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Insecticidal activity of Silica, Zinc and Copper nanoparticles against the German cockroach, *Blatella germanica* (L.) (Dictyoptera: Blattellidae)

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ABSTRACT

Blatella germanica is a major domiciliary pest associated with public health. Synthetic insecticides have hazardous effects on humans and the environment. This study aimed to evaluate the efficiency of three Nano formulations against the German cockroach. Silicon dioxide (SiO_2), Zinc oxide (ZnO) and Copper oxide (CuO) nanoparticles (NPs) were synthesized and screened for insecticidal activity against adults of the German cockroach by contact and feeding methods. The synthesized nanoparticles were attained in a powder form and characterized using UV-Vis spectrophotometer, High-Resolution Transmission Electron Microscopy (HRTEM), Dynamic light scattering (DLS) and zeta potential. The size range of the prepared NPS was 5.16-14.72 nm for SiO_2, 26.50-52.56 nm for ZnO-NPs and 10.04-39.7 nm for CuO-NPs. Results of UV-Vis spectroscopy, HRTEM, DLS and Zeta potential confirmed the successful formation of nanoparticles. Results clearly showed that the SiO_2-NPs had strong insecticidal activity against adults of German cockroaches with LC_{50} values of 10.36 mg by contact and 4.91 mg by feeding methods. While the LC_{50} values of ZnO- and CuO-NPs were 13.02 & 17.35 mg by contact and 5.94 & 6.19 mg, respectively by feeding methods. On the other hand, the crude powder of the three metals induced non-significant toxic effects. The LC_{50} values were 87.49, 179.27 and 233.24 mg by contact, and 9.31, 17.99 and 19.21 mg by feeding for Silica, Zinc and Copper powders, respectively after 7 days of treatment. The stability of the prepared NPs was studied after 4 months of storage under laboratory conditions. SiO_2-NPs were the most stable, followed by ZnO-NPs and CuO-NPs. The efficacy and stability of the prepared NPs made these products suitable candidates for controlling the German cockroach.

INTRODUCTION

The German cockroach is the most common cockroach species worldwide. It is considered one of the most important pests associated with public health, especially in indoor environments such as kitchens, bathrooms and food storage places (Said, 2017). This pest walks and feeds on human and animal food and may transmit several pathogens such as that cause dysentery and typhoid fever (Fotedar *et al*., 1991 and Kim & Jeon, 1995). Additionally, the cockroaches can cause allergic reactions and give an impression of dirtiness and displeasure as a result of the presence of their feces, excretion, exuviae and egg sacks (AbdEl-Raheem & Eldafrawy, 2016). Nanotechnology is a promising research field in different fields including pesticides (Ragaei and Sabry, 2014). Nanotechnology could provide efficient green alternatives for the management of insect pests without harming the environment (Haroun *et al*., 2020)

The NPs derived from metals and metal oxides are effective promising candidates in the industry of pesticides (Wang *et al*., 2010). Several methods have been used to prepare SiO_2-NPs (Abdelsalam *et al*., 2019 and Dahlous *et al*., 2019). One of these is the sol-gel method. This method is extensively used to produce homogenous silica products in a powder form that is non-toxic to non-target organisms and suitable to be used in several fields, especially in the field of pest control (El-Naggar *et al*. 2020). Silicon dioxide NPs have proved to be effective for several insect pests (Debnath *et al*., 2011; Haroun *et al*., 2020 and Thabet *et al*., 2021). Solution Combustion synthesis of metal oxide NPs is a relatively new method that occurs in an aqueous medium. The powder materials are solved in a solution forming a very homogeneous distribution of the materials (Tharani and Nehru, 2020). Zinc oxide NPs are popular among the significant metal oxides due to their physical and chemical peculiarity (Khooshe-Bast *et al*., 2016). ZnO-NPs have proved to possess enormous potential against insect pests (Haroun *et al*., 2020 and Pittarate *et al*., 2021). The development of Nano-pesticides derived from Copper and Copper oxide has received considerable attention in the pesticide industry in recent years (Benilli *et al*., 2017). This study aimed to prepare SiO_2, ZnO- and CuO- NPs and to evaluate their efficiency as alternatives and effective Nano formulations for the control of German cockroaches.

MATERIALS AND METHODS

Test Insect:

The German Cockroach *Blattella germanica* L. (Dictyoptera: Blattellidae) was obtained from a laboratory strain in the laboratory of the Research Institute of Medical Entomology (Ministry of Health & Population), Dokki, Giza, Egypt, and reared under laboratory conditions (27±2 ^{0}C and 70 ± 5% R.H.) according to the method described by Abd El-Raheem and Eldafrawy (2016).

Preparation of Nanoparticles:

Three raw powders of silica, zinc and copper and other chemicals were purchased from El Nasr pharmaceutical chemicals company, in Egypt.

The SiO_2-NPs were synthesized via the sol-gel method according to El-Naggar *et al*. (2020). The obtained white silica particles were ground in rapid mills for 30 seconds. While, ZnO- and CuO-NPs were synthesized by the solution combustion method as described by Tharani and Nehru, (2020).

