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Efficacy of silica and tin doped silica nanoparticles on the fourth larval instar of *Culex pipiens*

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Abstract

Mosquito-borne diseases represent a growing health challenge over time. Therefore, silicon oxide and tin-doped silica, with three different ratios of tin, nanoparticles were synthesized via sol-gel/combustion and hydrothermal methods, respectively and evaluated for insecticidal activity against the 4th larval instar of *Culex pipiens* at different concentrations (25, 50, 100, 200, 400, and 800 ppm) in the sunlight, artificial light, and dark at different time intervals. The prepared nanoformulations were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The crystal size of silicon oxide and tin-doped silicon oxide increases from 1.1 to 9.3 nm by increasing the dopant concentration to overcome quantum confinement to enhance its absorption for sunlight. Moreover, the siloxane bond appeared in both silicon dioxide and tin-doped silica nanoparticles. The highest concentration (800 ppm) induces 80% and 100% mortality in sunlight, 68.8% and 100% mortality in artificial light, 10.4% and 17.6% mortality in darkness after 3 and 6 h, respectively. As a result, doped nanostructures show high potential larvicidal action in sunlight and may serve as effective alternatives for chemical pesticides.

Keywords: *Sunlight; artificial light; Darkness; XRD; Doped nanoparticles; Culex pipiens.*

1. Introduction

Mosquitoes, the most significant blood-feeding dipterans, serve as primary vectors for numerous severe and highly infectious human diseases, including malaria, filariasis, Japanese encephalitis, dengue, and yellow fever, resulting in a substantial number of fatalities (1, 2). The Culicidae family, which includes over 3200 species of common mosquitoes, divides into three subfamilies: Anophelinae, Culicinae, and Toxorhynchitinae. These subfamilies further classify into forty genera, distributed worldwide (3, 4). *Culex* mosquitoes, the most prevalent species, thrive in tropical and temperate regions (5-8).

Conventional pesticides are no longer the optimal solution for insect control due to several considerations, including detrimental effects on human health and non-target organisms, as well as high operational costs (9). Additionally, insects have developed resistance to the majority classes of insecticides, such as organophosphates, organochlorines, carbamates, and even pyrethroids (10, 11). Given these issues, it is crucial to search for effective alternatives to synthetic chemical pesticides.

Nanotechnology, a promising interdisciplinary research field, provides applications in various scientific fields, including agriculture, pharmaceuticals, and insecticides (12-14). Nanomaterial-based insecticides may act as potential alternatives for pest management (15). Different nanoparticles, including those made of silver, gold, carbon, silica, alumina, titanic, and zinc oxide, have demonstrated diverse insecticidal effects against insects (16). Metal oxide nanoparticles will make it easier to deliver pesticides precisely and get rid of pests that destroy crops and their yields and medical insects as well (17).

Efficacy of doped nanoparticles have been assessed against *Culex* species such as *Culex quinquefasciatus, Aedes aegypti,* and *Anopheles stephensi* (18, 19). These nanoparticles have widespread applications, including plant protection and controlling medical insects (18, 20). Newly based nanoparticle materials such as pesticides are expected to reduce application volume and energy consumption due to anticipated changes in matter structure (size, shape, and disparity) (21, 22).

Employing solar spectra, which serves as a stimulant for excitation of electrons and insects as well introduces a highly promising avenue for integrated control programs (23). Therefore, this study aims to investigate the toxicity of tin doped silica nanoparticles against fourth larval instar of *Culex pipiens*.

2. Material and methods

2.1. Chemicals

Silica gel, sodium hydroxide, nitric acid, starch, hydrous tin chloride, tetraethyl orthosilicate (TEOS), urea and ethanol applied in the experiments was purchased from El-Gomhouria company for Trading Chemicals and Medical Appliances.

2.2. Preparation of silica nanoparticles

a. Undoped silicon dioxide nanoparticles

Silica nanoparticles were prepared via the sol–gel/combustion method. Four grams of silica gel were dissolved in 50 mL of sodium hydroxide aqueous solution (3 M) and magnetically stirred at 80 °C for two hours. 5.9 M of nitric acid aqueous solution was added dropwise till the formation of white gel. The produced gel was subsequently washed three times with 5.9 M nitric acid solution, and then separated by centrifugation at 2400 rpm for 4 min. To this separated gel, 50 mL of nitric acid solution (5.9 M) was added. Furthermore, 2 g of starch fuel aqueous solution dissolved in 10 mL distilled water was added to the gel under magnetic stirring for 5 min. Afterwards, the washed gel was dried at 100 ^{o}C for 4 h. Later, the stir bar was removed, then the reaction mixture has undergone combustion process at about 350 °C for 10 min. After the combustion reaction, the product was washed three times with warm distilled water, dehydrated at 100 ^{o}C for 4 h and calcined at 800 ^{o}C for 2 h, producing silicon dioxide nanoparticles denoted as SiO_2.

