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Eco-Friendly Low-Cost Insecticidal Formulation Extracted from Orange Peel Essential Oil and ZnO Nanoparticles against *Tribolium castaneum*

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Abstract
This study investigated the insecticidal potential of *Citrus sinensis* (L.) essential oil derived from orange peels, its emulsifiable concentrate (EC), and zinc oxide (ZnO) nanoparticles alone and in combination with *C. sinensis* oil against *Tribolium castaneum* (Herbst). GC/MS analysis of orange peel oil identified 31 compounds, with limonene (45.8%), α-pinene (16.38%), β-pinene (10.49), and γ-terpinene (10.01%) being the most prevalent. EC formulation of *C. sinensis* oil exhibited good emulsion stability and foam formation, with a separation layer of 1 mL and foam formation of 2 mL. Characterizations of prepared nanoparticles revealed mean sizes of 433.2 nm for zinc oxide nanoparticles (ZnO NPs) and 458.4 nm for ZnO-oil nanoparticles. Toxicity assays demonstrated that both *C. sinensis* essential oil and its EC formulation exhibited insecticidal activity against *T. castaneum*, with LC_{50} values of 0.246 and 0.215 g/kg, respectively. ZnO with essential oil NPs formulation achieved 100% mortality at lower concentrations and shorter exposure times than ZnO NPs alone or bulk ZnO. These findings suggest that *C. sinensis* waste, specifically the peel, can be effectively utilized as a source of natural insecticides. The combination of essential oil and ZnO nanoparticles, showcasing synergistic effects, presents a promising approach for developing sustainable and environmentally friendly pest control solutions for stored grains.

Keywords: *Citrus sinensis*, Zinc oxide, Botanicals, Emulsifiable concentrate, Nanoparticles, Nanoencapsulation.

1. Introduction

T. castaneum Herbst (Coleoptera: Tenebrionidae) is a cosmopolitan pest of stored grains that causes significant economic losses and food contamination worldwide [1]. The conventional control methods for this pest rely on synthetic insecticides and fumigants, which have drawbacks such as resistance development, environmental pollution, and human health hazards [2]. In response to these challenges, there has been an increased demand for safe and eco-friendly pest control methods. Research on naturally occurring toxicants from plants as new alternative pesticides is gaining traction due to essential oils' low mammalian toxicity, complete biodegradability, multifunctionality, and environmental safety [3].

Essential oils have been found to possess various bioactive properties, including insecticidal, ovicidal, antifeedant, oviposition inhibition, and repellency effects against numerous insect pests [4]. Citrus essential oils, particularly those derived from citrus peels, have demonstrated strong insecticidal activity against *T. castaneum*. These oils exhibit both contact toxicity and fumigant effects. Studies have reported that different citrus oils, such as those from *Citrus paradisi* Macfad. (grapefruit) and *Citrus reticulata* Blanco (mandarin), can effectively kill various life stages of the beetle, including larvae and adults. The efficacy varies depending on the type of citrus oil and its concentration used in the tests [5, 6]. Citrus essential oils also act as repellents to *T. castaneum*. Research highlighted that these oils can deter beetles from infesting stored products, thereby functioning as a preventive measure in pest management [7]. The obtained essential oil from orange peel, *C. sinensis* L. (Sapindales: Rutaceae) has been the subject of several investigations due to its functionality as the first pick for many biopesticides, mainly because of their various bioactivities, such as antibacterial, antioxidant, anti-inflammatory, cytotoxic, and anticancer [8]. *C. sinensis* is widely cultivated; however, orange peels have been reported as an excellent raw material for various value-added products. The essential oil with insecticidal properties against multiple pests, including *T. castaneum* [9, 10]. *C. sinensis* essential oil contains mainly monoterpenes, such as limonene, β-pinene, and myrcene, which can affect

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insects' nervous and respiratory systems [11]. The obtained essential oil from orange peel (*C. sinensis*) has been the subject of several investigations due to its functionality as the first pick for many biopesticides, mainly because of their various bioactivities, such as antibacterial, antioxidant, anti-inflammatory, cytotoxic, and anticancer [8].

Zinc oxide (ZnO) is a metal oxide used as a fungicide, bactericide, and insecticide in agriculture and industry [12].