Characterization of the Synthesized Nanoparticles:

The prepared NPs were characterized using a UV-visible spectrophotometer (Shimadzu UV-3600PC Series) with a wavelength range of 200–800 nm. High-Resolution Transmission Electron Microscope JEOL (JEM-2100 TEM) was used in order to clarify, the particles' shape, size and distributions. Three different magnifications (200, 100 and 50 nm) were used to clarify the actual shape of the synthesized nanoparticles. Dynamic light scattering (DLS) was used to confirm the particles size distribution and Zeta potential was measured to provide information about the stability of the nanoparticles against aggregation. The instrument (PSS, Santa Barbara, CA, USA) using the 632 nm line of a He Ne laser as the incident light with an external angle of 90^o for DLS and 18.9^o for Zeta potential. DLS and Zeta potential were measured at the Nanomaterial Investigation Lab., Central Laboratory Network (CLN), National Research Centre (NRC), Cairo, Egypt. Samples were prepared with 0.2g / 5ml Millipore water and sonication for 5 minutes.

Toxicity Bioassay:

To study the effect of SiO_2-, ZnO- and CuO-NPs and powders, five different concentrations (5, 10, 20, 40 and 80 mg) were applied to the adult stage of the German cockroach by contact and feeding methods. In contact test: ten adults were kept in a Petri dish (15 cm in diameter) containing one of the previously mentioned concentrations and left for 24 hours, after that time the insects were transferred to wooden cages containing their food. In feeding test: ten insects were kept in a wooden cage. The concentrations were administered orally to the adult cockroaches by feeding them on a biscuit weighing 5 grams mixed finely with the various concentrations. On the other hand, the control group was fed biscuits that were not mixed with any material. Each treatment was replicated five times. The mortality percentages were determined after 3, 5 and 7 days. The adult weights were recorded from the surviving insects after 3 days.

To determine the stability of the prepared NPs, they were stored for a period of four months under laboratory conditions (27±2 ^{0}C & 70 ± 5% R.H.) and were evaluated against adult cockroaches as previously mentioned. Adults were exposed to 80 mg of each tested compound by contact and feeding methods under laboratory conditions. The mortalities were recorded after 5 days of treatment.

Statistical Analysis:

Data were analyzed using one-way analysis of variance (ANOVA) and the means were compared by Duncan's multiple range test using version 21, SPSS program (Crop, 2012). The Statistical significance was established at $P \leq 0.05$ for all analyses. The probit analysis technique (Finney, 1971) was used to determine the LC_{50}.

RESULTS AND DISCUSSION

The SiO_2-, ZnO- and CuO-NPs were successfully prepared. The formation of nanoparticles was demonstrated by UV-Vis spectroscopy and the formed nanoparticles were characterized by TEM and Zeta potential.

UV-Vis Spectrophotometer Analysis:

The characteristic absorption peaks of the formed NPs in the UV-Vis spectra were 350 nm for SiO_2-NPs, 368 nm for ZnO-NPs and 668 nm for CuO-NPs which were generated due to the surface Plasmon resonance (SPR) of the formed NPs (Fig. 1). Similar absorption ranges for the prepared NPs were found by, Singh *et al*. (2012), Pudukudy and Yaakob (2014) and Shamhari *et al*. (2018). They found that the absorption peak for ZnO-NPs is between 357-378 nm. Morales *et al*. (2019) reported that SiO_2-NPs had an absorption peak of 325 nm. The absorption peaks for CuO-NPs have been reported to be in the range of 500–670 nm (Gondwal and Pant, 2018; Kesbi *et al*., 2018; Vivekanandhan *et al*., 2021b).

TEM Analysis:

Results revealed that SiO_2-NPs have a spherical shape and are well dispersed in a polymer matrix, the size range was 5.16-14.72 nm (Fig.2, a, b & c). ZnO-NPs with polymorphic structure, well dispersed and the size range was 26.50-52.56 nm (Fig.2 d, e & f). CuO-NPs have a spherical shape with some clusters and the size range was 10.04-39.7 nm (Fig. 2 g, h & i). Similar observations have been reported by TEM analysis of SiO_2-NPs (El-Naggar et al., 2020), CuO-NPs (Vivekanandhan *et al*., 2021a) and ZnO-NPs (Eskin & Nurullahoglu, 2022).

Dynamic Light Scattering and Zeta Potential:

DLS technique was used to assess the particle size distribution. The average particle diameter of SiO_2-NPs was 165.6 nm (Fig. 3a), ZnO-NPs with average diameter 129.4 nm (Fig. 3b), whereas the average diameter of CuO-NPs was 177.1nm (Fig. 3c). Results in agreement with the average particle diameters measured by other authors such as, Cao *et al*.

(2019) for ZnO-NPs, El-Naggar *et al*. (2020) for SiO_2-NPs and Kongor *et al*. (2021) for CuO-NPs.

