RESEARCH PAPER

The Effect of Copper Nano-capsules on the Control of Two Spotted Spider Mite (*Tetranychusurticae*)

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ABSTRACT

Common bean (*Phaseolus vulgaris L.*) is one of the most important and widely cultivated Legume in the world. The two-spotted spider mite (TTSM), is one of the most important agricultural pests. This research provided some evidence of the applicability of CuO nano particles and nano capsule for controlling TTSM. To evaluate the effect of copper nano-capsules on the populations of TSSM from red beans, Akhtar variety was used. This bean is a susceptible variety. To evaluate the effect of copper nano-capsules on the populations of TSSM from red beans, Akhtar variety was used. This bean is a susceptible variety. Five experiments were carried out, including spraying with copper nanocapsule (Cu_2O) at 5 levels of concentration (1) without nano-capsule copper (2) nanocapsules 1 g / l (3) nano capsules 2.5 g / l (4) nano capsules 4 Grams per liter 5. Nanocapsule was 5.5 grams per liter. The time of spraying was the simultaneous appearance of the first flower buds in each plant. According to the results, the use of copper nanocapsules has a significant effect on decreasing population of the pest. This can be different by change the concentration of nanocapsules. Copper oxide nanoparticles were first synthesized via a fast precipitation method. The prepared products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transform infrared (FT-IR) spectroscopy.

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INTRODUCTION

Common bean (*Phaseolus vulgaris L.*) is one of the most important and widely cultivated Legume in the world [1]. Beans are the most important nutrient source, calories, protein, fiber, minerals and vitamins for millions of people worldwide for developed and developing countries.

In the America, the main producing countries are Brazil (2.5 million tonnes), followed by the United States (1.3 million tonnes) and Mexico (0.98 million tonnes). In Asia, China, Iran, Japan and Turkey are the most important bean production areas. In Africa, Brady, Ethiopia and Malawi, and in Europe, the Albanian countries, Belarus, Bulgaria, Croatia and Greece are among the most important countries in the production of beans. In Iran, under cultivation, the area under cultivation was reported to be about 105000 hectares and 230,000 tons in the 2012cropping (anonymous, 2014). The most important bean producing provinces in Iran are Fars, Lorestan, Markazi, Chaharmahal and Bakhtiari, Zanjan. Two-spotted

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spider mite (TSSM), *Tetranychusurticae*Koch(Acari: Tetranychidae)mite is the most important pest of beans in Iran [2,3]. TSSM (Fig. 1), is one of the most important agricultural pests that annually make a lot of damage and is the most important specie from 1200 species of Tetranychidae family [4,5]. It can proliferate and propagate very quickly and also this species can be adapted to different environmental conditions. Furthermore they had a broad host range [6]. Until now this pest showed resistance to 80 types of pesticides and its economical restriction because of increase in its resistance to pesticides and its growth rate is growing daily [7]. Nanotechnology is a rapidly growing field with its application in science and technology for the purpose of manufacturing new materials at the nano scale level [8-10]. In modern agriculture, extensive use of pesticides to preserve crops from pests has raised serious public concern because of the high neurotoxicity of pesticides putting our healthiness, environment safety and food safety in danger [11]. Nanotechnology has been used in many agricultural fields such as production, processing, storing, packaging and transport of agricultural products [12,15]. Nano encapsulation of therapeutic agents increases their efficacy, specificity and targeting ability [16]. Encapsulation is the only possibility for stability (photosensitivity) and increasing the longevity (slow release) of compounds [17-19]. Encapsulation refers to a process in which one substance becomes entrapped within another substance, leading to the production of particles with diameters ranging from a few nanometers to several millimeters. The reservoir type has a shell surrounding the active agent and is also known as capsule, single-core, mono-core or core-shell. If pressure is applied to reservoir encapsulates, they can break, thereby releasing their contents [20,21].