b. Tin doped silicon dioxide nanoparticles

Hydrothermal technique was employed to fabricate tin doped silicon dioxide nanoparticles. Reaction starts by mixing 0.097 mmol of $SnCl_2$, 10.60 mmol of TEOS and 98.73 mmol of urea in 60 mL of distilled water under magnetic stirring followed by ultrasonication for 15 min. Shortly thereafter, this solution was transferred to an autoclave at 180 ^{o}C for 12 h. The yield was subsequently washed 5 times with distilled water and twice with ethanol (70%) at 2400 rpm for 5 min., dehydrated at 60 ^{o}C overnight and calcined at 800 ^{o}C for 3 h. It is worth mentioning that the synthesized nanoparticles were denoted as Sn-SiO_2-R1. Parallel experiments were carried out using 0.079 mmol of $SnCl_2$, 10.63 mmol of TEOS, and 99.06 mmol of urea which was denoted as Sn-SiO_2-R2. Meanwhile, the experiment involves using 0.057 mmol of $SnCl_2$, 10.65 mmol of TEOS and 99.23 mmol of urea denoted as Sn-SiO_2-R3.

2.3. Characterization of the synthesized nanoparticles

Nanoparticles was characterized by XRD analysis to study the composition, crystallinity and the phase purity, FT-IR for investigating the chemical composition of functional groups of the yield.

Mosquito bioassay

Laboratory rearing of *Culex pipiens*

Culex pipiens were obtained from Medical and Molecular Entomology Section, Entomology department, Faculty of Science, Benha University. They were maintained at 27 ± 2°C, 75±5% RH under a photoperiod of 14:10 h (light/dark) in the insectary. Larvae were fed on fish food (Tetramin®) with grinded bread in the ratio of 3:1. Pupae were transferred from the enamel pans to a cup containing de-chlorinated tap water and placed in screened cages (35 × 35 × 40 cm dimension) where the adults emerged. The adult colony was provided with 10% sucrose solution and was periodically taken a blood-fed. The engorged female mosquitoes oviposited egg rafts on small cups that containing dechlorinated tap water. Two developmental stages, larvae and adult females, were continuously available for the experiments and were maintained at the same laboratory conditions (24).

Larvicidal bioassay

Activities of silica nanoparticle were performed with 4th larval instars of *Culex pipiens* under laboratory conditions. 1 g of silica nanoparticles in 1000 mL of distilled water using ultrasonicator to prepare various concentrations, where the silica nanoparticles larvicidal activity were tested at 25, 50, 100, 200, 400, and 800 ppm concentrations. Twenty-five larvae per concentration were transferred to 500 mL glass beaker containing 250 mL of distilled water used for all the experiments. The experiment was replicated three times with an untreated control group. Mortalities were recorded after 1, 2, 3, 6 h of the exposure period.

2.4. Statistical analysis

The data were analyzed using SPSS V23 (IBM, USA) to conduct Probit analyses for calculating lethal concentration (LC) values and to conduct one-way analysis of variance (ANOVA) with Post Hoc/Tukey's HSD test. The critical thresholds were established at $P<0.05$ (25, 26).

3. Results and Discussion

Silicon dioxide and tin-doped silicon dioxide nanoparticles were successfully prepared by sol-gel/combustion and hydrothermal methods, respectively, and characterized by XRD and FTIR analysis.

3.1. Characterization of nanomaterials

X-ray diffraction (XRD)