The Zeta potential value of SiO_2-NPs was -37.87 mV (Fig. 4a). In the case of ZnO-NPs Zeta potential was 9.02 mV (Fig. 4b), whereas the Zeta potential of CuO-NPs was -47.74 mV (Fig. 4c). These values mean that, the prepared nanoparticles are stable and can be kept away from further aggregation. Our results are in accordance with zeta potential values measured by other authors for the same materials (El-Naggar *et al*., 2020 for SiO_2-NPs, Vivekanandhan *et al*., 2021b for CuO-NPs and Eskin & Nurullahoglu, 2022 for ZnO-NPs.

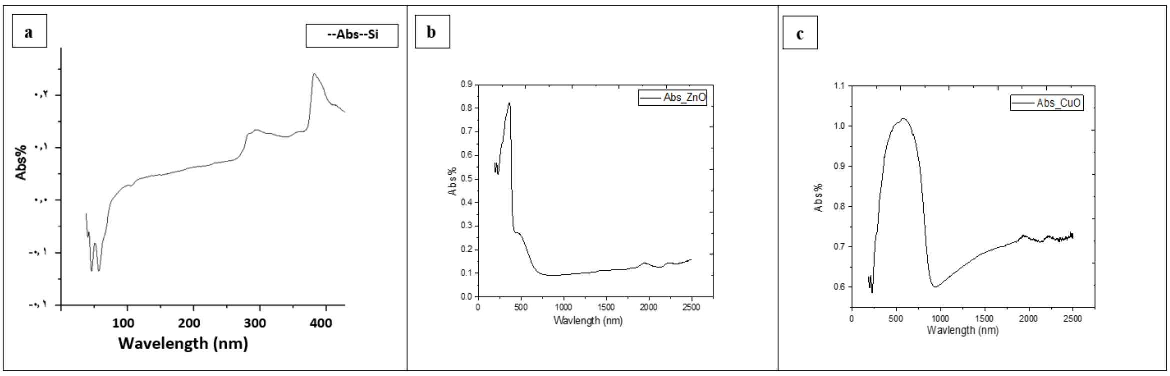

Fig. 1: UV-Vis spectroscopy of nanoparticles; SiO_2-NPs (a), ZnO-NPs (b) and CuO-NPs(c)

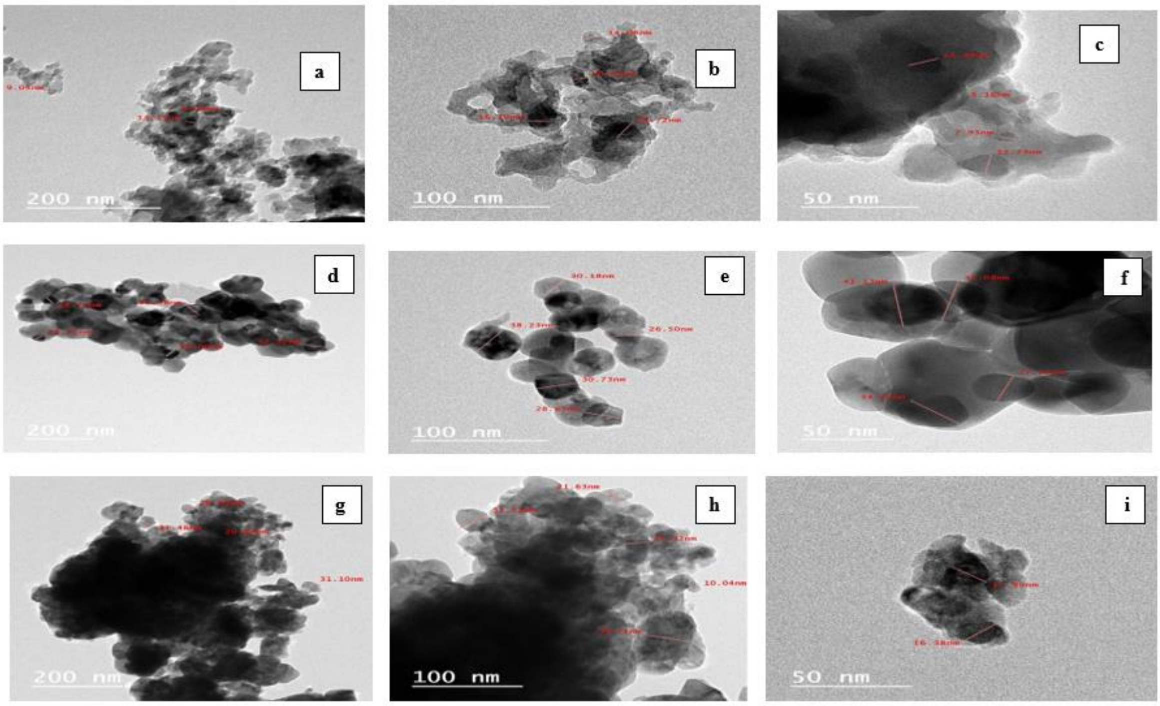

Fig. 2: TEM images at three magnifications; SiO_2-NPs (a, b and c), ZnO-NPs (d, e and f) and CuO-NPs (g, h and i).