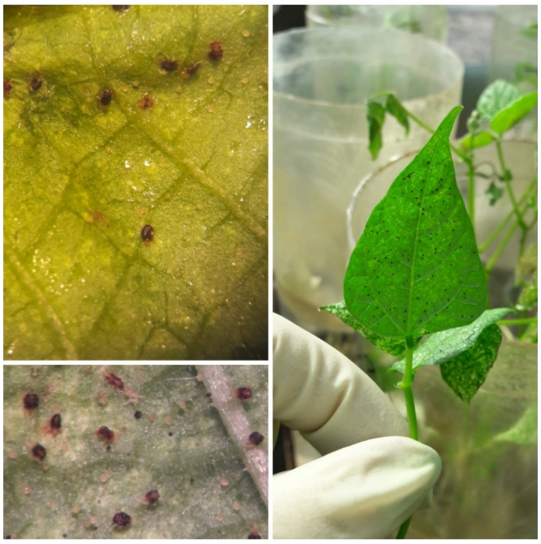

Fig. 1. Two-spotted spider mite

Copper, as copper sulfate and other chelated or complexed forms are effective pesticides for use in agriculture and direct application to aquatic systems with no toxicity concerns to humans when used according to label directions [22]. From control of fungi in citrus, potentially toxic algae (cyanobacteria) in drinking water to nuisanceaquatic weeds in flood and irrigation canals, copper-based pesticides are among the oldest and most widely used pest management solutions [23,24].

Unlike for the reservoir type, the active agents in the matrix type of encapsulate are normally present at the surface as well, unless encapsulate has an extra coating. For simplification, only spherically shaped encapsulates are shown in (Fig. 2), but the shapes can also be cylindrical, oval or irregular. Originally, various encapsulation methods were developed for the needs of medicine, where the ability to gradually release the encapsulated active substances of medicines in particular was discovered; a significant increase

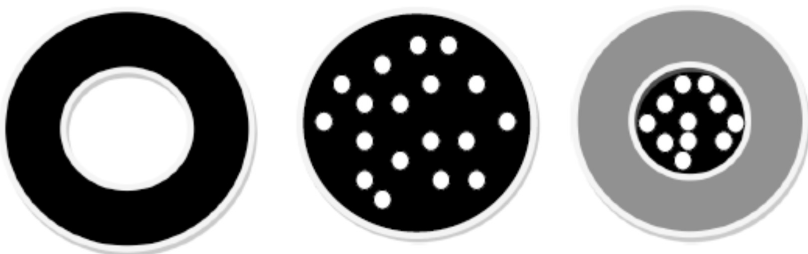

Fig. 2. Reservoir type (left), matrix type (middle), and coated matrix type (right) encapsulates.

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in the duration of their effects or their targeted release was thereby obtained. Besides in medicine, encapsulation has found its application in the food industry as a method suitable for enhancing some quality parameters of foods, e.g. for maintaining the stable taste and aroma of the foods [17, 25].

Nevertheless, encapsulation methods have been successfully used in the past in the development of insecticides, including larvicides based on microorganisms (e.g. *Bacillus thuringiensis*) [16], plant substances (e.g. Azadirachtin) [26] andsynthetic insecticidal substances (e.g. Temephos, Imidacloprid) [27].

Until now, limited research provided some evidence of the applicability of CuO nanoparticles and nanocapsule for controlling plant pest.

The first two are combined to create the third one. Although only spherically shaped encapsulates are shown, other forms are possible as well. The active material is indicated here in white, and the carrier material in gray. The active material in matrix encapsulates can be either in small-droplet form or dispersed throughout the particle at the molecular level.

MATERIALS AND METHODS

Synthesis of CuO nanoparticles

In this method, 24.9 g of Copper(II) sulfate was dissolved in 100 ml water. In order to adjust the pH of the solution to pH 10, NaOH (2 M) was added drop-wise while stirring. A blue crystalline precipitate of copper oxide was obtained, which is washed repeatedly with water, filtered and dried in an oven at 90°C to obtain the CuO nanoparticles dark powder (Fig. 3).

Synthesis of CuO nano capsules

4 g of sodium alginate dissolved in 100 ml distilled water at 50 °C and the resulting mixture was stirred for 10 minutes using a magnetic stirrer.1 g chitosan added in to acetic acid 5% and for 1 hour stirred at 90°C. After preparation this material 50 ml sodium alginate solution , 20 ml chitosan solution and 2 gr of CuO nano particles added and mixed and set pH. A blue crystalline precipitate of copper oxide capsule was obtained, which is washed repeatedly with water, filtered and dried in an oven at 90°C (Fig. 4).