Fig. 1. shows x-ray diffraction patterns of the undoped silicon dioxide (SiO_2) and tin doped silicon dioxide (Sn-SiO_2-R1, Sn-SiO_2-R2 and Sn-SiO_2-R3)

nanoparticles products. This figure indicated that the SiO_2 products were in conformity with the tetragonal phase of SiO_2 nanoparticles [No. 01-082-1410; space group: P41212]. Moreover, no other reflections for impurities had been observed which confirmed the pure phase of SiO_2 (27) which gives an indication of proper doping of tin within the matrix of silicon dioxide (28). It is worth noting that the calculated crystal size (D, nm) for silica nanoparticles (SiO_2 and Sn-SiO_2 R1) was found at Ca. 1.1 and 9.3 respectively, using the Debye-Scherrer equation (Jenkins and Snyder, 1996)

$$D = 0.9\lambda / \beta \cos\theta B$$

Where, λ (nm) is the X-ray radiation wavelength, β the full width of the diffraction peak at half maximum (FWHM), and θB is the Bragg diffraction angle. However, Sn-SiO_2 R2 and Sn-SiO_2 R3 products were almost amorphous. Doping is one of the techniques which are commonly used to control the size of some nanoparticles to tune their properties. However, when tin is doped into silicon dioxide nanoparticles, their size increases from 1.1 nm to 9.3 nm. It is crystal clear that the dopant can produce a sufficiently strong hybridization effect to overcome quantum confinement (29). Therefore, the significant increase in the average crystal size may lead to a decrease in the band gap, which indicates that tin-doped silicon dioxide can be excited by ultraviolet radiation from the solar spectrum. This result is consistent with the results published earlier that indicated that the band gap of manganese-doped tin oxide decreases from 3.89 eV to 3.63 eV as the manganese doping concentration increases (30).

3.2.Infrared spectroscopy (FT-IR)

In the present study, FT-IR spectra used to characterize the chemical function groups of undoped silicon dioxide (SiO_2) and tin doped silicon dioxide (Sn- SiO_2 R1, Sn- SiO_2 R2, Sn- SiO_2 R3) (**Fig. 2**). The bands appear at ca. 3420, 3437, 3439 and 3444 cm^{-1} in all the products correspond to the vibrations of O–H stretching. Meanwhile, bands which were present at ca. 1626 cm^{-1} may be attributed to H–O–H bending. Bands that appear at ca. 613, 810, 1104, 1108 and 1133 cm^{-1} can be assigned to the stretching vibrations of the siloxane Si-O-Si bond. Remarkably, the absorption bands at ca. 471 and 475 cm^{-1} may be attributed to the siloxane bond (Si-O-Si) bending vibration (31). Furthermore, the absence of characteristic peaks of tin refers to the proper phase formation.

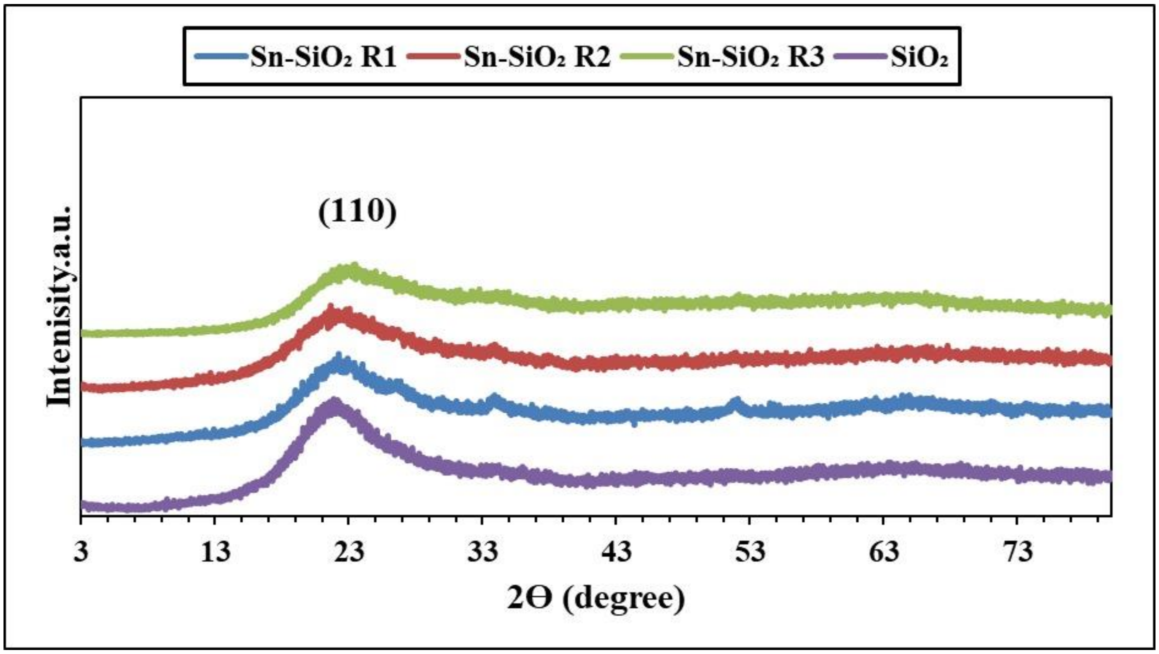

Fig. 1. XRD patterns of SiO_2 and Sn- SiO_2 (R1, R2 and R3) nanoparticles; prepared by sol-gel/combustion and hydrothermal method, respectively