Nanotechnology has been applied to various fields of science and technology, including agriculture and pest management. Nanotechnology can be used in the development of pesticides that are more efficient, effective, safe, and eco-friendly than conventional pesticides. Nanotechnology can enhance pesticides' delivery, targeting, stability, solubility, and biodegradability and reduce their toxicity, dosage, and environmental impact [13]. ZnO NPs have shown significant insecticidal efficiency against stored-product insects, particularly *T. castaneum*. Research indicates that ZnO NPs exhibit a toxic effect on *T. castaneum* adults over time post-exposure [14]. The toxicity of ZnO nanoparticles can be attributed to their ability to generate reactive oxygen species, which lead to oxidative stress in insects. This oxidative stress alters cellular functions and can compromise overall insect health, leading to lethality [15]. Additionally, the sharp edges of ZnO NPs can cause physical damage to the insect cuticle upon contact. This leads to increased permeability and dehydration, ultimately resulting in mortality [16, 17]. The combined effects of physical damage to the cuticle and increased dehydration are significant factors in the insecticidal properties of ZnO nanoparticles, leading to increased mortality rates in insect populations exposed to these materials [12]. The implementation of ZnO nanoparticles in stored product protection is not only limited to their standalone application but can also be integrated with other pest management strategies [18]. Their potential for biosynthesis through eco-friendly methods emphasizes their role in sustainable agricultural practices, further enhancing their appeal for use in managing storage pests like *T. castaneum.*

-This study aimed to evaluate the toxicity of *C. sinensis* peel essential oil, bulk ZnO or ZnO NPs individually, and the combination of ZnO and *C. sinensis* oil NPs as eco-friendly low-cost substances against *T. castaneum* adults.

2. Materials and methods

2.1. Chemicals

Pure ZnO was supplied by El-Nasr Pharmaceutical Chemicals Co.

2.2. Plant materials

Fresh fruits of orange, *C. sinensis* byproducts after extracted juice were collected from Al Shams Agro-Group (Station 22 Wadi Al--Molak, Al--Tal Al--Kaber, Ismailia, Egypt) from September to November 2021.

2.3. Extraction of essential oil

A Clevenger-type apparatus was used to extract the essential oil from the citrus plant's fresh peels. According to Egyptian Pharmacopeia 1984, two kilograms of fresh peels were hydro-distilled for 3 hours. Anhydrous sodium sulphate was used to dehydrate the resultant essential oil, which was then stored in a deep freezer at -20 ºC for GC-MS analysis.

2.4. Characterization of essential oil through GC-MS

~~A~~ Thermo Scientific Trace GC Ultra/-ISQ Single Quadrupole MS, TG-5MS fused silica capillary column (30 m, 0.251 mm, 0.1 mm film thickness) was utilized to conduct the GC-MS study. The procedure and conditions were followed exactly as stated [19]. A tentative identification of the compounds was carried out by comparing the compounds respective retention times and mass spectra to published data from NIST, the GC-MS system's WILLY library, and/or public data [20].

2.5. Insect rearing

T. castaneum adults were reared and kept in a lab setting with 27 ± 2 °C, 60 to 65% relative humidity, and a 12 h light/dark cycle without any pesticide exposure. *T. castaneum* cultures were kept in big plastic containers with tiny holes for aeration, and the culture medium consisted of wheat flour combined with yeast (10:1, w: w). Adults without sex who had experienced delusions for two to four weeks were used.

2.6. EC formulation of *Citrus sinensis* essential oil

The compound was naturally prepared as an emulsifiable concentrate formulation of 5% EC (V/V) by mixing *C. sinensis* essential oil with appropriate amounts of emulsifier (IS emulsifier from the Egyptian starch yeasts & detergents co.) and natural solvent (mineral and vegetable oils, "sesame oil").

2.7. Physico-chemical properties of the prepared formulation.s

2.7.1. -Emulsion stability test

The test was conducted in compliance with WHO guidelines [21]. 75–80 mL of distilled water was added to a 250 mL beaker and heated to 30 ± 1°C. The EC was prepared using a pipette and a glass rod spinning at roughly four revolutions per second. With constant swirling, tested water was added to the beaker until the volume reached 100 mL. Immediately pour the beaker's contents into a dry, clean, graduated 100 mL cylinder. Three min passed between the start of the EC addition and the pouring of the emulsion into the 100 mL cylinder. After an hour at 30-31 °C, the cylinder was checked for creaming or separation.

2.7.2. Foam test

2.7.2. Foam test

The emulsion stability test was performed to determine the foam amounts generated on the surface of the emulsion in the cylinder after 5 min [21].

