shafiqhi Y, Ziaee M, Ghosta Y (2014) Diatomaceous earth used against insect pests, applied alone or in combination with *Metarhizium anisopliae* and *Beauveria bassiana*. *J Plant Prot Res* 54(1):62–66
- Sheny DS, Mathew J, Philip D (2012) Synthesis characterization and catalytic action of hexagonal gold nanoparticles using essential oils extracted from *Anacardium occidentale*. *Spectrochim Acta A Mol Biomol Spectrosc* 97:306–310
- Shojaaddini M, Moharramipour S, Sahaf B (2008) Fumigant toxicity of essential oil from *Carum copticum* against Indian meal moth, *Plodia interpunctella*. *J Plant Prot Res* 48:411–419
- Stadler T, Buteler M, Weaver DK (2010) Novel use of nanostructured alumina as an insecticide. *Pest Manag Sci: Formerly Pestic Sci* 66(6):577–579
- Stadler T, Buteler M, Weaver DK, Sofie S (2012) Comparative toxicity of nano structured alumina and commercial inert dust for *Sitophilus oryzae* (L.) and *Rhyzopertha dominica* (F.) at varying ambient humidity levels. *J Stored Prod Res* 48:81–90
- Statistix 8.1 (2003) User's Manual. Analytical Software, Tallahassee, USA
- Stejskal V, Hubert J, Aulicky A, Kucerova Z (2015) Overview of present and past and pest associated risks in stored food and feed products: European perspective. *J Stored Prod Res* 64:122–132
- Wazid SN, Prabhuraj A, Naik RH, Shakuntala NM, Sharanagouda H (2018) Effect of Biosynthesized Zinc Oxide Green Nanoparticles on Pulse Beetle, *Callosobruchus analis* (Coleoptera:Chrysomelidae). *Int J Curr Microbiol App Sci* 7:503–512
- White NDG, Leesch JG (1996) Chemical control. In *Integrated Management of Insects in Stored Products*; Subramanyam B, Hagstrum DW Eds Marcel Dekker New York NY USA 287–330
- Yasir M, Mankin RW, ul Hasan M, Sagheer M (2021) Residual Efficacy of Novaluron Applied on Concrete, Metal, and Wood for the Control of Stored Product Coleopteran Pests. *Insects* 12(1):7. <https://doi.org/10.3390/insects12010007>
- Yasir M, Sagheer M, Abbas SK, ul-Hasan M, Ahmad S, Ijaz M (2019) Bioactivity of Lufenuron against *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae) *Sains Malaysiana* 48(1):75–80
- Ziaee M, Ganji Z (2016) Insecticidal efficacy of silica nanoparticles against *Rhyzopertha dominica* F. and *Tribolium confusum* Jacquelin du Val. *J Plant Prot Res* 56(3):250–256

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.