Greenhouse test

To evaluate the effect of copper nano-capsules on the populations of TSSM from red beans, Akhtar variety was used. This bean is a susceptible variety. The pots were made of plastic with a diameter of 15 cm and a height of 20 cm and with an approximate capacity of 2 kg of soil. The soil was in a pot containing a 1: 1 ratio of compust and lomesoils. The temperature range in the

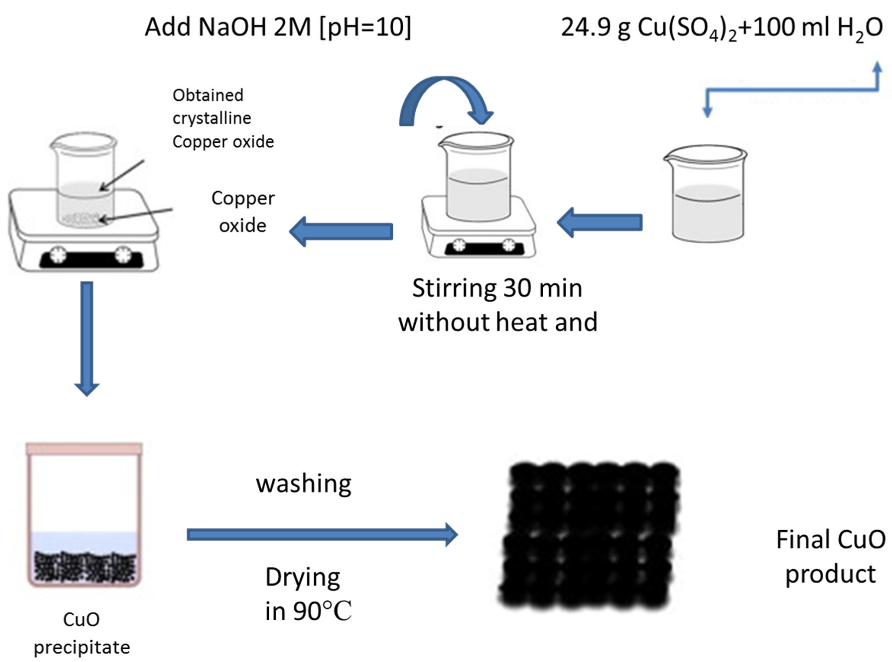

Fig. 3. Schematic preparation of CuO nanoparticles

greenhouse was 25-15 °C.The light period was considered in greenhouse conditions according to sunrise and sunset. In order to match the initial density of the mite, at the end of the vegetative growth stage (V4) and before the first flower bud in the plant, each plant was infected with 50 mature adult mothers by means of a zero number brush.

Experimental treatments

Five experiments were carried out, including spraying with copper nanocapsule (Cu_2O) at 5 levels of concentration (1) without nano-capsule copper (2) nanocapsules 1 g / l (3)nano capsules 2.5 g / l (4)nano capsules 4 Grams per liter 5. Nanocapsule was 5.5 grams per liter. The time of spraying was the simultaneous appearance of the first flower buds in each plant. For each treatment, three pot and each pot were considered as a repeat. In each pot, 3 plants were planted and evaluated. .

Sampling

Each plant in a three-leaf pot was randomly selected and from each leaf area of 2×2 cm of contaminated points were counted mite. The average number of ticks in three leaves per plant and three plants per pot was considered as the population of each replicate.Sampling was carried out at 0 (before spraying), 24, 48, 72, 96 and 120 hours after spraying.

Growth mite colony

Primary population was prepared from the greenhouse of the plant protectionsectionof the Agricultural Research and Education Center of the Agricultural and Natural Resources of Markazi Province. The mite colony in the greenhouse was grown on Akhtar variety at a temperature of 26-22 ° C, relative humidity of 45 ± 10%, and a light period of 16 hours of light and eight hours of darkness.