2.8. Fabrication of ZnO NPs

After adding 1.8 g of Zn $(NO_3)_2.6H_2O$ to 100 mL of deionized water, the mixture was agitated for 30 min. After that, NaOH (1 M) was added to the solution to bring its pH down to 10. Water circulation was used to ultrasonicate the solution for two hours. After being rinsed, the precipitate was dried.

2.9. Preparation of ZnO and nanoencapsulation of essential oils with ZnO

The pure essential oil that was utilized to blend with ZnO did not differ much from its EC formulation. ZnO nanoencapsulation of essential oil required 1.8 g Zn (NO3)2.6H2O dissolution in 90 mL of water. After that, the prepared solution was added to the EO (1 mL) and ethanol (9 mL) mixture and agitated for 60 min. NaOH (1 M) was added to the solution to decrease its pH to 10. Using a Bandelin model HD 3100, the precipitate was ultrasonically treated for 120 min while water was circulated. The sample was dried after rinsing the acquired material with ethanol and water.

2.10. Characterizations of zinc oxide nanoparticles

2.10.1. Dynamic light scattering (DLS)

The particle size of the zinc oxide nanoparticles was measured and analyzed using a particle size analyzer (Nano-ZS, Malvern Instruments Ltd. , UK) to establish the average diameter, size distribution, and zeta potential. Before the zeta potential measurement, the samples underwent sonication for 30-60 min.

2.10.2. Transmission electron microscopy (TEM)

The morphology of the stable nanoparticles was analyzed using a JEOL TEM model JEM-1230 in Tokyo, Japan. A tiny quantity of the nanoparticles was combined with deionized water and spread out on a carbon-coated copper grid. After a minute of treatment with a phosphotungstic acid solution, the sample was left to dry at room temperature before being examined and photographed. ImageJ 1.53 t was used to determine the droplet size of the prepared nanoparticles (Wayne Rasbandand Contributors, National Institutes of Health, USA).

2.11. Toxicity bioassay

The toxicity of *C. sinensis* essential oil and ZnO against *T. castaneum* adults was evaluated using direct contact assay [17]. A series of concentrations, 0.03, 0.1, 0.5, 1, and 2 g kg^{-1} of the essential oil and ZnO, were mixed separately with 50 g of wheat in 200 mL plastic vessels. The control treatment contained 50 g of wheat only. Twenty adults of *T. castaneum* were placed in each of the vessels. Each treatment had four replicates of both treated and untreated wheat. Treatments and control mortality were observed 2 and 5 days after treatment.

2.12. Data analysis

A statistical tool, SPSS software version 27.0 (SPSS, Chicago, IL, USA), was used to perform the statistical analysis of the lethal concentration causing 50% mortality (LC_{50}). According to the probit analysis, the log concentration-–response curves were utilized to calculate the LC_{50} for the bioassays [22]. Using the XLSTAT add-on 2019.2.2 program, mortality percentages were first submitted to a one-way analysis of variance and then Duncan's multiple range tests. The mean and standard error for each treatment were determined using a minimum of four replicates. If there was no overlap between the 95% confidence limits, the results were deemed to be significantly different.

3. Results

The chemical constituent of C. sinensis essential oil extracted from orange peel was analyzed using GC/MS chromatogram (Fig. 1). From the data presented in Table 1, it was clear that GC/MS analysis of the volatile oil of standard Baladi orange yielded 31 compounds representing 97.78-% of the total peak area of identified compounds. The major volatile constituents were identified as limonene 45.8%, α–pinene16.38%, *β*-pinene10.49%, ɣ-Terpinnene10.01%, Sabinene 8.95%, and some other remaining volatile constituents with low percentages.

Table 1: Chemical composition of the volatile oil of orange waste byproduct (*Citrus sinensis*) extracted by cold-pressing

No	R_t	Compounds	BP	M+	Molecular formula	Relative %
1	8.09	α- Pinene	93	136	$C_{10}H_{16}$	16.38
2	9.36	Sabinene	93	136	$C_{10}H_{16}$	8.95
3	9.98	β- Pinene	93	136	$C_{10}H_{16}$	10.49
4	11.11	Limonene	67	136	$C_{10}H_{16}$	45.8
5	12.21	ɣ-Terpinnene	93	136	$C_{10}H_{16}$	10.01
6	13.47	Linalool	71	154	$C_{10}H_{18}O$	0.30
7	14..86	Citronellal	69	154	C10 H18 O	0.08

