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Repurposing chicken eggshells, *Gallus gallus domesticus*, as nanoparticles to manage red flour beetles, *Tribolium castaneum*

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ABSTRACT

The red flour beetle (RFB), *Tribolium castaneum*, is one of the most serious pests on stored grains and in high-value grain products such as milled flour and baked products. They may cause significant problems in stored grain by direct feeding, damaging the grain, which may cause mold to increase and cause flour to change color. Currently, the management of RFB relies on insecticides with various modes of action which has resulted in pesticide resistance in beetles. Therefore, safer and more effective ways to treat stored product pests are needed. This research examined the use of chicken eggshell nano-powder alone and eggshell nano-powder combined with the biopesticide Spinosad in treated glass vials to control RFB adults and larvae. Laboratory trials with eggshell nano-powder alone at 0.04 mg/mm^2 and 0.13 mg/mm^2 were applied to glass vials adult RFBs were killed at or close to 100%. When RFB larva was exposed to eggshell nano-powder at 0.04 mg/mm^2, it had a mortality rate of only 48 ± 13 % after 7 days. Spinosad alone, when exposed to RFB larva had a mortality rate of only 56 ± 4 % after 7 days. When the eggshell nano-powder was combined with 1 ppm of commercial Spinosad, RFB larval mortality increased to 98 ± 2 % after 7 days. Thus, the eggshell nano-powder alone was sufficient to kill RFB adults, but in order to kill the RFB larvae, Spinosad had to be added to the eggshell nano-powder. The addition of Spinosad to nano-powder eggshells had an additive effect on the mortality rate of RFB larvae.

1. Introduction

In the United States of America (USA), 6 billion kilograms of eggshells are produced annually as a byproduct of poultry and egg farming (Ngayakamo and Onwualu, 2022). The U.S. Environmental Protection Agency (EPA) has identified eggshells as the 15th most significant food-related pollutant (Shang et al., 2022). Despite being a byproduct of the food industry, eggshells should be recognized as a highly sophisticated composite material (Waheed et al., 2020). Repurposing waste eggshells into valuable commodities is a promising endeavor (Nagayama and Onwualu, 2022). Efforts to repurpose eggshells for commercial, medical and industrial applications due to the characteristics of the eggshell such as being porous and composed of 93–97 % calcium, have been made (Torres-Mansilla et al., 2023). Previous studies have shown that eggshells, in the form of a powder with particles smaller than 90 μm, can be effective as a pesticide against stored pests such as *Sitophilus zeamais* in maize seeds, with a mortality rate LC 90 of 0.72 g/100 g (Olagunju et al., 2022). Here, we investigated the use of eggshells in a nano-powder formulation for use as a pesticide for stored product insect pests.

Nanomaterials have been used in various applications, such as medicine, energy, and biology (Amina and Bin, 2020). They have many advantages, but one of their primary advantages is the high surface-to-volume ratio, which makes them biocompatible (Moulton et al., 2010). One growing application of nanomaterials is pesticides. For example, Norton et al. (2023) showed that a zein micro carrier with silver nanoparticles works as a pesticide for mosquito larvae at levels as low as 1 ppm in an aquatic habitat. The use of nanomaterials for stored product pests, such as red flour beetles (RFB), *Tribolium castaneum* (Herbst), has primarily focused on silica-based materials like diatomaceous earth (DE) (Sabb our, 2015), and in combination with essential oils (Sabbour, 2020).

Eggshells were selected for this project as a safe and readily available agricultural waste material, suitable for use with stored food products.

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Comprised of calcium carbonate ($CaCO_3$), eggshells effectively absorb both water and pesticides such as Spinosad, which is certified organic by the USDA and FDA. This natural method offers a promising solution for managing *T. castaneum* and other pests associated with stored products. produced by a soil bacterium and was chosen due to its organic label by the USDA and FDA ("Spinosad General Fact Sheet," access 2024). A naturally occurring organic substrate such as eggshells that can kill crawling insects will make a powerful new tool for managing *T. castaneum* and perhaps other stored product pests. The objective of this research was to investigate the use of eggshell nano-powder with and without the naturally-derived insecticide Spinosad, as a new approach for controlling *T. castaneum*, a common stored product insect.

