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Synthesis and Characterization of ZnO@SiO_2 Nanocomposite Using Gum Arabic and its Larvicidal activity on Malaria vectors

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ABSTRACT

Green synthesis of ZnO@SiO_2 nanocomposite was performed using Gum Arabic. The green synthesized nanocomposite was characterized using Fourier Transform Infrared Spectrophotometer (FTIR), The Scanning Electron Microscopy (SEM), UV-Visible spectrophotometer, Dynamic Light Scattering (DLS), and X-Ray Fluorescence (XRF). The toxicity study was conducted for 24 h on 1st to 4th larval instars of malaria vectors at various concentrations (10, 20 and 25 mg/L). The LC_{50} and LC_{90} for the 1st-4th larval instars were found to be in the range of 9.11-18.288 mg/L and 157.254-126.132 mg/L respectively. A strong positive correlation between concentrations of the nanocomposite and mortality of larval instars (0.945-0.997). These values indicate that the mortality rates increased with an increase in concentrations. ZnO@SiO_2 nanocomposite is a potential nano-larvicide for malaria vector control in tropical countries with high malaria incidence.

Keywords: Green synthesis, ZnO@SiO_2, Nanocomposite, Malaria vectors, Gum Arabic.

INTRODUCTION

Malaria is one of the common life-threatening diseases mostly found in the tropics. Over 100 hundred countries were reported to be at risk of transmission of this disease. It is caused by protozoan parasites of the genus *Plasmodium*. Most human malaria is caused by four different species of the *Plasmodium* parasite: *Plasmodium falciparum*, *P. malariae*, *P. ovale* and the *P. vivax*[1]. The world malaria report indicated that 228 million malaria cases were reported worldwide, out of which 405,000 died. Africa accounted for the majority of the malaria cases and deaths, amounting to 213 million and 94% respectively[2]. Several species of mosquitoes belonging to the genus *Anopheles* are known to transmit malaria. In the African continent, *Anopheles gambiae*, *An. coluzzii*,

An. arabiensis and the *An. funestus* were reported to be the major malaria vectors[3]. Other members of the *An. gambiae* complex includes *An. bwambae*, *An. melas*, *An. merus*, *An. quadriannulatus* and *An. amharicus*. All were noted to exhibit genetic differences, behavioural and ecological that can affect their vectorial capacity[4]. Over the years, vector control has contributed immensely to the management of malaria and other vector-borne infectious diseases[5]. Several control measures are employed against the mosquitoes. The control measures are either targeted at the adults or the larvae. The control measures against the adults are majorly chemical-based used in either Long Lasting Insecticide Nets (LLINs) or as Indoor Residual Spray (IRS)[2]. Whereas the larvae are controlled biologically employing larvivorous fishes such as the *Gambusia spp* or through the use of toxic chemical formulations or plant extracts[6]. The major constraint with the chemical-based control measures is the resistance development by the vectors. Successive usage of chemical-based insecticides over time resulted to the development as well as the widespread resistance in vector populations[7,3]. Another challenge with chemical control reported is the potentiality of the insecticides to cause environmental and human health toxicity[8]. Consequent to the failure of the aforementioned control strategies, the need of a novel and safer eco-friendly strategy is required to have effective control of the vector with minimal toxicity effect on the environment and human health. The emergence of nanotechnology is seen as a prospect for alternative vector control by many vector biologists. Nanotechnology deals with the synthesis and application of nanosized particles with configurations ranging from 1 to 100nm in dimension. These particles are referred to as nanoparticles (NP)[9,7]. Generally, due to their small size, nanoparticles can pass through the larvae's body wall into the cell and alter the physiological function of the larvae which causes death[10]. Ingestion of nanoparticles by larvae and absorption of nanoparticles are two ways in which nanoparticles penetrate the cuticle cells[10]. These are referred to as mechanisms of action of nanoparticles against mosquito larvae. Findings have shown that there is limited proof of toxicity towards non-target organisms of nanoparticles synthesized through the green route against mosquito larvae[11]. For instance,[12] reported no toxicity effect of the silver nanoparticles synthesized using *Vinca rosea*-synthesized against *P. reticulata*, when exposed to the dosages toxic against *Anopheles stephensi* and the *Cx. quinquefasciatus* for 72 hours. In the same way,[13] reported that there was no detection of toxicity of the silver nanoparticles synthesized using the dried green fruit of *Drypetes roxburghii* against the insect *P. reticulata*, after exposure for 48 h to LC_{50} of the 4th instars of *Anopheles stephensi* and *Culex quinquefasciatus* larvae. It was also reported that nanoparticles synthesized using *Solanum nigrum* berry extracts against the larvae of *Anopheles stephensi* and *Culex quinquefasciatus* were also toxic to some predators of mosquito (e.g. Toxorhynchites larvae and the *Diplonychus annulatum*) and larvae of *Chironomus circumdatus*[14]. Nanoparticles and other inert dust were suggested to serve as alternative strategy to the current broad-spectrum insecticides used in the management of pest populations. This is recommended since most pests are developing resistant to the chemical-based conventional pesticides[15].