8	16.32	Decanal	41	156	$C_{10}H_{20}O$	0.72
9	17.34	β-Citronellol	41	156	$C_{10}H_{20}O$	0.14
10	18.15	Neral (z citral)	69	152	$C_{10}H_{16}O$	0.38
11	18.24	*trans*- Ocimenone	135	150	$C_{10} H_{14} O$	0.07
12	20.84	α –Copaene	105	204	$C_{15}H_{24}$	0.29
13	21.26	β – Elemene	67	204	$C_{15}H_{24}$	0.13
14	21.64	Dodecanal	41	184	$C_{12} H_{24} O$	0.24
15	21.94	Caryophyllene beta	41	204	$C_{15}H_{24}$	0.1
16	22.18	β **-** Cedrene	161	204	$C_{15} H_{24}$	0.21
17	22.85	β -Farnesene	69	204	$C_{15}H_{24}$	0.25
18	23.46	Germacrene -D	41	204	$C_{15}H_{24}$	0.16
19	23.78	β - Selinene	161	204	$C_{15}H_{24}$	0.92
20	24.10	E,E)-α--Farnesene	93	204	$C_{15}H_{24}$	0.13
21	24.24	Butylated hydroxytoluene	205	220	$C_{15} H_{24}O$	0.14
22	24.52	δ-Cadenene	161	204	$C_{15}H_{24}$	0.35
23	25.12	Elemol	93	222	$C_{15}H_{26}O$	0.11
24	28.41	β-sinensal	93	218	$C_{15}H_{22}o$	0.96
25	30.71	Nootkatone	41	218	$C_{15}H_{22}o$	0.14
26	38.83	Octadecane	57	254	$C_{18}H_{38}$	0.06
27	39.44	Nonadecane	57	268	$C_{19}H_{40}$	0.08
28	40.62	Docosane	57	310	$C_{22}H_{46}$	0.05
29	41.05	Tricosane	57	324	$C_{23}H_{48}$	0.04
30	42.01	Tetracosane	57	338	$C_{24}H_{50}$	0.04
31	42.58	Pentacosane	57	352	$C_{25}H_{52}$	0.06
Total identified						**97.78**

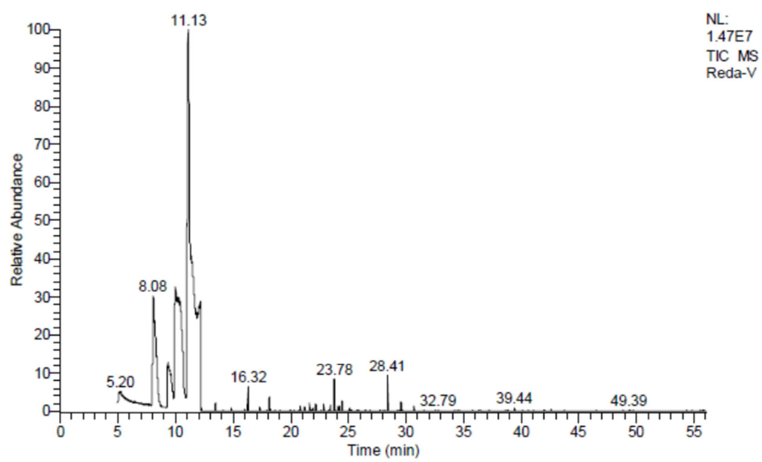

Figure 1: GC/MS chromatogram of orange peels volatile oil.

The characterizations of *C. sinensis* essential oil extracted from orange peel EC formulation are presented in Fig. 2. The compound had good emulsion stability, as the separation layer was 1 mL. In addition, the foam formation was 2 mL.