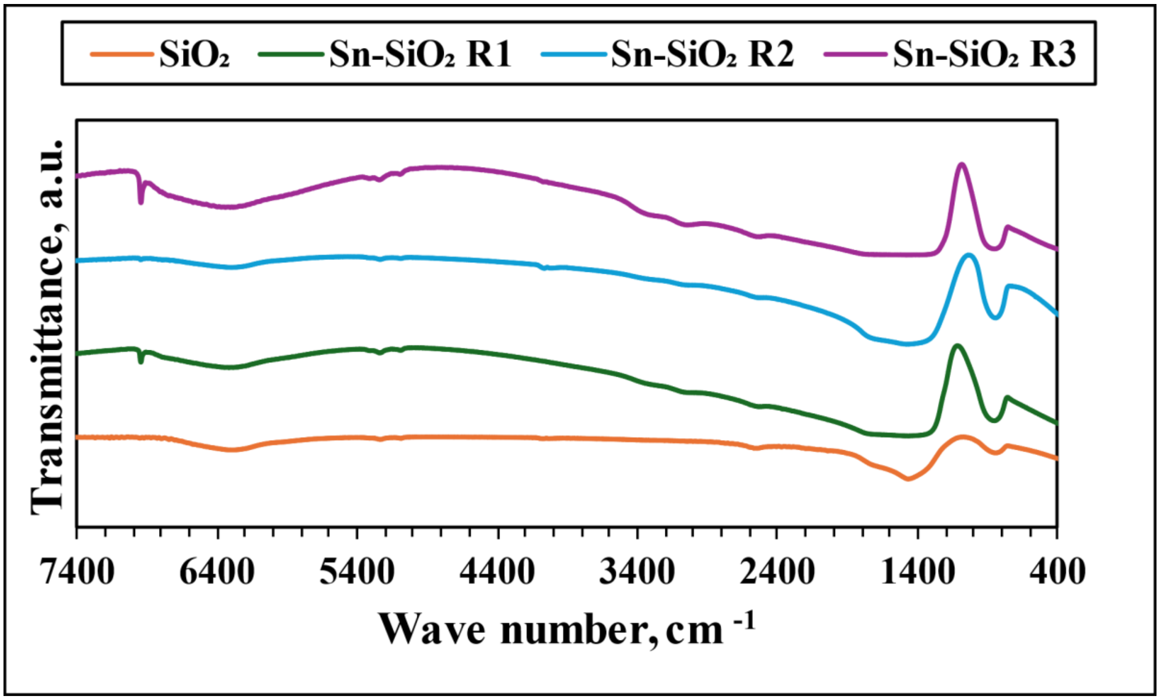

Fig. 2. FT-IR spectra of SiO_2 and Sn- SiO_2 (R1, R2 and R3) nanoparticles; prepared by sol-gel/combustion and hydrothermal method, respectively .

3.3. Toxicity of undoped silicon dioxide and tin doped silicon dioxide nanoparticles on the 4th larval instar of *Culex pipiens* in the direct sunlight

Larvicidal potency of the synthesized undoped silicon dioxide (SiO_2) and tin doped silicon dioxide nanoparticles ($Sn\text{-}SiO_2$) against 4th larval instar of *Culex pipiens* was shown in **Table 1**. The data indicated that mortality % increased by increasing concentration and time of exposure recording 80 and 100% mortalities in treated larvae after 3 and 6 h exposure, respectively, to the highest concentration (800 ppm) of tin doped silicon oxide ($Si\text{-}SnO_2$) compared to control (**Table 2)**. On the other hand, LC_{50} values for undoped silicon dioxide were 404.70 and 130.08 ppm (**Table 3**). As for tin doped silicon dioxide, LC_{50} values were 171.52 and 39.53 ppm (**Table 4**) after 3 and 6 h, respectively.