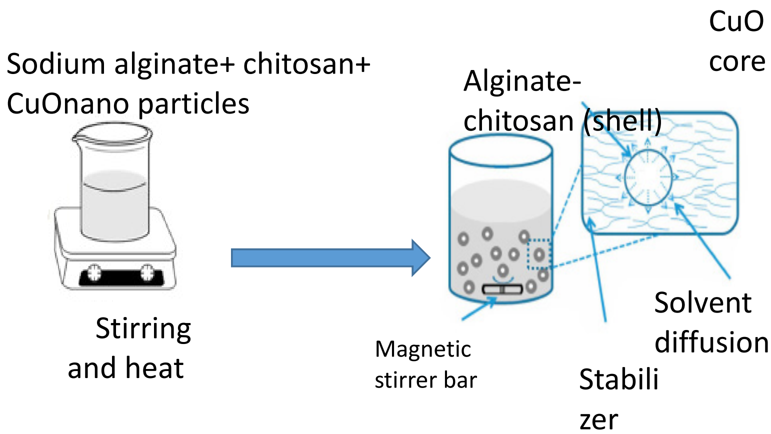

Fig. 4. Schematic synthesis of CuO nanocapsules

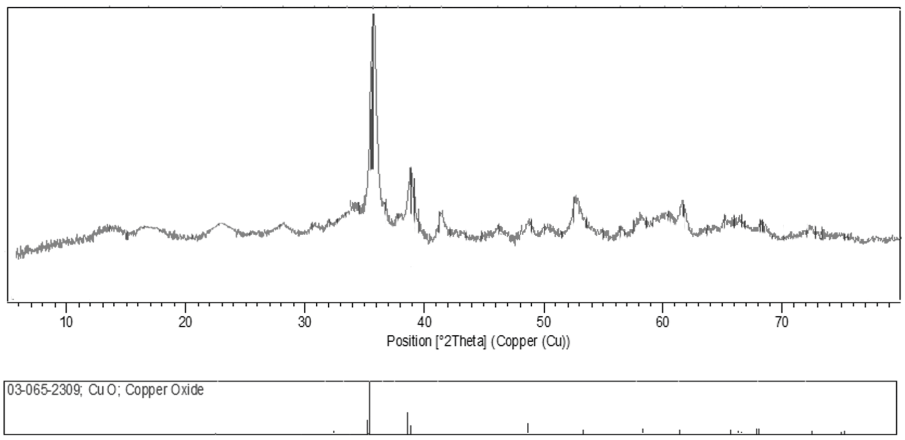

Fig. 5. XRD pattern of the copper oxide nanoparticles

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Matching the age mites

In order to simulate the mites, the bean leaf discs were first placed on soaked cotton peals in a nine-centimeter petrefuge, then 30 mature adult mites with brush on each of the discs The leaf of bean plant was transferred and after 24 hours the mite was removed.Petrefuges containing leaf and egg in a growth chamber with a temperature of 24 ± 2 ° C, relative humidity of 60 ± 10%, a light period of 16 hours and darkness for eight hours

RESULTS AND DISCUSSION

Fig. 5. illustrates XRD pattern of CuO product. Pure cubic phase of ferrite (JCPDS No.65-2309, Space group: Fd-3m) can be observed in this pattern. The crystalline sizes are calculated from Scherrer equation, $D_c=K\lambda/\beta Cos\theta$, where β is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the shape factor, which takes a value of about 0.89, and λ is the X-ray wavelength (CuK_α radiation, equals to 0.154 nm). The value of about 15nm was found for crystalline sizes of CuO nanoparticles.

Figs. 6 illustrate scanning electron microscopy images of as-synthesized CuO nanoparticles. The images indicate that the nanoparticles with average diameter size about 50 nm were prepared.

SEM images of the alginate/chitosan/CuO nano-capsules are shown in Fig. 7. According to SEM images nanoparticles less than 50 nm were prepared.

Transmission electron microscopy image of the CuO nanoparticles is illustrated in Fig. 8. The images confirm that the nanoparticles with mediocre diameter size about 50 nm were synthesized.

Fig. 9 shows the FT-IR spectrum of the as-prepared magnetite. The absorption bands at 435 and 490 and 650 cm^{-1} are assigned to the Cu-O (metal-oxygen bonds) stretching mode. The spectrum exhibits broad absorption a peak at 3390 and 3556 cm^{-1}, corresponding to the stretching mode of O-H group of adsorbed hydroxyl group and a weak band near 1381 cm^{-1} which is assigned to H–O–H bending vibration mode due to the adsorption of moisture on the nanoparticles surface.

Figs. 10 show the FT-IR spectra of the as-prepared alginate/chitosan/CuO nano-capsules. It can be observed that the strong absorption bands at 418 and 484cm^{-1} which are ascribed to absorptions of the metal-oxygen and a broad absorption peak at 3390, 3563 and 3583 cm^{-1} which are assigned to adsorbed O-H groups on the surface of nanoparticles. 1088, 1126 cm^{-1} which are assigned to adsorbed C-O bonds. There are no other significant peaks related to precursors and other impurities.