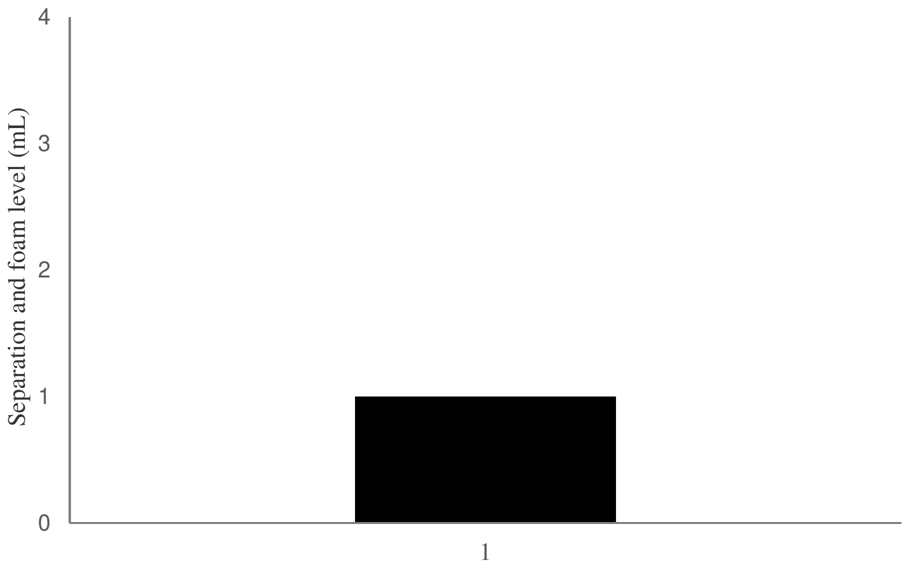

Fig.ure2: Emulsion stability and foam formation of EC formulation based on *Citrus cinensis* oil extracted from orange peels.

Investigations were conducted on the size and distribution of ZnO nanoparticle preparations. However, results confirmed that the mean droplet size diameters were 433.2 nm for ZnO NPs and 458.4 nm for ZnO with essential oil NPs preparation (Fig 3).

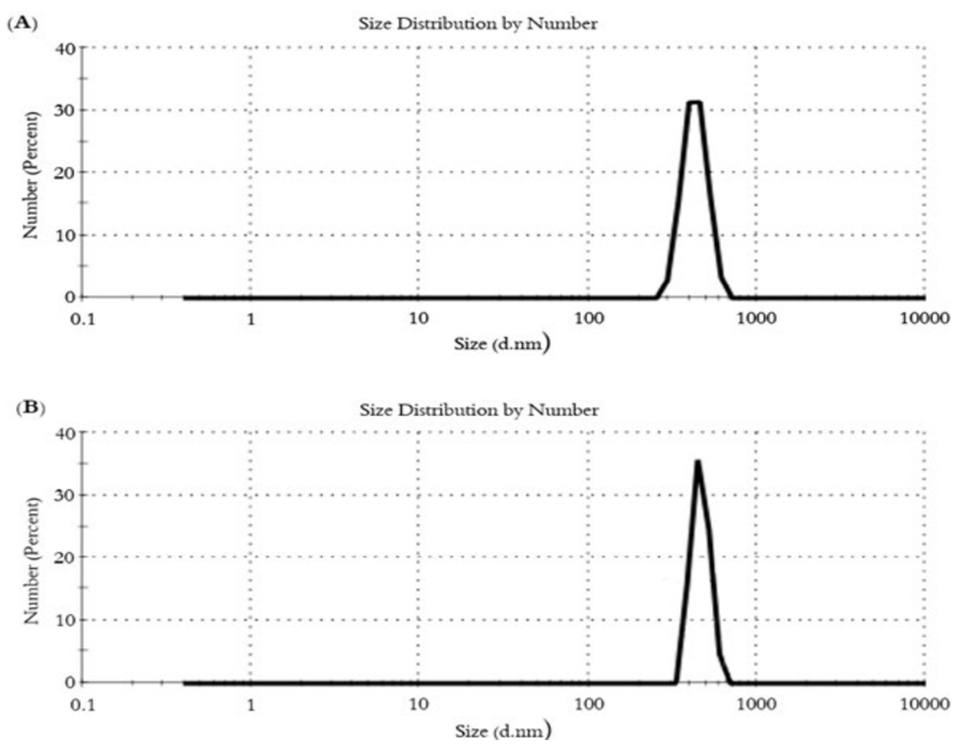

Figure 3: Nano-formulations particle size (A) ZnO with a size of 433.2 ± 19.46 nm; (B) ZnO + *Citrus cinensis* nanoparticle formulation with a size of 458.4 ± 21.23 nm.

Moreover, the polydispersity index (PDI) was 0.307 and 0.486 for ZnO NPs and ZnO with essential oil NPs, respectively. The zeta potential of the prepared nanoparticles was highly negative. They were -47.6 and -31.9 mV for ZnO NPs and ZnO with essential oil NPs, respectively (Fig. 4).