It was suggested that reliable data on the biological effects of nanoparticles and then the Physico-chemical behaviour of nanoparticles conditions provide a prospect for predicting the potential impacts of the nanoparticles in both environmental and biological systems[16]. Nanoparticles are basically synthesized in three ways; chemical, physical and green synthesis. Among these, green synthesis accords more advantages of cost-effectiveness and Eco-friendliness[17]. More so, the plant-mediated synthesis of nanoparticles has been proven to be a cheap, single step, requires less pressure, energy and temperature and uses less toxic chemicals in comparison to physical and chemical methods[18]. Consequently, there has been a growing number of plant-based green syntheses of metal nanoparticles in recent times and their wide applications in different spheres in industry, agriculture and biology[19]. Several reports indicated the toxicity of ZnO nanoparticles against microbes[20], fungi and mosquitoes[21]. The toxic effect of SiO_2 nanoparticles on insects, microbes and molluscs is also well documented[22-23]. However, there are limited toxicity reports on composite containing ZnONPs and SiO_2NPs against mosquito larvae. Gum Arabic is a hydrocolloid polysaccharide extracted from Acacia senegal var. the Senegal trees. Gum Arabic

are non-toxic and are used as, stabilizing agents, film formers, flocculants, thickeners, suspending agents, emulsifiers and surfactants[24-25]. Recently, the green sol-gel method with the aid of Gum Arabic has been reported for the synthesis of CuO@SiO_2[26] and NiO[27]. Here, we have reported the novel synthesis and the characterization of ZnO@SiO_2 nanocomposite using Gum Arabic. The toxicity of the nanoparticles on the larvae of the Anopheles gambiae complex was also revealed.

EXPERIMENTAL

MATERIALS AND METHOD

Chemicals and apparatus/instrument

All the reagents used in this study are analytical grade and DBH products. All the glassware and apparatus used in this study are pyrex products. For this research the following apparatus and chemicals were used: $Zn(NO_3)_2.6H_2O$, Silica gel, distilled water, Gum Arabic, mortar and the pestle, conical flasks, beakers, test tubes, Whatman filter paper, watch glass, measuring cylinder, oven, funnels, hot plate, petri dish, weighing balance, cotton wool, masking tape, spatula, glass rod stirrer, aluminium foil paper, syringes, Furnace, Ultraviolet-Visible spectrophotometer (model 6705), micropipette, FT-IR (PerkinElmer Spectrum Version 10.0309) and SEM/EDX(model PhenomWorld).

Collection of Gum Arabic Extrudes

A fresh *Acacia senegalensis* extrude was obtained from Billiri, a Local Government Area in Gombe state. The extrude was ground using mortar and pestle until it becomes powder. It was kept under room temperature [as reported by[26]] in the laboratory of the Department of Chemistry, Gombe State University.

Synthesis of ZnO@SiO_2 nanocomposite

The synthesis of the nanocomposite followed the prescription of[28]. A beaker containing 40 mL of 1 g of Gum Arabic was stirred for 10 min at the temperature of 90°C on a hotplate for complete dissolution. Following this, 2 g of Zinc nitrate and 2 g of the Silica gel were then added and stirred for 120 min and the same temperature was maintained. By the addition of copper nitrate and the silica, the solution was changed colour to blue-green. Subsequently, the solution becomes viscous. Cloudy formation at the bottom of the beaker indicates that resin is formed. Resin obtained was then transferred into a crucible and covered with paper foil and then placed in the laboratory furnace at 450°C for 2 h to get ZnO@SiO_2 Nanocomposite powder. The SiO_2 was also calcined at 450°C for 2 hours.