2. Material and methods

2.1. Reagents

Chemicals: Spinosad was acquired from Chem Service (West Chester, PA). Copper grids (200 mesh, (74 μm)) for Transmission Electron Microscopy (TEM), hydrochloric acid (HCl), and filter paper (10 cm) were all purchased from Sigma Aldrich (St. Louis, MO). Chicken eggs were purchased from a local grocery store.

2.2. Particle preparation

2.2.1. Egg microparticles preparation

Three chicken eggs were cracked, and all the contents were separated from the shell. The eggshells were rinsed in distilled water and placed in a food dehydrator (Commercial Chef, Spartanburg, SC) at 70 °F for 2 h. Sixteen grams of dried eggshells (5 cm) were crushed into small pieces using a mortar and pestle. The eggshell pieces (1 mm) were added to a 70 mL HCl (0.1 M) solution. The suspension was heated and stirred at 35 °F. After 10 min, the suspension formed two layers: a foam layer on top and a liquid layer with the eggshell pieces on the bottom. The suspension was stirred for an additional 20 min. Then, the eggshell suspension was decanted, leaving only the foam. This suspension was filtered through a 10 cm diameter filter paper disc in a Buchner funnel. The eggshell pieces were collected from the Buchner funnel and 0.5 g were placed in a Nano mill (Retsch Co., Newton, PA) that had a 50 mL stainless steel container with 50 stainless steel balls each of 5 mm dia. The stainless-steel container was filled with 25 mL of distilled water and milled at 15 Hz (900 rpm) for 30 min to create a nano eggshell suspension. After grinding the eggshells, the suspension was collected in a 50 mL Falcon® tube.

2.2.2. Preparation of spinosad solutions

Spinosad solutions were prepared in hexane at the following concentrations: 1 ppm vial concentration ($0.071\ mg/(L \times mm^2)$, and 0.1 ppm vial concentration $=(0.0071\ mg/(L \times mm^2))$, via serial dilution from a stock solution of 100 ppm Spinosad in hexane (Spinosad from Sigma Aldrich, St. Louis, MO, USA).

2.3. Characterization of particles

2.3.1. Sizing of particles

Scanning electron microscope (SEM) images were recorded on an SNE-Alpha high-resolution tabletop SEM with a 5-axis XYZRT stage at 5 nm resolution (Nanoimages, Lafayette, CA). Elemental mapping of Ca^{2+} was conducted using Energy Dispersive X-ray spectroscopy (EDAX) and recorded on an EDAX element EDS with APEX™ software (Nanoimages, Lafayette, CA).

The average size of the eggshell nanoparticles was 117 (±5 SE) nm ($n = 3$) as determined by SEM (Fig. 1).

2.3.2. Humidity absorbance of eggshells

The humidity absorption capacity of eggshells was measured using a gravimetric technique. In brief, 1 mL of eggshell solution at 0.1 g/L was added to 3 different vials with a dimension of 12.7 × 38.1 and a volume of 1.85 mL. The water was allowed to evaporate at room temperature. Once all the water had evaporated, the eggshell vials were placed in a desiccator with Drierite desiccant (W. H. Hammond, Xenia, OH, USA) for 48 h, and the weight recorded. The eggshell-filled vials were then placed in a water desiccator for 48 h and the weight was recorded again. The gravimetric measurements (dried and humid) were measured in triplicate.

2.3.3. Insect rearing

RFB larvae and adults were reared using methods previously reported (Cato et al., 2019). Rearing chambers were Ball 473-ml Wide Mouth glass canning jars, with a 90 mm piece of P8 filter paper (Thermo Fisher, Waltham, Ma) used for ventilation in place of the metal lid insert. The rearing medium was organic, stone-ground whole wheat flour (Great River Milling, Cochrane, WI, USA) supplemented with 5 % brewer's yeast (95:5 % by weight (company name and city)). Approximately 50 mixed-sex adult beetles were added to the rearing media in the glass jars and kept in growth chambers set at 27 °C and ∼65 % relative humidity (RH) with a photoperiod of 16:8 (L:D).