Toxicity of undoped silicon dioxide (SiO_2) and tin doped silicon dioxide ($Sn\text{-}SiO_2$) nanoparticles on the 4th larval instar of *Culex pipiens* in the artificial light

The data presented in **Tables 5 & 6** clearly demonstrated a higher mortality in doped nanomaterials compared to undoped ones. It recorded the highest mortality at the highest concentration (800 ppm), resulting in 100% mortality after 6 h exposure, while the undoped silicon dioxide showed 74.4% mortality after 6 h exposure. LC_{50} values for undoped silicon dioxide were 1190.53 ppm and 438.62 ppm (**Table 7**). As for tin doped silicon dioxide, LC_{50} values were 338.32 and 98.74 ppm **(Table 8)** after 3 and 6 h, respectively.

Toxicity of undoped silicon dioxide (SiO_2) and tin doped silicon dioxide ($Sn\text{-}SiO_2$) nanoparticles on the 4th larval instar of *Culex pipiens* in the dark

Data in **Table 9** indicated that the highest mortality (10.4%) after 6 h exposure was observed at the highest concentration (800 ppm) of undoped nanoparticles (SiO_2) compared to control. On the other hand, the mortality after 6 h exposure to the highest concentration (800 ppm) of doped nanomaterials was 17.6% compared to control **(Table 10)**.

From the previous results, it was clear that the fourth larval instar of *Culex pipiens* was more susceptible to doped nanomaterials ($Sn\text{-}SiO_2$) than undoped nanomaterials (SnO_2) and much more affected in sunlight than the artificial light and dark. It is worth to note that the mean mortality (%) of the 4th larval instar of *Culex pipiens* increased by increasing the concentration and the time of exposure in all light media.

A parallel study evaluated silica nanoparticles (SNPs) synthesized via sol-gel (A800) and sol-gel/combustion (B800) techniques at varying concentrations of 5, 25, 50, 100, and 200 ppm after 24 and 48 hours on *Culex pipiens* larvae. The authors found that silica nanoparticles (B800) had a strong larvicidal activity, with LC_{50} values of 19.7 ppm for the 1st larval instar, 37.4 ppm for the 2nd, 61.1 ppm for the 3rd, and 85.2 ppm for the 4th larval instar, and 234.8 ppm for the pupal stage at 24 hours (32).

The results of this study are in agreement to the another finding which indicated that silica nanoparticles are toxic to mosquito species like A*nopheles stephensi*, *Aedes aegypti*, and *Culex quinquefasciatus*, inducing mortality in both larvae and pupae. Moreover, the toxicity is high at low concentrations (112.5 and 225 ppm) (33).

Moreover, the current results are in accordance with similar studies (33, 34) which indicated that silica nanoparticles can be used as larvicides and pupicides on mosquito species including *Anopheles stephensi*, *Aedes aegypti*, and *Culex quinquefasciatus* with high toxicity at low doses (112.5 and 225 ppm). The obtained results were also compatible with that data published earlier which assessed the effects of two silicon dioxide nanoparticles of Aerosil® and Nanosav on adults of *Rhyzopertha dominica* and *Tribolium confusum* at 50, 100, 200, and 300 ppm after 7 days of exposure; the data showed that the mortality % for both species increased by increasing the concentration and time-exposure to each concentration and that the Aerosil® silicon dioxide nanoparticles were more effective than Nanosav silicon dioxide (35).

The doping process involves introducing dopants into the matrix of the photocatalyst to delay the recombination of photogenerated electrons from the conduction band to the valence band and extend the threshold wavelength response to the ultraviolet region of the solar spectrum (36).

Accordingly, the highest mortality in direct sunlight may be attributable doping that stimulates photocatalytic activity (37, 38). This finding could be interpreted as an excitation of electrons from the valency band to conduction band after being exposed to the ultraviolet radiation of the direct sunlight (39) which induces an oxidative stress (40). Oxidative stress arsing from an imbalance between the reactive oxygen species (ROS) and the biological systems' ability to repair the damage or even to detoxify the reactive intermediates. This data obtained is in conformity with the study that applied rose Bengal and methylene blue against *Aedes aegypti* and *Anopheles gambiae* as photosensitive insecticides. However, they added sand to the water in order to absorb more energy increasing stress on the larvae (41).

Table 1. Efficacy of undoped silicon dioxide on the 4th larval instar of *Culex pipiens* mortality after exposure to sunlight for 1, 2, 3, and 6 h (mean ± SE).