Characterization of ZnO@SiO_2 Nanocomposite, SiO_2 and Gum Arabic

The following techniques were used for the characterization: Fourier-Transform Infrared Spectrophotometer (FTIR), The Scanning Electron Microscopy (SEM), UV-Visible spectrophotometer, The Dynamic Light Scattering (DLS), and X-Ray Fluorescence (XRF).

Collection of *Anopheles gambiae* complex

The laboratory-reared larvae of *Anopheles gambiae* complex were obtained from the Gombe State Roll Back Malaria (Malaria Control Booster Insectary, Gombe, Nigeria) identified using[29]. The larvae were kept in and maintained at 25 ± 2°C and were stored in a dechlorinated water. A mixture of low-fat biscuit and yeast powder in the ratio of 3:1 was used to for feeding the larvae as per[30].

Toxicity test of ZnO@SiO_2 against *Anopheles gambiae* complex

To prepare the stock solution, 0.1 g of the ZnO@SiO_2 nanocomposite was measured and then diluted in distilled water using a 1000 mL volumetric flask and was shaken to obtain a 100 mg/L concentration. Then the toxicity of ZnO@SiO_2 against the larvae of *Anopheles gambiae* complex was assessed following[30] as per the method of[31], with minor modifications. Twenty-five larvae were then placed in 200 mL of the de-chlorinated water in a glass beaker (500 mL), and then 1 mL of the desired concentration of ZnO@SiO_2 nanocomposite was then added (10 mg/L, 20 mg/L, and 25 mg/L). Each concentration was tested against each of the larval instar accordingly, with control in each case containing distilled water. The percentage mortality was computed as follows:

$$\text{Percentage mortality} = \frac{\text{No. of dead larvae}}{\text{No. of larvae introduced}} \times 100$$

Statistical analysis

The average mortalities were calculated from the replicate and represented in percentages. The LC_{50} and LC_{90} were also computed. SPSS (Statistical software package) version 25.0 was used.

RESULT AND DISCUSSION

Toxicity test

The toxicity studies were carried out for 24 h on the four larval instars of the Malaria vectors (1st, 2nd, 3rd, and 4th). The larval instars were tested at various concentrations of 10, 20 and 25 mg/L of the nanocomposite Table 1. The percentage toxicity of 1st instar larvae at concentrations of 10, 20 and 25 mg/L were 50±11.31371, 65±7.071068 and 65±7.071068% respectively. The 2nd instar showed 40±2.828427, 55±7.071068 and 60±7.071068% mortality respectively when tested with concentrations of 10, 20, and 25 mg/L of the nanocomposite. The percentage mortality for 10, 20 and 25 mg/L concentrations were 40±2.828427, 55±7.071068 and 60±7.071068% respectively while the 4th instar indicated 35±4.242641, 50±7.071068, 60±2.828427% mortality for the respective concentrations.[32] reported variable toxicity between different kinds of nano-silica in larval toxicity test of *An. stephensi, Ae. aegypti*, and *Cx. quinquefasciatus*. The results were shown to be in the range of 93-100% mortality in 48 hours. The variation of this finding may be attributed to the fact that the nanoparticles in their study used one metal whereas in the present study, two different metals were used, Moreso, the method of the synthesis vary. Notably, the juvenile instars proved to be more susceptible to the nanocomposite just as reported by;[14,32]. The LC_{50} for the 1st, 2nd, 3rd and 4th instars were found to be 9.11, 15.85, 15.85 and 18.288 mg/L respectively whilst the LC_{90} for the 1st, 2nd, 3rd and 4th instars were found to be 157.254, 157.254, 157.254 and 126.132mg/L respectively.

Ultraviolet-Visible analysis

The absorption spectrum of the synthesized $ZnO@SiO_2$ nanocomposite at different wavelengths ranging between 260 and 380nm disclose the maximum absorption wavelength at 280nm, (Fig. 1). The maximum absorption wavelength of 300nm was reported for $CaO@SiO_2$ nanocomposite by[33]. The optical property reveals that they fall within the same range as the present study.