2.4. Bioassay

2.4.1. Preparation of vials for mortality assays with RFBs

Glass vials measuring 12.7 × 38.1 mm with a volume of 1.85 mL were treated as follows: an untreated control vial (water only), a high-concentration (H) eggshell vial with $13 \pm 2\ mg/cm^2$, a low-concentration (L) eggshell vial ($4 \pm 2\ mg/cm^2$), eggshell ((H) or (L)) + Spinosad (S) at concentrations of 1, or 0.1 ppm, and Spinosad only at

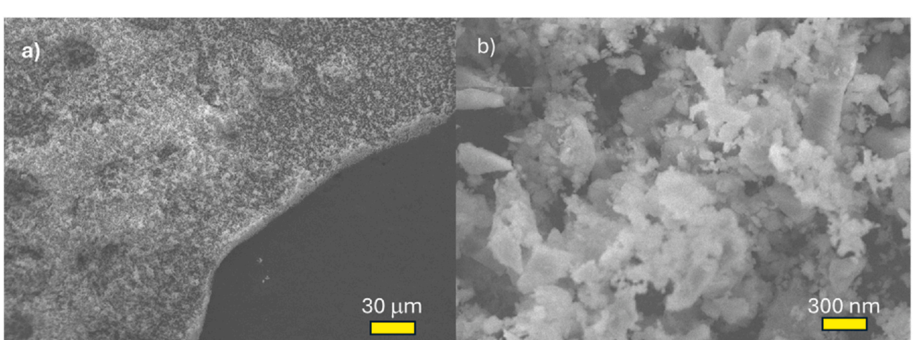

Fig. 1. SEM images of eggshell particles used in this research. All SEM samples were placed on a carbon tape, which was placed on a SEM stub. a) Image of a layer of ground eggshelss taken at 500-x, and b) clusters of ground eggshells at a magnification of 1000-x. Note from the 300 nm scale that many of the particles are 100 nm in diameter or smaller.

concentrations of 1 or 0.1 ppm. Eggshell-treated vials were prepared by adding 1 mL or 0.25 mL of an eggshell suspension of 0.1 g/L to the vial and allowing the liquid to evaporate. Spinosad (0.5 mL to the vial) was added after the water had evaporated from the eggshells, either at a concentration of 1 or 0.1 ppm. The Spinosad-treated vials were spun on a rotator (Scilogex MX-RL-E Tube Rotator - Analog Rotisserie, Fischer Scientific, Waltham, Ma) for 1 h to evaporate the Spinosad. The water was not spun because it took days for the water to evaporate. RFBs cannot climb vertical glass sides, so the treated surface for all treatments was the bottom floor of each vial.

Each treatment had five replicates, with ten RFB adults or RFB larvae/replicate vial. Second instar larvae were selected, the selection occurred using a sieving method. During exposure, there was no food in the treated vials. After seven or fourteen days of exposure, the beetles were placed on a clean surface before being counted. The adults and larvae were allowed to recover for 24 h with a small amount of rearing diet and then counted. For larval treatments, the larvae were placed on a clean surface with diet after 3- or 7-days exposure, then counted. (Hagstrum 2016).

2.4.2. *Experimental design and data analysis*

The treatments described in section 2.4.1 were analyzed using ANOVA testing. The experiments were set up using a general randomized block design. Table 1 is a summary of the average of results from the results described in section 2.4.1. ANOVA test was conducted with Origin (OriginLab Corporation, Northampton, MA). Post-hoc comparisons of the different treatments were compared at $P < 0.05$, using the Fischer-LSD mean-comparison test.