Treatment	Time (h)	Concentration (ppm)						
		0	25	50	100	200	400	800
Silicon dioxide	1	0 ± 0^{aG}	1.6 ± 0.98^{dF}	4.0 ± 1.79^{dE}	8.0 ± 1.26^{dD}	16.0 ± 2.19^{dC}	27.2 ± 1.50^{dB}	39.2 ± 2.33^{dA}
	2	0 ± 0^{aG}	2.4 ± 0.98^{cF}	5.6 ± 1.60^{cE}	12.8 ± 0.80^{cD}	22.4 ± 2.04^{cC}	32.0 ± 1.26^{cB}	44.8 ± 2.33^{cA}
	3	0 ± 0^{aG}	4.8 ± 0.80^{bF}	9.6 ± 1.60^{bE}	18.4 ± 1.60^{bD}	33.6 ± 2.04^{bC}	55.2 ± 1.50^{bB}	62.4 ± 2.04^{bA}
	6	0 ± 0^{aG}	9.6 ± 0.98^{aF}	18.4 ± 2.04^{aE}	35.2 ± 2.33^{aD}	60.0 ± 2.83^{aC}	85.6 ± 2.71^{B}	100 ± 0.00^{aA}

a, b & c: There is no significant difference ($P>0.05$) between any two means for each treatment, within the same column have the same superscript letter. A, B & C: There is no significant difference ($P>0.05$) between any two means, within the same row have the same superscript letter.

Table 2. Efficacy tin doped silicon dioxide on the 4th larval instar of *Culex pipiens* mortality after exposure to sunlight for 1, 2, 3, and 6 h (mean ± SE).

Treatment	Time (h)	Concentration (ppm)						
		0	25	50	100	200	400	800
Tin-Silicon dioxide	1	0 ± 0^{aG}	4.0 ± 1.26^{dF}	12.0 ± 0.00^{dE}	18.4 ± 0.98^{dD}	28.0 ± 2.83^{dC}	39.2 ± 3.44^{dB}	54.4 ± 3.71^{dA}
	2	0 ± 0^{aG}	8.8 ± 1.50^{cF}	15.2 ± 1.50^{cE}	22.4 ± 2.04^{cD}	34.4 ± 0.98^{cC}	45.6 ± 3.49^{cB}	60.0 ± 4.56^{cA}
	3	0 ± 0^{aG}	17.6 ± 2.04^{bF}	28.8 ± 2.33^{bE}	42.4 ± 3.71^{bD}	48.8 ± 4.08^{bC}	63.2 ± 2.33^{bB}	80.0 ± 3.35^{bA}
	6	0 ± 0^{aG}	29.6 ± 2.99^{aD}	61.6 ± 2.99^{aC}	84.0 ± 2.83^{aB}	100 ± 0.00^{aA}	100 ± 0.00^{aA}	100 ± 0.00^{A}

a, b & c: There is no significant difference ($P>0.05$) between any two means for each treatment, within the same column have the same superscript letter. A, B & C: There is no significant difference ($P>0.05$) between any two means, within the same row have the same superscript letter.

Table 3. Lethal concentrations (ppm) of undoped silicon dioxide against the 4th larval instar of *Culex pipiens* after exposure to sunlight for 1, 2, 3, and 6 h post-treatments.

Treatment	Time (h)	LC$_{50}$ (Low-Up.)	LC$_{90}$ (Low-Up.)	LC$_{95}$ (Low-Up.)	Slope ±	Chi (Sig.)	R (0.8111)
Silicon dioxide	1	1284.02 (876.04-2289.48)	13740.87 (61174.89-49604.43)	26905.06 (10665.64-119464.32)	1.2449 ±0.1520	0.078 (0.999)	0.019
	2	971.08 (688.23-1600.19)	11515.38 (5421.62-37273.24)	32313.27 (9649.55-91769.13)	1.1933 ±0.1376	0.475 (0.975)	0.997
	3	404.70 (328.12-522.76)	3346.39 (2109.49-6391.36)	6090.44 (3526.55-13174.26)	1.3969 ±0.1274	1.972 (0.740)	0.994
	6	130.08 (96.67-174.20)	498.26 (377.13-836.44)	729.10 (540.25-1339.93)	2.1974 ±0.1479	9.559 (0.048)	0.950

Table 4. Lethal concentrations (ppm) of tin doped silicon dioxide against the 4th larval instar of *Culex pipiens* after exposure to sunlight for 1, 2, 3, and 6 h post-treatments.