Table 1: Toxicity status of $ZnO@SiO_2$ nanocomposite against first to fourth instars larvae of Anopheles gambiae complex

Life cycle	Conc.(mg/L)	%Mortality and SD	%Control	Mortality LC_{50}	LC_{90}	χ^2	r
1st Instar	10	50±11.31371	0.00	9.11	157.254	0.084	0.945
	20	65±7.071068	0.00				
	25	65±7.071068	0.00				
2nd Instar	10	40±2.828427	0.00	15.85	157.254	0.00	0.999
	20	55±7.071068	0.00				
	25	60±7.071068	0.00				
3rd Instar	10	40±2.828427	0.00	15.85	157.254	0.00	0.999
	20	55±7.071068	0.00				
	25	60±7.071068	0.00				
4th Instar	10	35±4.242641	0.00	18.288	126.132	0.0920.997	
	20	50±7.071068	0.00				
	25	60±2.828427	0.00				

LC_{50}=Lethal concentration that kills upto 50% of the larvae exposed, LC_{90}= Lethal concentration that kills upto 90% of the larvae exposed, χ^2=chi square value, r=correlation coefficient; SD= Standard deviation

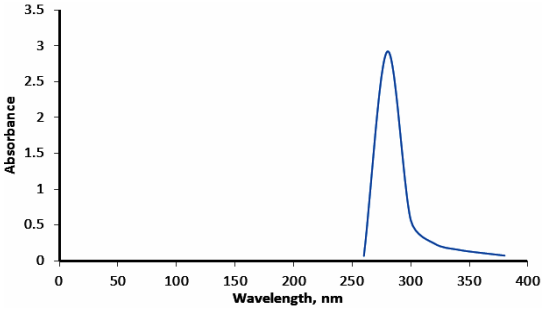

Fig. 1. The UV-Visible spectrum for $ZnO@SiO_2$ nanocomposite

FT-IR Analysis

The FT-IR spectrum of Gum Arabic, SiO_2 and $ZnO@SiO_2$ nanocomposite is shown in Fig. 2, 3 and 4 respectively. The prominent peaks for Gum Arabic are 3242.8, 2933.4, 1606.5, 1416.4 and 1200-900 cm^{-1} which represents; O-H stretching of the glucosidic ring, the C-H stretching, the COO-symmetric stretching, COO-asymmetric stretching, and fingerprint of carbohydrate respectively. For SiO_2, the band at the 1067.44 cm^{-1} conform to the asymmetric stretching vibration of Si-O-Si bond. While peaks at 972.8 and 797.7 cm^{-1} correspond to Si-OH

bond as reported by several findings[34-37]. The peak at 3753.4-3403.1 cm^{-1} denotes H-O-H stretching mode (for the silanol group and the adsorbed water)[34-38]. For ZnO@SiO_2 nanocomposite, almost peaks in the spectrum of SiO_2 and Gum Arabic remains except the new peak at 670.9 cm^{-1} which correspond to Zn-O and Si-O bond[34-38]. Thus, the formation of ZnO@SiO_2 nanocomposite was confirmed.