3. Results

3.1. *RFB adult and larva bioassays with eggshells*

Eggshells alone without Spinosad caused mortality to adult RFBs at both treatment levels and for each exposure time (Table 1). Adult mortality at seven days was 94 % for the 4 mg dose, and 100 % at 14 days. The higher dose of 13 mg eggshells elicited 100 % mortality of adults following both exposure times. A dose-response curve of adult RFB mortality for eggshells across a range of application rates at the two-exposure times is in Fig. 2. Eggshells were much less effective on larvae. Three-day exposures of larvae to the two eggshell treatments of 4 or 13 mg elicited average mortality of 6 % and 18 %, respectively. The same two eggshell treatments (4 or 13 mg treatments) for larvae after 7 days resulted in 48 % and 74 % mortality at the same treatment levels. Spinosad applied mortality rate at adults at both the low and high

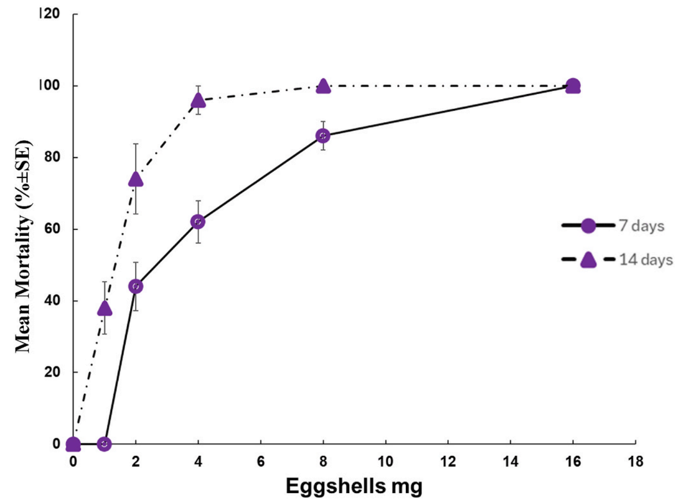

Fig. 2. Dose-response curve for mortality of RFB adults from 0 to 16 mgs of eggshells after 7 days (circles), and 14 days (triangles).

application rates after 7 days had a mortality rate of 0 % but killed nearly 50 % of adults following the 14-day exposure. Similarly, both concentrations of Spinosad alone did not affect larvae after three days, but after 7 day there was 18 % kill for the 0.1 ppm and 56 % to the 1.0 ppm. All adult beetles, as expected, were killed at both exposure times for all combinations of the application rates of eggshell with Spinosad. However, RFB larvae remained very tolerant to the eggshell-Spinosad combinations after 3 days of exposure. The higher levels of eggshells combined with both Spinosad concentrations elicited 100 % larval mortality after 7 days of exposure.

3.2. *RFB interaction with eggshells*

SEM analysis was conducted on RFB adults and larvae after eggshell exposures (Fig. 3). The eggshells were deposited on the surface of the RFB like a powder. EDAX analysis confirmed that the powder on the surface of the RFB adults and larvae contained Ca^{2+}; calcium was not present in the control sample. Differences were seen between the mouthparts of RFB adults treated with eggshells, but nothing like the eggshells showed on the untreated RFBs. The deposition on the mouthparts was not as pronounced as elsewhere and showed signs of damage in the treated samples.

Table 1
Percent mortality of adults and larvae of the red flour beetle after exposure to ground eggshells at two levels, with or without the addition of the Spinosad.

Treatment	Adults[A]			Larvae[B]				
	7 days		14 days	3 days		7 days	ANOVA	
							Effect	P value
Untreated Control	0[a]		0[a]	0[a]	*	24.0 (±11.7)[de]	Treatment	<0.01
Eggshells 4 mg	94.0 (±6.0)[b]		100[d]	18.0 (±8.0)[ab]	*	48.0 (±13.2)[cd]	Day	<0.01
Eggshells 13 mg	100[b]		100[d]	52.0 (±5.8)[c]	*	74.0 (±8.1)[abc]	T × D	0.03
Spinosad 0.1 ppm	0[a]	*	18.0 (±3.7)[b]	0[a]	*	18.0 (±8.0)[e]		
Spinosad 1.0 ppm	0[a]	*	54.0 (±5.1)[c]	0[a]	*	56 (±4.0)[c]		
ESs 4 mg + 0.1 ppm Spin.	100[b]		100[d]	32.0 (±5.8)[bc]	*	70 (±4.5)[bc]		
ESs 4. mg + 1.0 ppm Spin.	100[b]		100[d]	52.0 (±5.8)[c]	*	98.0 (±2.0)[ab]		
ESs 13 mg + 0.1 ppm Spin.	100[b]		100[d]	50.0 (±4.5)[c]	*	100[a]		
ESs 13 mg + 1.0 ppm Spin.	100[b]		100[d]	56.0 (±6.0)[c]	*	100[a]		