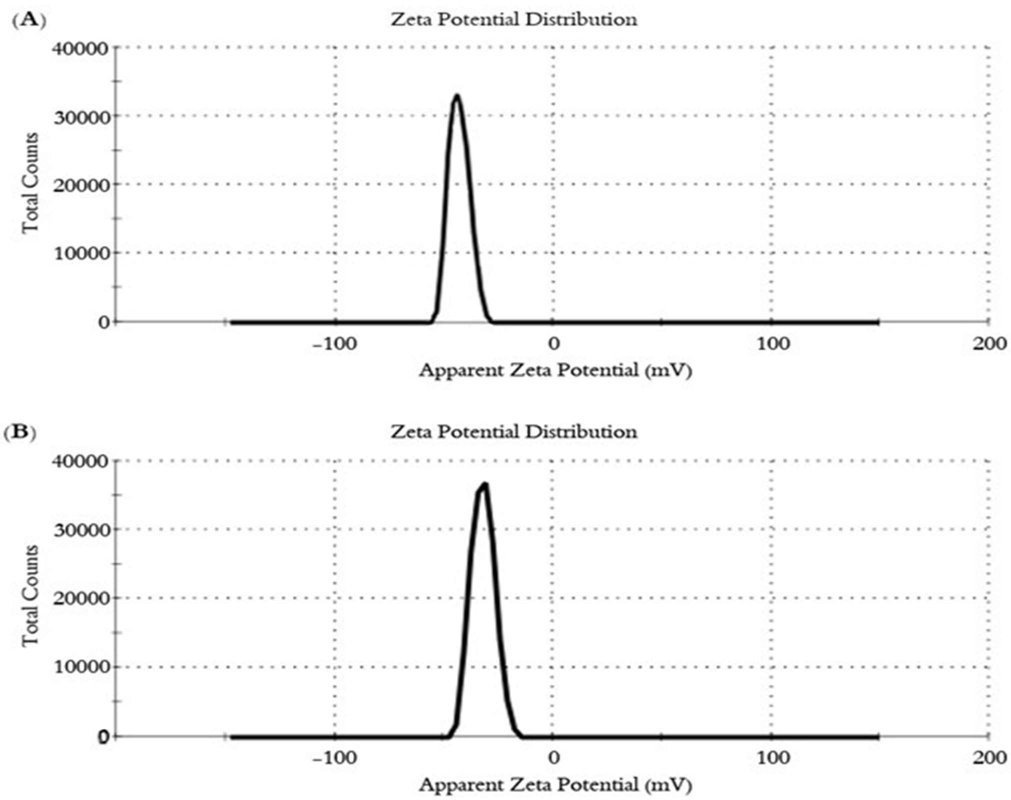

Figure 4: Nano-formulations zeta potentials (A) ZnO with a zeta potential value of -47.6; (B) ZnO + *Citrus cinensis* formulation with a zeta potential value of -31.9.

The nanoparticle morphology was investigated using TEM characterization as shown in Fig. 5. The droplet size of ZnO NPs was found to be in the range of 201-367 nm and 365-425 nm for ZnO NPs and ZnO with oil NPs, respectively.

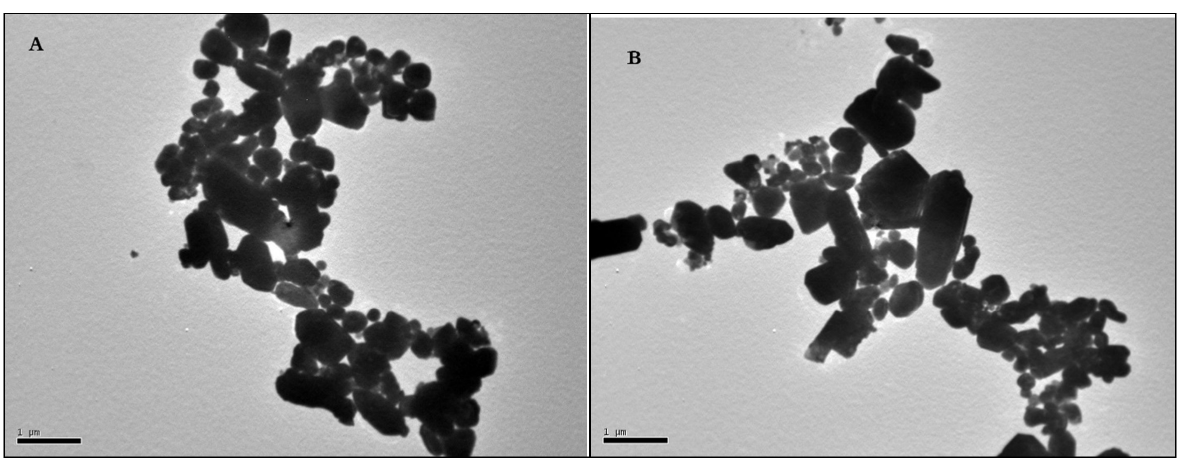

Figure 5: Transmission electron micrograph (TEM) of ZnO NPs (A) and ZnO with essential oil NPs (B).