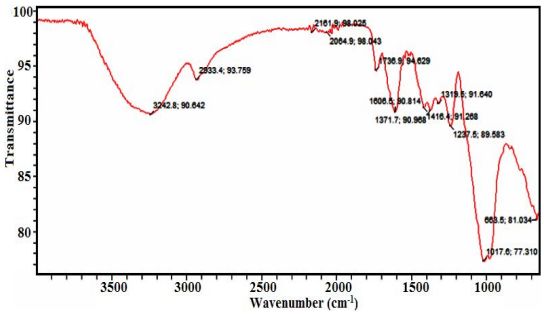

Fig. 2. FT-IR spectrum of Gum Arabic

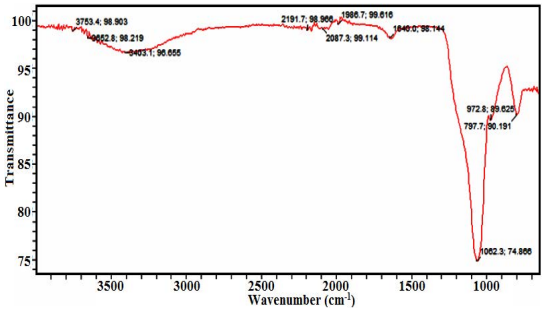

Fig. 3. The FT-IR spectrum of SiO_2

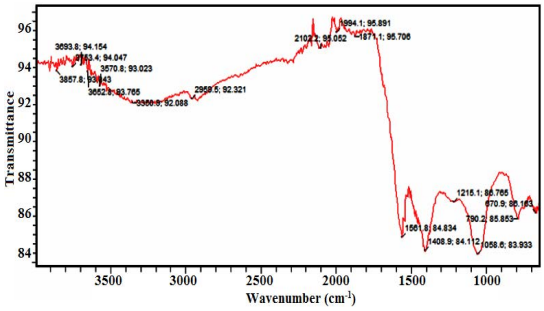

Fig. 4. The FT-IR spectrum of ZnO@SiO_2 Nanocomposite

Scanning Electron Microscopy and Dynamic Light Scattering Analysis

Figure 5A and Figure 5B shows the SEM image of ZnO@SiO_2 nanocomposite and SiO_2 respectively. The image from SEM showed large irregular particles and the coating of the silica on the ZnO is seen when compared to the SEM image of silica. Also, the SEM image of SiO_2 showed irregular large particles, Figure 5B.

The measurement of the particle sizes were done using Zetasizer (Malvern Instrument Ltd, Worcestershire, UK) at 25°C based on the laser Doppler velocimetry and the DLS techniques. The DLS gives the polydispersity index (PDI), which suggests the width of the particle size distribution, is calculated thus: the square root of peak (standard deviation/average size). PDI<0.1 suggests the sample is monodisperse while PDI>0.1 indicate the sample is polydispersed. If When PDI is lies between 0.1-0.4, the sample would then have a moderate polydispersed distribution of particle size. The PDI>0.4 shows that the sample would then have a wide particle size distribution. In this research, size distribution by intensity was found to be 88.1nm (76.3%), 410.8nm (20.9%) and 5387nm (2.7%) for peak 1, peak 2 and peak 3 respectively, Fig. 6. The average size distribution was found to be 147.6nm. The polydispersity index (PDI) for peak 1, peak 2 and peak 3 were found to be 0.5, 0.96 and 1.5 respectively. The polydispersity index (PDI) shows that the sample is polydispersed with a wide distribution of particle size. These findings correlate well with the SEM result.

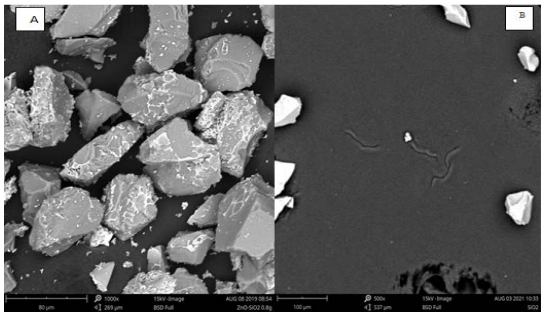

Fig. 5. A; SEM image of ZnO@SiO_2 nanocomposite, B; SEM image of SiO_2

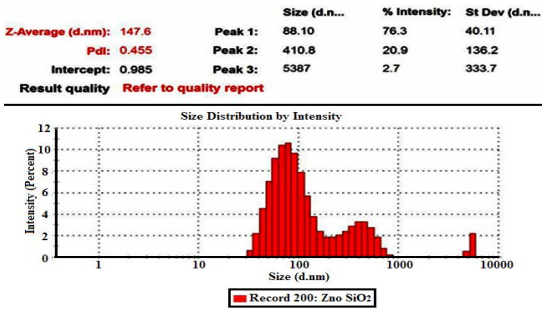

Fig. 6. DLS result for ZnO@SiO_2 nanocomposite

X-Ray Fluorescence (XRF) Analysis

The elemental composition of Gum Arabic, SiO_2, and ZnO/SiO_2 nanocomposite are presented in

Table 2. Various elements with a different percentage such as Si, Zn, Al, O2, S, Cl, Ca, Ti, K, V, Cr, Fe, Co, Mn, Ni, Cu, Nb, Zr, Mo, W and Ag were found in both Gum Arabic and SiO_2 sample. Gum Arabic has been earlier reported to contain Al, Ca, Ba, Fe, Mg, K, Mn, P, Sr and S[39]. The elemental composition of the nanocomposite almost followed the same trend with the precursors (Gum Arabic and SiO_2). This indicates that other impurities in the nanocomposite are from the precursors (Gum Arabic and SiO_2). The components composition of SiO_2 and ZnO/SiO_2 nanocomposite are presented in Table 3. For SiO_2 components, SiO_2 contains 97.361% whereas other components made up 2.639%. For the ZnO/SiO_2 nanocomposite, ZnO is 42.068% and SiO_2 is 44.794%. Overall, the nanocomposite is made up of 86.862% while other components are 13.138%.