Treatment	Time (h)	LC$_{50}$ (Low-Up.)	LC$_{90}$ (Low-Up.)	LC$_{95}$ (Low-Up.)	Slope ±	Chi (Sig.)	R (0.8111)
Tin -Silicon dioxide	1	650.74 (481.91-984.20)	8744.52 (4342.93-25347.31)	18263.62 (8005.81-64404.05)	1.1358 ±0.1244	0.814 (0.936)	0.993
	2	484.59 (364.82-708.24)	7831.39 (3879.70-22811.97)	17234.76 (7467.48-61988.41)	1.0605 ±0.1166	0.136 (0.997)	0.999
	3	171.52 (137.28-216.92)	2502.93 (1506.70-5217.79)	5351.15 (2868.18-13315.97)	1.1009 ±0.1103	1.831 (0.766)	0.992
	6	39.53 (34.30-44.72)	110.08 (94.05-135.12)	147.16 (121.67-190.17)	2.8815 ±0.2600	4.470 (0.346)	0.939

Table 5. Efficacy of undoped silicon dioxide on the 4th larval instar of *Culex pipiens* mortality after exposure to artificial light for 1, 2, 3, and 6 h (mean ± SE).

Treatment	**Time (h)**	**Concentration (ppm)**						
		0	25	50	100	200	400	800
Silicon dioxide	1	0.0 ± 0^{aE}	0.0 ± 0^{aE}	0.0 ± 0.0^{bE}	1.6 ± 2.19^{dD}	6.4 ± 0.98^{dC}	14.4 ± 0.98^{dB}	22.4 ± 1.60^{dA}
	2	0.0 ± 0^{aE}	0.0 ± 0^{aE}	0.0 ± 0.0^{bE}	2.4 ± 3.58^{cD}	9.6 ± 2.71^{cC}	18.4 ± 2.04^{cB}	28.8 ± 1.96^{cA}
	3	0.0 ± 0^{aE}	0.0 ± 0^{aE}	0.8 ± 0.80^{bE}	5.6 ± 3.58^{bD}	13.6 ± 2.40^{bC}	27.2 ± 1.96^{bB}	47.2 ± 2.33^{bA}
	6	0.0 ± 0^{aE}	0.0 ± 0^{aE}	5.6 ± 0.98^{aE}	12.0 ± 4.00^{aD}	24.0 ± 2.53^{aC}	40.0 ± 3.35^{aB}	74.4 ± 3.49^{aA}

a, b & c: There is no significant difference (P>0.05) between any two means for each treatment, within the same column have the same superscript letter.; A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

Table 6. Efficacy of tin doped silicon dioxide on the 4th larval instar of *Culex pipiens* mortality after exposure to artificial light for 1, 2, 3, and 6 h (mean ± SE).

Treatment	**Time (h)**	**Concentration (ppm)**						
		0	25	50	100	200	400	800
Tin-Silicon dioxide	1	0.0 ± 0^{aG}	0.0 ± 0.00^{dF}	5.6 ± 0.98^{dE}	10.4 ± 3.58^{dD}	18.4 ± 1.60^{dC}	28.8 ± 1.96^{dB}	48.0 ± 2.53^{dA}
	2	0.0 ± 0^{aG}	1.6 ± 0.98^{cF}	7.2 ± 1.50^{cE}	16.0 ± 4.90^{cD}	27.2 ± 1.96^{cC}	38.4 ± 2.99^{cB}	56.8 ± 2.94^{cA}
	3	0.0 ± 0^{aG}	8.0 ± 1.26^{bF}	17.6 ± 2.04^{bE}	29.6 ± 4.56^{bD}	36.8 ± 2.94^{bC}	51.2 ± 4.27^{bB}	68.8 ± 3.67^{bA}
	6	0.0 ± 0^{aG}	15.2 ± 1.50^{aF}	28.0 ± 2.19^{aE}	46.4 ± 6.07^{aD}	69.6 ± 2.40^{aC}	87.2 ± 3.88^{aB}	100 ± 0.00^{aA}

a, b & c: There is no significant difference (P>0.05) between any two means for each treatment, within the same column have the same superscript letter.; A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

Table 7. Lethal concentrations (ppm) of undoped silicon dioxide against the 4th larval instar of *Culex pipiens* after exposure to artificial light for 1, 2, 3, and 6 h post-treatments