3Means within a column followed by the same letter in a column are not significantly different ($P > 0.05$). A × symbol between values in adjacent columns signifies a significant difference between the two means ($P < 0.05$).

[A] Kruskal-Wallis test was applied for Adults data.

[B] Fixed effects including treatment, day, and T × D two-way interaction for larvae data were analyzed using two-way analysis of variance (ANOVA) model. Model residuals were checked for normality using Shapiro-Wilk test ($P > 0.05$). Tukey's multiplicity adjustment was applied when comparing mortality among treatment groups for 3 days or 7 days, respectively.

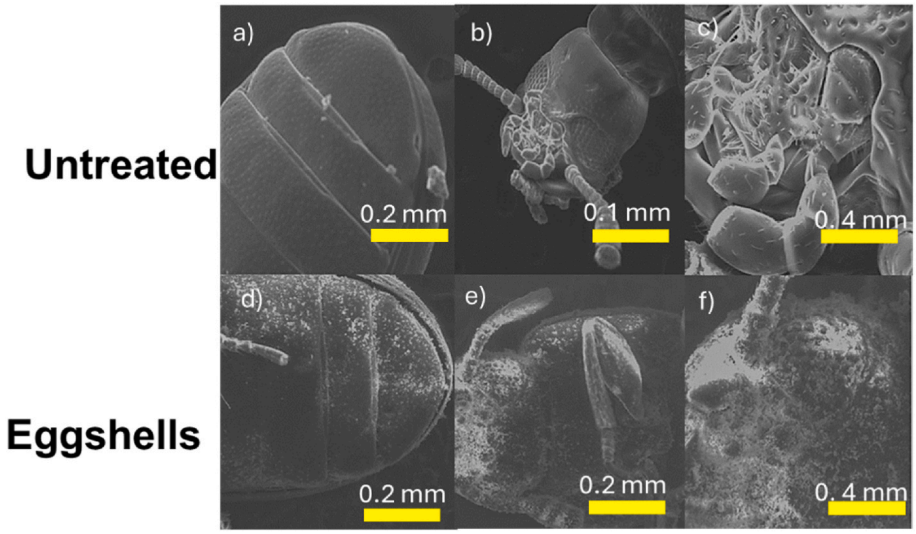

Fig. 3. SEM images of RFB adult a-c control d-f exposed to eggshells. All SEM samples were placed on a carbon tape, which was placed on an SEM stub.

4. Discussion

Eggshell particles were selected because of their unique ability to absorb water, due to their composition of calcium carbonate ($CaCO_3$). It has been determined that $CaCO_3$ from eggshells can absorb 1.8 g of water per gram (Ivanovich et al., 1967), rendering eggshells an effective natural source of $CaCO_3$. Eggshells, composed of 93–97 % $CaCO_3$, possess a porous structure that makes them an ideal substrate for pesticides. Although eggshells have been used in the remediation of pesticides, their practical application as a natural pesticide is somewhat limited. (Mittal et al., 2016; Kınaytürk et al., 2021).

Spinosad is a naturally-occurring insecticide derived from a soil bacterium, has been certified organic by the EPA since 1997 (Bunch et al., 2014). Spinosad has also been used as an insecticide towards other stored pests such as *Callosobruchus maculatus* (Lü et al., 2017), *Cadra cautella* (Sammani et al., 2020) and *Rhyzopertha dominica* (Dissanayaka et al., 2020). For the purpose of this study, we focus on the RFB. However, its effectiveness against RFB varies between 0 and 84 % for adults and 0–34 % for larvae depending on the surface it has been applied (Fang, Subramanyam, and Arthur, 2002; Huang and Subramanyam, 2007; Athanassiou et al., 2010; Hertlein et al., 2011).