Data illustrated in Table 2 shows the toxicity of *C. sinensis* essential oil extracted from peel and its EC formulation, against the adults of *T. castaneum*. The results indicate that both compounds have insecticidal activity against *T. castaneum*. The values of LC_{25} and LC_{50} of *C. sinensis* (EC) were slightly lower than those of the pure essential oil, with no significant differences (based on non-overlap in 95% confidence limits of LC_{25} and LC_{50} values). The LC_{25} and LC_{50} were 0.172 and 0.246 g kg^{-1}, respectively, of *C. sinensis* peel essential oil and 0.145 and 0.215 g kg^{-1}, respectively, of *C. sinensis* (EC).

Table 2: Toxicity of the tested compounds against the adults of *Tribolium castaneum*

Compounds	LC_{25} (g kg^{-1})[a]	LC_{50} (g kg^{-1})[b]	Slop ± (SE)[c]	Intercept ± (SE)[d]	*df*	(χ^2)[e]
Citrus sinensis oil	0.172 (0.138 - 0.199)	0.246 (0.214 - 0.278)	4.39 ± 0.63	2.67 ± 0.38	13	9.90
Citrus sinensis (EC)	0.145 (0.112 - 0.173)	0.215 (0.183 - 0.248)	3.95 ± 0.55	2.63 ± 0.35	13	8.82

[a,b] Concentration triggering 25 and 50% mortalities, respectively.
[c] Slope of concentration fatality regression line.
[d] Intercept of the regression line.
[e] Chi-square value.

The mortality of ZnO, ZnO NPs, and ZnO with *C. sinensis* peel essential oil NPs against *T. castaneum* at different concentrations and time intervals was presented in Table 3. Mortality of *T. castaneum* increased with increasing exposure time and concentrations of ZnO treatments (ZnO, ZnO NPs, and ZnO with *C. sinensis* peel essential oil mixture NPs). At a concentration of 0.03 g/kg, both bulk ZnO and ZnO NPs had low mortality rates ranging from 0-3.3% after 2 days, while the mortality induced by ZnO with *C. sinensis* peel essential oil NPs was 30%. The highest concentration of 2 g/kg at the same duration was 41, 43.3, and 70% of ZnO, ZnO NPs, and ZnO with peel essential oil NPs, respectively. The bulk ZnO recorded 100% mortality after 14 days at the highest application rate of 2 g/kg. ZnO NPs also gave complete mortality at a lower duration of 7 days at the same application rate. Moreover, ZnO with essential oil NPs lowered the concentration required to achieve the complete mortality to 1 g/kg. ZnO with *C. sinensis* peel essential oil NPs resulted in higher significant mortality than bulk ZnO or ZnO NPs.

Table 3: Mean adult mortality of bulk ZnO, ZnO nanoparticles, and ZnO with *C. sinensis* peel essential oil mixture nanoparticles against *Tribolium castaneum.*

Treatments (Concentration, g kg-1)	Mean mortality (%) ± SE		
	2 days	7 days	14 days
Cont.	0.0 ± 0.0g	3 ± 0.6h	5.0 ± 0.6i
ZnO (0.03)	0.0 ± 0.0g	5.0 ± 1.0h	13.3 ± 1.5h
ZnO (0.1)	5.7 ± 0.9g	33.3 ± 1.2g	43.3 ± 1.9f
ZnO (0.5)	17.3 ± 1.2f	44.0 ± 2.1e	87.0 ± 1.5c
ZnO (1)	34.3 ± 1.3de	57.3 ± 0.9d	95.0 ± 1.5b
ZnO (2)	41.0 ± 1.2c	70 ± 2.1c	100.0 ± 0.0a
ZnO NPs (0.03)	3.3 ± 0.3g	30 ± 2.9g	18.0 ± 1.2g
ZnO NPs (0.1)	16.7 ± 1.5f	31.3 ± 1.9g	55.3 ± 1.5e
ZnO NPs (0.5)	29.0 ± 6.1e	73.7 ± 1.8c	94.3 ± 1.2b
ZnO NPs (1)	39.3 ± 2.3cd	87.7 ± 1.5b	100.0 ± 0.0a
ZnO NPs (2)	43.3 ± 1.5c	100.0 ± 0.0a	100.0 ± 0.0a
ZnO with oil NPs (0.03)	30.0 ± 2.9e	39.0 ± 2.1f	45.3 ± 1.8f
ZnO with oil NPs (0.1)	31.3 ± 1.9e	47.7 ± 1.5e	70.0 ± 1.5d
ZnO with oil NPs (0.5)	44.0 ± 2.1c	84.3 ± 1.2b	97.3 ± 1.3ab
ZnO with oil NPs (1)	57.3 ± 0.9b	100.0 ± 0.0a	100.0 ± 0.0a
ZnO with oil NPs (2)	70.0 ± 2.1a	100.0 ± 0.0a	100.0 ± 0.0a
F value	92.28	454.92	867.15
P	< 0.0001	< 0.0001	< 0.0001