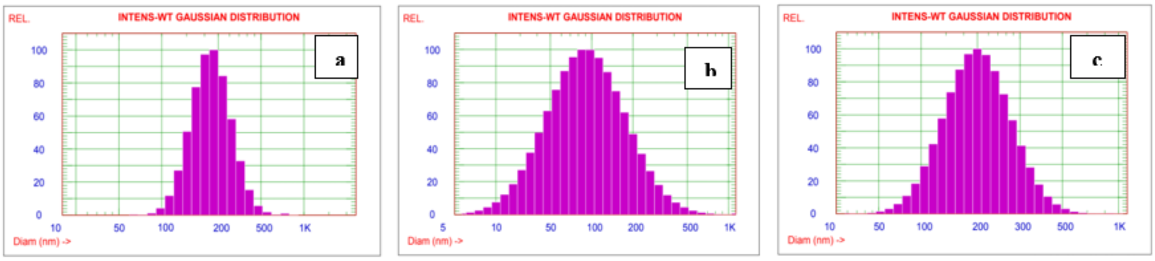

Fig. 3: Dynamic light scattering of SiO_2-NPs (a), ZnO-NPs (b) and CuO-NPs (c)

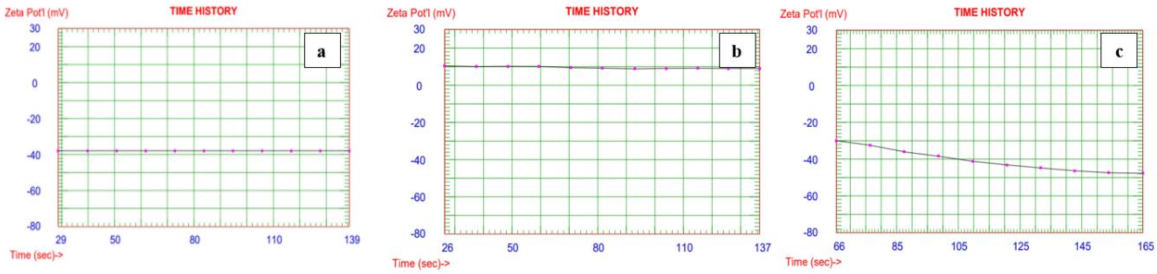

Fig. 4: (a) Zeta potential of SiO_2-NPs (-37.87 mV), (b) Zeta potential of ZnO-NPs (9.02 mV) and (c) Zeta potential of CuO-NPs (-47.74 mV).

Insecticidal Activity:

Silica, Zinc and Copper, powders and NPs were evaluated for their insecticidal activity against adult German cockroaches by contact and feeding methods. Results demonstrate that all metal powders have low insecticidal activity against adult cockroaches by contact. The recorded mortalities were 52.0, 34.0 and 30 % after 7 days for Silica, Zinc and Copper powders, respectively. On the other hand, the NPs of these metals affected adult mortality significantly in a concentration and time-dependent manner. The highest concentration (80 mg) induced 100 % mortality in adults treated with SiO_2- and ZnO-NPs after 7 days of treatment, while the CuO-NPs recorded 94% mortality at the same concentration (Table 1).

Table 1: Insecticidal activity of Silica, Zinc & Copper powders and nanoparticles against adult German cockroach by contact method.