Other factors that have been found to impact insecticidal properties are particle size. Chiu's (1939) study on "inert" dust, also known as silica found that particles larger than 100 μm had no effect on mortality while smaller particles caused the highest mortality. The importance of particle size lies in its ability to adhere to insects. This adhesion depends on the surface area exposed and the weight of the material. Since the surface of the insect is fixed, the Chiu study indicates that the effectiveness of "inert" dust for adhesion diminishes as particle size decreases. As particle size decreases, both weight and particle diameter also decrease, increasing the surface area relative to the insect.

The unit weight of a material is inversely related to its diameter; as the diameter of the particles decreases, their surface area increases while their weight decreases. Thus, the relationship between particle adhesion and surface area is inversely related to particle diameter and unit weight. In summary, smaller particles with a larger surface area tend to adhere more effectively to insects. In our study particle size of the eggshell nano-powder is 117 nm, which is well below the 100 μm cut off of the Chiu study.

Eggshells have been used as pesticides in two previous cases, with *Spodoptera littoralis* and *Sitophilus zeamais* (Nwaubani and Fasoranti, 2008). In the case of *S. littoralis*, the eggshells were treated in water, and the concentration required to cause 50 % mortality was 935 ppm after 11 days. In the case of *S. zeamais*, the eggshells were applied directly to maize seeds, and 5000 ppm (0.5 g/100 g) resulted in 90 % mortality after 7 days (Olagunju et al., 2022). However, the amount that was required here may be due to the size of the particles. This is the first report on eggshell nano-powder for the RFB, and after 7 days, 94 % mortality was achieved at was 0.04 mg/cm^2. The eggshells nano-powder alone achieve 100 % mortality at 2.5 mg/cm^2 at 7 days. The Spinosad alone achieved a mortality of 54 % from an application of 0.5 mL of a 1 ppm solution after 14 days. Eggshell nano-powder didn't kill 100 % in the larvae. However, the combination of eggshell nano-powder and Spinosad was able to achieve 100 % mortality after 7 days; the combination seems to have an additive effect.

As mentioned above, eggshell nano-particles nanoparticles may act as a desiccant against insects that cause death by itself or in combination with an insecticide. Future work should to determine the mode of action eggshells against insects, then it could be evaluated as a potential substitution for DE. One of the disadvantages to DE is that it reduces the bulk density of wheat and other grain, which affects the value of the commodity in marketing, and eggshells are a food source. On the other hand, eggshell nano-powder has the potential to be a marketable replacement for DE. There can also be a cost benefit to replacing DE with eggshell nano-powder, one kg of DE costs $79.95 in USD, while 1 kg of finely ground eggshells cost $9.00 estimated from our methods here, nearly a 9-fold difference in cost while upcycling a waste product.

5. Conclusions

Red flour beetles exposed to eggshell nanoparticles had a mortality rate of 100 % after 7 days at an 8 mg treatment to the bottom of vials. RFB larvae had to be exposed to Spinosad + eggshells to obtain 100 % mortality after 7 days (Table 1). The addition of the Spinosad was important when treating the RFB larvae. Future work is needed to determine if eggshell nanoparticles can be combined with low levels of commercial pesticides for effective treatment and much lower residues of insecticide. Eggshell nanoparticles alone could potentially be a replacement for DE as a desiccant to control grain pests and avoid the reduction in the bulk density of grain found with DE.

CRediT authorship contribution statement

Amie Norton: Writing – original draft, Conceptualization. **Lee W. Cohnstaedt:** Supervision, Resources, Conceptualization. **Jeff Whitworth:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **Xuan Xu:** Data curation, Formal analysis. **Thomas W. Phillips:** Writing – review & editing, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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