Treatment	Time (h)	LC_{50} (Low-Up.)	LC_{90} (Low-Up.)	LC_{95} (Low-Up.)	Slope ±	Chi (Sig.)	R (0.8111)
Silicon dioxide	1	2245.82 (1389.47-5316.78)	15371.88 (6202.59-84045.32)	26517.17 (9436.89-184622.64)	1.534 ±0.242	1.252 (0.869)	0.979
	2	1610.49 (1100.67-2987.22)	10283.30 (4891.37-36652.55)	17393.15 (7426.98-74990.41)	1.591 ±0.219	1.920 (0.750)	0.974
	3	1190.53 (883.47-1833.09)	8272.49 (4474.83-21424.47)	14331.52 (7040.66-43298.94)	1.522 ±0.173	2.612 (0.624)	0.986
	6	438.62 (372.37-531.82)	2033.55 (1472.13-3148.53)	3141.21 (2150.16-5269.24)	1.923 ±0.161	5.474 (0.242)	0.973

Table 8. Lethal concentrations (ppm) of tin doped silicon dioxide against the 4th larval instar of *Culex pipiens* after exposure to artificial light for 1, 2, 3, and 6 h post-treatments

Treatment	Time (h)	LC_{50} (Low-Up.)	LC_{90} (Low-Up.)	LC_{95} (Low-Up.)	Slope ±	Chi (Sig.)	R (0.8111)
Tin-Silicon dioxide	1	898.89 (669.17-1360.42)	7491.94 (4015.01-19283.20)	13666.03 (6619.13-41216.64)	1.391 ±0.151	2.477 (0.648)	0.947
	2	595.95 (466.29-821.30)	5051.12 (2954.44-10990.99)	9257.67 (4934.20-23170.43)	1.380 ±0.136	1.183 0.880	0.991
	3	338.32 (268.58-448.60)	4161.71 (2398.77-9245.80)	8477.01 (4381.30-2202.37)	1.175 ±0.116	1.328 (0.856)	0.994
	6	98.74 (85.42-113.47)	437.28 (354.58-568.36)	666.74 (518.49-918.70	1.982 ±0.140	5.980 (0.200)	0.950

Table 9. Efficacy of undoped silicon dioxide on the 4th larval instar of *Culex pipiens* mortality in dark after 1, 2, 3, and 6 h (mean ± SE)

Treatment	Time (h)	Concentration (ppm)						
		0	25	50	100	200	400	800
Silicon dioxide	1	0.0±0^{aB}	0.0±0^{aB}	0.0±0^{aB}	0.0±0^{aB}	0.0±0^{cB}	0.0±0^{dB}	1.6±0.98^{dA}
	2	0.0±0^{aC}	0.0±0^{aC}	0.0±0^{aC}	0.0±0^{aC}	0.0±0^{cC}	0.8±0.80^{cB}	2.4±0.98^{cA}
	3	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{aD}	0.8±0.80^{bC}	3.2±0.80^{bB}	5.6±0.98^{bA}
	6	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{aD}	3.2±0.80^{aC}	6.4±0.98^{aB}	10.4±0.98^{aA}

a, b & c: There is no significant difference (P>0.05) between any two means for each treatment, within the same column have the same superscript letter. A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

Table 10. Efficacy of tin doped silicon dioxide on the 4th larval instar of *Culex pipiens* mortality in dark after 1, 2, 3, and 6 h (mean ± SE).

Treatment	Time (h)	Concentration (ppm)						
		0	25	50	100	200	400	800
Tin-Silicon dioxide	1	0.0±0^{aC}	0.0±0^{aC}	0.0±0^{aC}	0.0±0^{bC}	0.0±0^{dC}	2.4±0.98^{dB}	3.2±0.80^{dA}
	2	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{bD}	2.4±0.98^{cC}	3.2±0.80^{cB}	5.6±0.98^{cA}
	3	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{aD}	0.0±0^{bD}	4.0±1.26^{bC}	5.6±2.04^{bB}	10.4±1.60^{bA}
	6	0.0±0^{aE}	0.0±0^{aE}	0.0±0^{aE}	2.4±0.98^{aD}	7.2±0.80^{aC}	9.6±0.98^{aB}	17.6±1.60^{aA}

a, b & c: There is no significant difference (P>0.05) between any two means for each treatment, within the same column have the same superscript letter. A, B & C: There is no significant difference (P>0.05) between any two means, within the same row have the same superscript letter.

4. Conclusion

The current study assessed the effectiveness of silicon dioxide and tin doped silicon dioxide against the 4th larval instar of *Culex pipiens*. The results indicated that *Culex pipiens* was more susceptible to tin doped silicon dioxide than silicon dioxide which open new horizons to nano-based pesticides. In anticipation of the pressing need for effective integration pest management strategies, nano-based insecticides may be involved without disturbing the environmental balance.

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