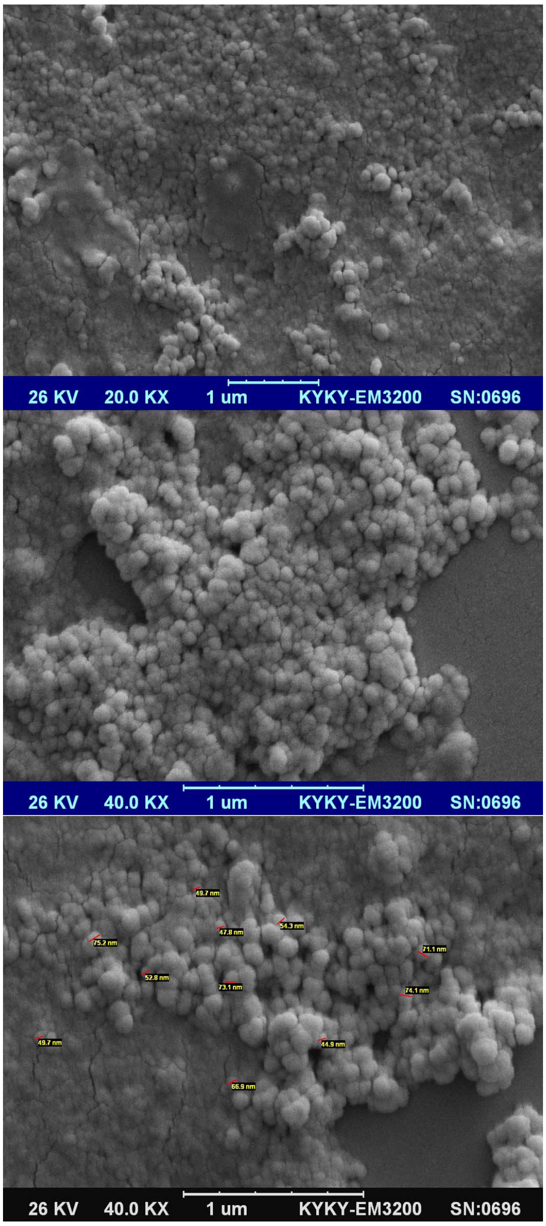

Fig. 6. SEM images of the copper oxide nanoparticles

The results of the experiment were evaluated based on the density of mite at different times after spraying and then analysis of variance and statistical comparison of the means.

Analysis of variance

Table 1 shows the results of variance analysis of the evaluated traits. Based on the population

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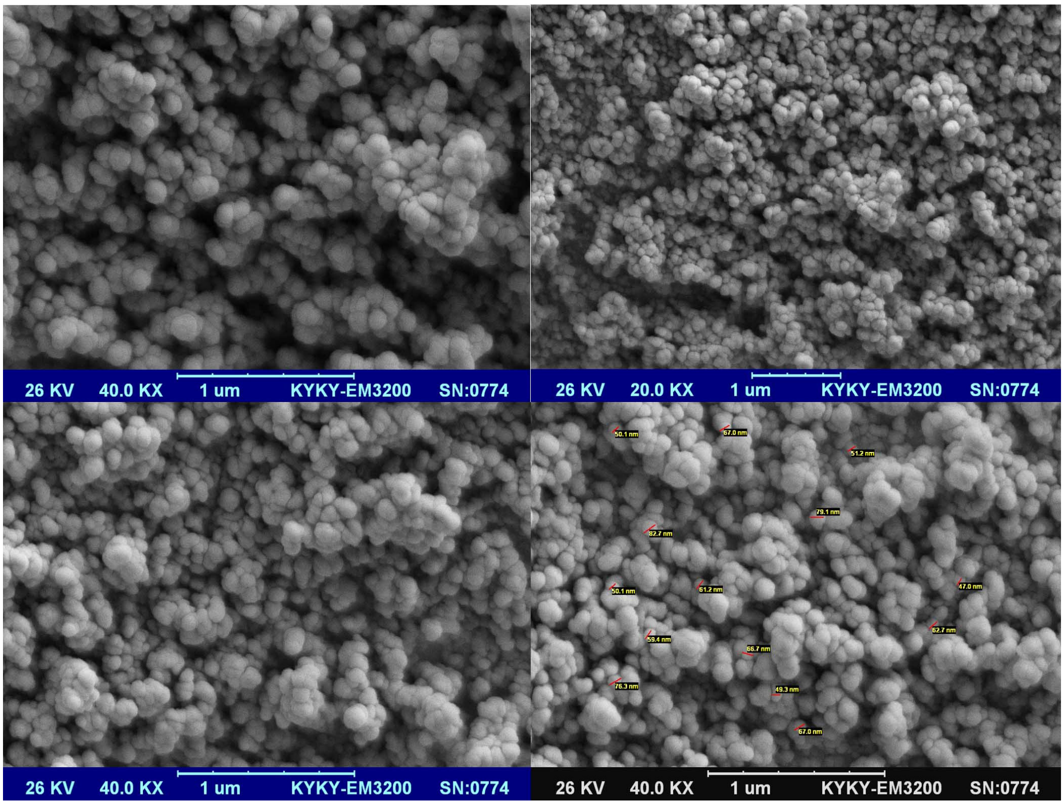