Values with different letters in the same column are significantly different at p < 0. 05 according to Duncan's multiple range test with degree of freedom equal to 15 and 32.

4. Discussion

These findings about the chemical composition of *C. sinensis* peel essential oil are consistent with previous studies on the chemical composition of *C. sinensis* peel essential oil, which have reported similar major volatile constituents [23, 24]. The basic components exhibited considerable or marginal variation in their concentration. Geographic location, seasonal factors, environmental conditions, plant nutrition levels, and other potential factors could influence the chemical composition of vegetable oils [25, 26]. The results of the physical and chemical analysis of the examined *C. sinensis* EC preparation indicated that the volume of the creaming layer was not more than 2 mL, and the volume of the foam was not over 5 mL. In accordance with established standards, if there is a cream layer, it should not be more than 2 mL [21] and the foam layer volume should not exceed 5 mL [27]. The results also showed that ZnO NPs were prepared with and without adding *C. sinensis* peel essential oil. ZnO nanoparticles are widely used as carriers for essential oils due to their high surface area, biocompatibility, and photocatalytic activity [28, 29]. The nanoparticles had a negative Zeta potential, which means they repel each other and prevent aggregation. The nanoparticles were also characterized by their size, shape, and PDI, which measures the uniformity of the size distribution. Nanoemulsion is defined as an emulsion with droplet size less than 500 nm [2, 30]. The addition of *C. sinensis* peel essential oil slightly increased the size and PDI of the nanoparticles, but did not change their morphology, which was spherical. The droplet nanoemulsions are less uniform when the PDI values are greater than 0.3. The zeta potential of the nanoparticles was less than -30 mV, as this work has indicated. A zeta potential of less than -30 keeps the system steady and prevents the particles from aggregating [25, 26]. Data obtained from TEM images confirm consistent nanoparticle size and morphology. The results further show that both *C. sinensis* peel essential oil and its EC formulation have insecticidal activity against *T. castaneum*. The EC formulation was slightly more effective than the pure essential oil, but the difference was insignificant. The results also show that ZnO nanoparticles, alone or in combination with *C. sinensis* peel essential oil, have insecticidal activity against *T. castaneum*, depending on the concentration and exposure time. These results could be due to their smaller size, larger surface area, and higher reactivity, which can cause oxidative stress and insect cell damage [31]. Combining ZnO and C. sinensis peel essential oil nanoparticles was the most effective, achieving 100% mortality at a lower concentration and shorter time than ZnO nanoparticles alone or bulk ZnO. This suggests a synergistic interaction between ZnO and *C. sinensis* peel essential oil that enhances their insecticidal activity against *T. castaneum*. The mechanism of this synergy could be related to the increased penetration, absorption, or distribution of the compounds at the insect body surface [32].

5. Conclusion

This study investigated the insecticidal potential of *C. sinensis* essential oil derived from orange peels, its emulsifiable concentrate (EC), and ZnO nanoparticles against *T. castaneum*. The combination of orange peel essential oil and ZnO nanoparticles exhibited a synergistic effect, achieving higher insecticidal activity than individual treatments. This novel approach, utilizing agricultural waste and nanotechnology, demonstrates the potential for developing sustainable and low-cost pest control solutions. The EC formulation of *C. sinensis* oil exhibited good emulsion stability and foam formation. Furthermore, the ZnO nanoparticle formulations, particularly when combined with essential oil, exhibited increased efficacy against *T. castaneum* at significantly lower concentrations compared to bulk ZnO. This highlights the potential of nanoformulations to enhance penetration and uptake, leading to faster and more effective insect mortality. These findings suggest that *C. sinensis* waste, specifically the peel, can be effectively utilized as a source of natural insecticides. The synergistic effect of the combined formulation, combined with its enhanced efficacy and reduced application rates, presents a promising approach for developing eco-friendly pest control solutions for stored grains.

6. Conflict of interest

The authors have no conflict of interests.

7. Acknowledgment

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