Tested compounds	Conc. (mg)	Mortality % (Mean ± SE)								
		Silica			Zinc			Copper		
		3 days	5 days	7 days	3 days	5 days	7 days	3 days	5 days	7 days
Metal powders	Control	0.00±0.0^{dA}	0.00±0.0^{eA}	0.00±0.0^{fA}	0.00±0.0^{cA}	0.00±0.0^{dA}	0.00±0.0^{dA}	0.00±0.0^{cA}	0.00±0.0^{dA}	0.00±0.0^{dA}
	5	0.00±0.0^{dB}	4.0±2.45^{dA}	4.0±2.45^{eA}	0.0±0.0^{cA}	2.00±2.0^{cdA}	2.00±2.0^{dA}	0.00±0.0^{cA}	0.00±0.0^{dA}	0.00±0.0^{dA}
	10	2.0±2.0^{dC}	6.0±2.45^{dB}	10.0±3.1^{dA}	0.0±0.0^{cC}	4.00±2.45^{cB}	8.00±2.0^{cA}	0.00±0.0^{cB}	4.00±2.45^{cA}	6.00±2.45^{cA}
	20	6.0±2.45^{cC}	10.0±3.1^{cB}	16.0±4.0^{cA}	2.00±2.0^{cC}	6.00±2.45^{cB}	10.0±3.16^{cA}	0.00±0.0^{cC}	4.00±2.45^{cB}	8.00±2.00^{cA}
	40	12.0±4.9^{bC}	18.0±4.9^{bB}	26.0±4.0^{bA}	6.00±4.0^{bC}	10.0±4.47^{bB}	20.0±3.16^{bA}	4.0±2.45^{bC}	8.00±3.74^{bB}	16.0±2.45^{bA}
	80	24.0±4.0^{aC}	34.0±5.1^{aB}	52.0±4.9^{aA}	16.0±4.0^{aC}	22.0±3.74^{aB}	34.0±5.10^{aA}	10.0±4.47^{aC}	16.0±5.10^{aB}	30.0±3.16^{aA}
Nanoparticles	Control	0.00±0.0^{fA}	0.00±0.0^{fA}	0.00±0.0^{eA}	0.00±0.0^{fA}	0.00±0.0^{fA}	0.00±0. 0^{fA}	0.00±0.0^{fA}	0.00±0.00^{fA}	0.00±0.00^{fA}
	5	8.00±3.7^{eC}	16.0±4.0^{eB}	22.0±3.7^{dA}	6.00±4.0^{eC}	14.0±5.10^{eB}	18.0±3.74^{eA}	4.00±2.45^{eC}	10.0±5.48^{eB}	14.0±5.10^{eA}
	10	18.0±3.7^{dC}	26.0±6.7^{dB}	42.0±7.3^{cA}	12.0±4.9^{dC}	20.0±7.07^{dB}	34.0±5.10^{dA}	10.0±3.16^{dC}	18.0±5.83^{dB}	26.0±4.00^{dA}
	20	26.0±6.0^{cC}	42.0±5.8^{cB}	76.0±5.1^{bA}	22.0±3.7^{cC}	38.0±5.83^{cB}	64.0±5.10^{cA}	18.0±2.00^{cC}	26.0±6.78^{cB}	54.0±4.00^{cA}
	40	48.0±4.9^{bC}	72.0±3.7^{bB}	100±0.0^{aA}	30.0±7.7^{bC}	60.0±5.48^{bB}	90.0±4.47^{bA}	28.0±5.83^{bC}	54.0±5.10^{bB}	80.0±9.49^{bA}
	80	90.0±4.4^{aC}	96.0±0.0^{aB}	100±0.0^{aA}	70.0±8.9^{aC}	92.0±3.74^{aB}	100±0.00^{aA}	52.0±2.00^{aC}	86.0±5.10^{aB}	94.0±6.00^{aA}

Means within a column and followed by the same superscript small letter are not significantly different (P>0.05), Means within a raw and followed by the same superscript capital letter are not significantly different (P>0.05), SE: standard error.

The toxicity results in Table (2) clearly show that the crude powder of the three metals induced non-significant mortalities after 3 and 5 days by feeding method, but the mortality rates increased over time till reached 100, 94 and 90 % after 7 days of treatment. While, the NPs had high insecticidal activity and the mortality ranges were 14–100 % (df 4; X^2 = 1.000; p < 0.01), 14-92 % (df 4; X^2 = 0.3649; p < 0.05) and 12-90 % (df 4; X^2 == 2.098;

$p < 0.05$) for insects treated with SiO_2-NPs, ZnO-NPs and CuO-NPs, respectively after 3 days of treatment. After 7 days, 100 % mortality was achieved in all treatments with the lowest concentration used (20 mg). The previous results indicate that NPs kill roaches faster than metal powders.

The toxicity of metals and metal NPs to insects may be due to their ability to disrupt the cuticular lipids that act as a water barrier, and in this way prohibit death through dehydration. Meanwhile, metal NPs and due to the small volume may be easily absorbed into the cuticular lipids and thus causes insect death. The higher efficiency of NPs as insecticides was also observed by many investigators as El-Naggar *et al*. (2020) who verified the use of SiO_2-NPs as Nano pesticides and suggested the same killing mechanism. Baghban *et al*. (2014) and Eskin & Nurullahoglu (2022) reported that zinc and copper bind to cytosol metallothionein in the midgut in many insects and can be toxic at high concentrations. Abd El-Raheem and Eldafrawy (2016) tested silver NPs against *B. germanica* and observed that the mortality occurred quickly when cockroaches were treated by the feeding method and mortality rates increased over time when treated by the contact method. In contrast with our results, Ayoub *et al*. (2017) reported that the mortality of *Spodoptera littoralis* larvae treated with SiO_2-NPs by surface contact was faster than by feeding method. This contradiction may be due to the difference in the integument structure between *S. littoralis* larvae and cockroach adults.

Table 2: Insecticidal activity of Silica, Zinc & Copper powders and nanoparticles against adult German cockroach by feeding method