Fig. 7. SEM images of the alginate/chitosan/CuO nanocapsules

table, the effect of replication for all the period was not significantly different.

Pest populations were significantly different in terms of experimental treatments at the period except for control treatment. It thus becomes distinguished that the use of copper nano-capsule affects the population of mites.

Table 2 shows the comparison of the average number of mites at the period of evaluation based on copper nanocapsule treatments. No significant differences were observed in all of the treatments based on the population of the mite at the pre-spraying stage Twenty four hours after spraying, the highest density of mite was observed in control (without spraying). For other treatments, the lowest number of mite was observed in treatments 4 (4 g / l nanocapsules) and 5 (5.5 g / l nanocapsules). These two treatments did not significant difference. Treatments 3 (nano capsules 2.5 g / l) and 2 (nano capsules 1 g / l) were at 7.7 and 11.7, respectively.

The population of the mite after 72 hours showed that the highest number of mite was related to the control treatment (26.7) and the lowest treatment was 5 (5.5 g / l nano capsule) with 1 mites. Treatments 4 and 3 were also 1.3 and 4.3 at the next stages, which did not show any significant difference. Treatments 2 with 11 mites showed a significant difference with control.

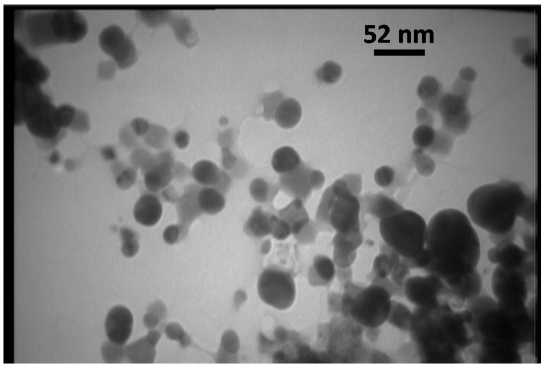

Fig. 8. TEM image of the CuO nanoparticles

Mite population after 96 hours showed that the highest number of mite was related to the control treatment (46) and the lowest treatment was 5 (5.5 grams liters nano capsule) with 1mite. Treatments 4 and 3 were 2.3 and 5.3 at the next stages, which did not show any significant difference. Treatment 2 showed a significant difference with 13.4 mites with control.

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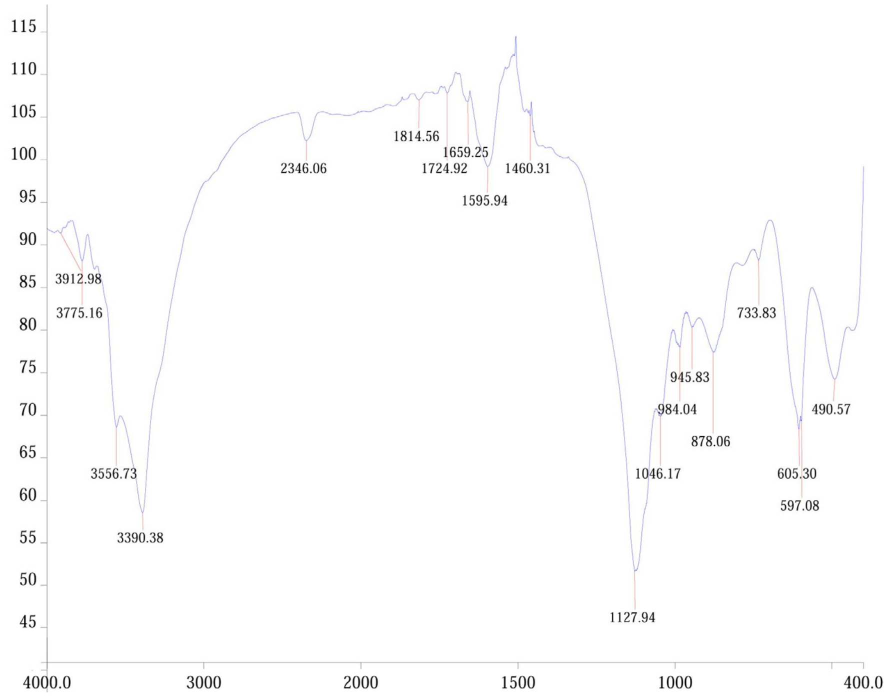