Mechanism of formation of ZnO/SiO_2 NPs using green sol-gel method

The chains of Arabic Gum which are larger are polysaccharides that are natural, forming complexes with Zn^{2+} ions that interact with functional groups like –COOH, –OH and $–NH_2$ during gel formation[40]. The gel complexes formed lead to nucleation and growth of ZnONPs. The simple explanation for the mechanism of the formation and the growth of ZnO in the presence of the Arabic Gum and Silica is illustrated thus:

Table 2: Elemental composition of Gum Arabic, SiO_2, and ZnO/SiO_2

S/N	Elements	Gum Arabic(wt.%)	SiO_2(wt.%)	ZnO/SiO_2(wt.%)
1	O	29.508	52.641	35.661
2	Si	3.090	45.511	20.939
3	Zn	0.174	0.002	33.796
4	Mg	6.831	-	-
5	Al	5.236	0.766	1.678
6	S	0.219	-	0.062
7	Cl	4.288	0.783	0.906
8	K	16.450	-	1.188
9	Ca	27.077	0.142	1.297
10	Ti	0.284	0.013	0.017
11	V	0.060	0.004	0.010
12	Cr	0.068	0.012	0.015
13	Mn	4.172	0.016	0.106
14	Fe	1.034	0.032	0.050
15	Co	0.113	-	0.001
16	Ni	0.013	0.003	-
17	Cu	0.828	0.028	0.019
18	Zr	0.011	0.004	0.250
19	Nb	0.172	0.003	2.955
20	Mo	0.056	0.001	-
21	Ag	0.226	0.005	-
22	Ba	-	0.021	0.052
23	Ta	-	0.007	0.324
24	W	0.049	0.004	0.674

Table 3: Compounds composition of SiO_2, and ZnO/SiO_2

S/N	Components	SiO_2(wt.%)	ZnO/SiO_2(wt.%)
1	SiO_2	97.361	44.794
2	ZnO	0.002	42.068
3	Al_2O_3	1.448	3.171
4	K_2O	-	1.431
5	CaO	0.198	1.815
6	Nb_2O_3	0.004	3.719
7	Cr_2O_3	0.018	0.022
8	V_2O_5	0.007	0.019
9	MnO	0.021	0.136
10	Fe_2O_3	0.046	0.072
12	CuO	0.035	0.023
13	MoO_3	0.002	-
14	WO_3	0.005	0.850
15	SO_3	-	0.154
16	BaO	0.024	0.058
17	Ta_2O_5	0.008	0.395
18	TiO_2	0.022	0.029
19	Cl	0.783	0.906
20	ZrO_2	0.005	0.337
21	NiO	0.004	-
22	Ag_2O	0.005	-

$$Zn(NO_3)_2 \xrightarrow{Aqueous\ solution} Zn^{2+} + NO_3^- \quad (1)$$

$$Zn^{2+} + GA \xrightarrow{\text{Aqueous solution}} [Zn(AG)]^{2+} \quad (2)$$

$$[Zn(GA)]^{2+} + SiO_2 \xrightarrow{\text{Heat}} [Zn(GA)/SiO_2]^{2+} \xrightarrow{\text{Calcination at 400 o}_C} ZnO/SiO_2 \quad (3)$$

CONCLUSION

This work reported the novel synthesis of $ZnO@SiO_2$ nanocomposites using Gum Arabic. SEM, XRF, UV-spectrophotometric analysis, DLS and FT-IR were employed for characterization of the nanocomposite. The toxicity of the nanocomposite against the larval instars of Malaria vectors was tested and the LC_{50} and LC_{90} were computed. The $ZnO@SiO_2$ nanocomposites could be a potential larvicide for the control of malaria vectors.

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Conflict of Interest

There was no conflict of interest between the authors.

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