Tested compounds	Conc. (mg)	Mortality % (Mean ± SE)								
		Silica			Zinc			Copper		
		3 days	5 days	7 days	3 days	5 days	7 days	3 days	5 days	7 days
Metal powders	Control	0 ± 0^{fA}	0 ± 0^{fA}	0 ± 0^{fA}	0 ± 0^{fA}	0 ± 0^{fA}	0 ± 0^{fA}	0 ± 0^{fA}	0 ± 0^{fA}	0 ± 0^{fA}
	5	8 ± 3.74^{eC}	14 ± 2.45^{eB}	34 ± 5.10^{eA}	4 ± 2.45^{eC}	10 ± 3.16^{eB}	18 ± 2.00^{eA}	4 ± 2.45^{eC}	8 ± 2.00^{eB}	18 ± 2.00^{eA}
	10	14 ± 5.10^{dC}	22 ± 3.74^{dB}	48 ± 5.83^{dA}	10 ± 3.16^{dC}	16 ± 2.45^{dB}	26 ± 2.45^{dA}	8 ± 2.00^{dC}	12 ± 2.00^{dB}	22 ± 5.83^{dA}
	20	20 ± 5.48^{cC}	32 ± 3.74^{cB}	72 ± 7.35^{cA}	14 ± 2.45^{cC}	22 ± 3.74^{cB}	50 ± 4.47^{cA}	14 ± 2.45^{cC}	22 ± 3.74^{cB}	50 ± 6.32^{cA}
	40	32 ± 2.00^{bC}	58 ± 5.83^{bB}	90 ± 5.48^{bA}	20 ± 5.48^{bC}	32 ± 3.74^{bB}	74 ± 4.00^{bA}	18 ± 2.00^{bC}	30 ± 5.48^{bB}	74 ± 5.10^{bA}
	80	50 ± 3.16^{aC}	82 ± 3.74^{aB}	100 ± 0.00^{aA}	32 ± 2.00^{aC}	56 ± 8.12^{aB}	94 ± 4.00^{aA}	26 ± 4.00^{aC}	54 ± 7.48^{aB}	90 ± 3.16^{aA}
Nanoparticles	Control	0 ± 0^{fA}	0 ± 0^{dA}	0 ± 0^{cA}	0 ± 0^{fA}	0 ± 0^{eA}	0 ± 0^{dA}	0 ± 0^{fA}	0 ± 0^{eA}	0 ± 0^{dA}
	5	14 ± 2.45^{eC}	22 ± 2.00^{cB}	52 ± 4.90^{bA}	14 ± 3.74^{eC}	20 ± 0.00^{dB}	36 ± 4.00^{cA}	12 ± 2.45^{eC}	22 ± 2.00^{dB}	34 ± 4.00^{cA}
	10	32 ± 5.83^{dC}	74 ± 8.12^{bB}	98 ± 2.00^{aA}	26 ± 3.74^{dC}	52 ± 4.90^{cB}	86 ± 4.00^{bA}	18 ± 2.45^{dC}	46 ± 4.00^{cB}	82 ± 7.35^{bA}
	20	54 ± 5.10^{cB}	98 ± 2.00^{aA}	100 ± 0.00^{aA}	46 ± 4.90^{cC}	96 ± 2.45^{bB}	100 ± 0.00^{aA}	42 ± 5.10^{cC}	90 ± 4.47^{bB}	100 ± 0.00^{aA}
	40	90 ± 4.47^{bB}	100 ± 0.00^{aA}	100 ± 0.00^{aA}	84 ± 6.78^{bB}	100 ± 0.00^{aA}	100 ± 0.00^{aA}	80 ± 5.48^{bB}	98 ± 2.00^{aA}	100 ± 0.00^{aA}
	80	100 ± 0.00^{aA}	100 ± 0.00^{aA}	100 ± 0.00^{aA}	92 ± 3.74^{aB}	100 ± 0.00^{aA}	100 ± 0.00^{aA}	90 ± 4.47^{aB}	100 ± 0.00^{aA}	100 ± 0.00^{aA}

Means within a column and followed by the same superscript small letter are not significantly different ($P>0.05$), Means within a raw and followed by the same superscript capital letter are not significantly different ($P>0.05$), SE: standard error**.**

The sensitivity of *B. germanica* to the crude metals by the contact method was demonstrated by the LC_{50} values (Table 3). After 7 days of treatment, the LC_{50} values were 87.49, 179.27 and 233.24 mg for Silica, Zinc and Copper powders, respectively. Meanwhile, the LC_{50} values of SiO_2-, ZnO- and CuO-NPs were 10.36, 13.02 and 17.35 mg, respectively. Based on the LC_{50} values, the relative efficacies of the tested NPs compared with that of the metal powders as reference materials indicated that, SiO_2-, ZnO- and CuO-NPs are more effective than powders of the same metals.

Table 3: The relative efficiency of the tested compounds against the German cockroach by contact method

Treatment	Mineral	LC_{50} (LCL-UCL)	LC_{90} (LCL-UCL)	LC_{95} (LCL-UCL)	Slope ± SE	$X^2(df=4)$ (Sig.)	Relative Efficacy
Powder	Si	87.49 (65.72-133.04)	663.63 (352.83-1823.14)	1178.62 (563.35-3861.56)	1.4564±0.1777	2.4352 (0.4871)	1
	Zn	179.27 (111.86-408.99)	1906.09 (712.12-11650.99)	3725.34 (1196.26-30291.83)	1.2484±0.1920	1.3380 (0.7201)	1
	Cu	233.24 (134.74-647.41)	2590.69 (855.29-22255.37)	5126.45 (1436.60-60984.04)	1.2257±0.2035	0.9296 (0.8183)	1
Nanoparticles	Si	10.36 (7.04-14.14)	27.20 (21.54-51.14)	35.77 (28.57-76.20)	3.0568±0.2477	8.8784 (0.0310)	8.445
	Zn	13.02 (11.47-14.67)	40.03 (33.72-49.74)	55.04 (44.86-71.74)	2.6269±0.2023	4.5838 (0.2049)	13.77
	Cu	17.35 (15.16-19.80)	64.62 (52.55-84.38)	93.81 (73.20-129.95)	2.2444±0.1752	1.59.23 (0.6611)	13.44

LCL: lower confidence limit; UCL: upper confidence limit; X^2: Chi-square value; *df* : degrees of freedom; Significant at $p < 0.05$ level; SE: standard error.

As indicated in Table (4) LC_{50} values of Silica, Zinc and Copper powders by feeding method were 9.31, 17.99 and 19.21mg, respectively. While SiO_2-, ZnO- and CuO-NPs recorded the lowest LC_{50} values (4.91, 5.94 and 6.19 mg, respectively). Based on the LC_{50} values, the relative efficacies of the tested NPs by feeding compared with that of the metal powders as reference materials indicated that SiO_2-, ZnO- and CuO-NPs were about 1.9, 3.03 and 3.1times more effective than the metal powders at the same concentrations. From the previous results, we can conclude that the German cockroach is more highly susceptible to SiO_2-NPs than ZnO- and CuO-NPs and the feeding method is more effective in controlling cockroaches than the contact method. The high efficiency and toxicity of NPs against the German cockroach in the present results were observed by many other investigators against the German cockroach and other insect species. Gonzalez *et al*. (2016) demonstrated that LC_{50} values of polymer-based essential oil NPs for the German cockroach were significantly lower than the essential oils alone. Abd El-Wahab *et al.* (2016) reported that SiO_2-NPs have more insecticidal activity than Silica powder against three different aphid species. Sabbour and Hussein (2016) tested the effect of both silica gel and silica gel NPs against *Tuta absoluta* and found that the silica gel NPs had more effect against *Tuta absoluta*Other. The higher efficiency of SiO_2-NPs against different species of insects was reported by Many studies such as *Sitophilius oryzae* (Patil *et al*., 2018), *Tenebrio molitor* (Rankic *et al*., 2019), *Bemisia tabaci* and *Aphis gossypii* (Mehana *et al*., 2019). Haroun *et al.* (2020) reported that SiO_2-NPs have a higher insecticidal activity than ZnO-NPs against *Callosobruchus maculatus* and *Tribolium castaneum*.

Table 4: The relative efficiency of the tested compounds against the German cockroach by feeding method.

Treatment	Mineral	LC_{50} (LCL-UCL)	LC_{90} (LCL-UCL)	LC_{95} (LCL-UCL)	Slope ± SE	$X^2(df=4)$ (Sig.)	Relative Efficacy
Powder	Si	9.31 (7.79-10.84)	38.31 (31.27-50.01)	57.21 (44.56-80.27)	2.0856±0.1857	5.4382 (0.1424)	1
	Zn	17.99 (15.54-20.75)	77.84 (61.45-106.28)	117.92 (88.61-172.28)	2.0142±0.1656	5.2014 (0.1576	1
	Cu	19.21 (16.54-22.29)	123.68 (68.61-123.68)	136.15 (100.28-205.88)	1.9343±0.1624	5.1618 (0.1603)	1
Nanoparticles	Si	4.91 (4.42-5.32)	7.66 (6.92-9.06)	8.69 (7.67-10.80)	6.6483±1.0441	1.000 (0.00)	1. 9
	Zn	5.94 (5.35-6.50)	10.74 (9.56-12.67)	12.70 (11.04-15.62)	4.9876±0.5767	0.3649 (0.0474)	3.03
	Cu	6.19 (5.56-6.78)	11.60 (10.29-13.73)	13.87 (12.00-17.11)	4.6911±0.5198	2.0986 (0.050)	3.10

LCL: lower confidence limit; UCL: upper confidence limit; X^2: Chi-square value; *df* : degrees of freedom; Significant at $p < 0.05$ level; SE: standard error**.**

In a study on *Spodeoptera litura*, with ZnO- and CuO-NPs, Abd El- Wahab and Anwar (2014) observed that 0.01 g of ZnO-NPs resulted in 100% mortality, whereas the same concentration of CuO-NPs resulted in 33.3% mortality. Khooshe-Bast *et al*. (2016) tested ZnO-NPs on *Trialeurodes vaporariorum*, the LC_{50} value was 7.35 mg and the mortality rate was 91.6% at 20 mg**.** Ramadan *et al*. (2020) reported that the latent biological responses of *Schistocerca gregaria* treated with ZnO were more than that of CuO-NPs. Pittarate *et al*. (2021) and Eskin & Nurullahoğlu (2022) also concluded that ZnO-NPs have toxic effects on *Spodoptera frugiperda and Galleria mellonella*. Other authors reported the toxic effects of CuO-NPs against different mosquito species (Vivekanandhan *et al*. 2021a, b) and *Spodoptera frugiperda* (Rahman et al., 2022).

Effects of the Tested Nanoparticles on Adult Weights of *B. germanica*:

The effects of the tested NPs on adult weights of *B. germanica* are presented in Table (5). SiO_2-NPs significantly decreased the weights of adults treated with 40 and 80 mg concentrations, while ZnO- and CuO-NPs induced a non-significant decrease by contact method. When NPs were applied by the feeding method, the adults fed on SiO_2-NPs treated food at all concentrations weighed much less than adults from the control group. While the low concentrations of ZnO- and CuO-NPs had no significant effect on adult weights. The decrease in adult weights may be due to the toxic effects of NPs. When NPs are taken into the insect body with the diet, they may cause a decrease in the energy stored (adipose tissues and glycogen) of the insect by creating stress on the insect. Overcoming this stress condition requires a high amount of energy. A similar explanation was suggested by Eskin and Nurullahoğlu (2022) in a study investigating the effect of ZnO-NPs on the pupal weight of *Galleria mellonella*. Weight decreases in insects treated with ZnO-NPs were also recorded by Pittarate *et al*., (2021).

Table 5: Effect of SiO_2-, ZnO- and CuO-NPs on adult weights of the German cockroach after 3 days of treatment.

Treatment Conc.(mg)	Adult weights in mg (mean ± SE)					
	Contact method			Feeding method		
	SiO_2-NPs	ZnO-NPs	CuO-NPs	SiO_2-NPs	ZnO-NPs	CuO-NPs
Control	123.2 ± 5.20^{aA}	123.2 ± 5.20^{aA}	123.2 ± 5.20^{aA}	124.2 ± 10.1^{aA}	124.2 ± 10.1^{aA}	124.2 ± 10.1^{aA}
5	120.4 ± 6.67^{abA}	122.8 ± 8.22^{aA}	122.9 ± 3.98^{aA}	117.6 ± 8.90^{bB}	120.9 ± 7.42^{aAB}	123.0 ± 6.50^{aA}
10	120.8 ± 6.68^{abA}	126.7 ± 9.30^{aC}	126.6 ± 9.21^{aC}	114.0 ± 10.12^{bB}	119.5 ± 5.45^{bAB}	121.6 ± 7.47^{aA}
20	114.0 ± 8.64^{bAD}	122.6 ± 8.00^{aC}	121.6 ± 7.30^{aC}	103.0 ± 7.50^{cB}	116.0 ± 4.37^{bA}	117.2 ± 6.08^{bA}
40	111.4 ± 5.03^{bA}	121.3 ± 6.50^{aC}	122.8 ± 4.45^{aC}	77.20 ± 6.55^{dB}	111.0 ± 3.86^{cA}	114.4 ± 6.20^{bA}
80	97.40 ± 5.34^{cAB}	119.1 ± 7.60^{aD}	120.2 ± 2.22^{aD}	42.20 ± 8.01^{eC}	92.10 ± 5.90^{dB}	102.5 ± 4.83^{cA}

Means within a column and followed by the same superscript small letter are not significantly different ($P>0.05$), Means within a raw and followed by the same superscript capital letter are not significantly different ($P>0.05$) SE: standard error.

Stability of the Prepared NPs:

The efficiency of the prepared NPs was tested after storing them for four months is represented in Table (6). SiO_2-NPs at 80 mg concentration caused 100% mortality by contact and feeding methods. Mortality % caused by ZnO-NPs were slightly decreased to 90 and 98% by contact and feeding methods, respectively compared to 92 and 100% for the freshly prepared NPs. CuO-NPs were less stable than SiO_2- and ZnO-NPs, the recorded mortalities were 66.67 and 76% compared with 86 and 100% for the freshly prepared NPs by contact and feeding methods, respectively. The stability and efficiency of SiO_2-NPs were also observed by El-Bendary (2017).

Table 6: Mortality % of *B. germanica* exposed to 80 mg of SiO_2-, ZnO- and CuO-NPs after four months storage under laboratory conditions

Method of treatment	Period of storage	Mortality % (mean± S.E.)			
		Control	SiO_2-NPs	ZnO-NPs	CuO-NPs
Contact	At zero time	0.00±0.0	100±0.00	92.0±3.74	86.0±5.10
	After 4 months	2.00±0.3	100±0.00	90.0±3.20	66.67±4.6
Feeding	At zero time	0.00±0.0	100±0.00	100±0.00	100±0.00
	After 4 months	0.00±0.0	100±0.00	98.0±1.30	76.0±4.10

CONCLUSION

Silicon dioxide (SiO_2), Zinc oxide (ZnO) and Copper oxide (CuO) nanoparticles (NPs) were synthesized and screened for insecticidal activity against adults of the German cockroach by contact and feeding methods. Low concentrations of Silicon dioxide and Zinc oxide NPs caused remarkable insecticidal effects against adults of Blattella germanica by contact or feeding methods compared to the crude metal powders. Both products were stable and retained insecticidal activity after storage for four months under laboratory conditions. The physical mode of action of NPs makes insects unlikely to become physiologically resistant; hence, the use of these nanoparticles as unconventional insecticides constitutes a new approach to combat this pest, which has become resistant to conventional chemical insecticides. Further studies are needed to find out the mechanism of action and non-target toxicity of these products.

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