Fig. 9. FTIR spectrum of the CuO nanoparticles

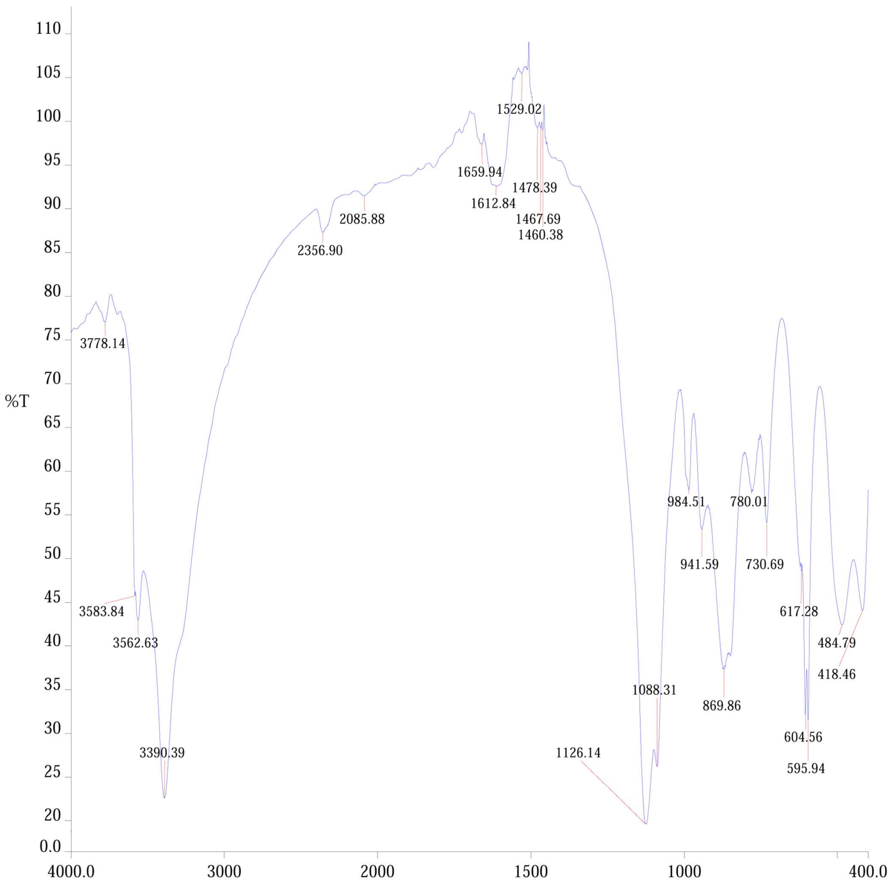

Fig. 10. FTIR spectrum of the CuO nanocapsules

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Table 1. Analysis of variance of the number of mite under CuO nanocapsules.

S.O.V	df	T0	T24	T72	T96	T120
Rep	2	649.9^{ns}	1.68^{ns}	1.5^{ns}	14.8^{ns}	1.56^{ns}
Treat	4	830^{ns}	84.2**	1.6**	1060**	1933**
Error	8	647	1.5	3.2	12.7	46
CV(%)		25	12	18	35	21

** Significantat 1percent and ns shows non-significant.

Table 2. Comparison of average number of mite under CuO nanocapsules

Treatment	T0	T24	T72	T96	T120
1	14.3a	16.7a	26.7a	46a	49a
2	14a	11.7b	11b	13.4b	18.7b
3	15.3a	7.7c	4.3c	5.3bc	8.7bc
4	17.3a	1.7d	1.3c	2.3c	4c
5	28.3a	2d	1c	1c	1c

Dissimilar letters in each column indicate a significant difference

After 120 hours, the mite population showed that the highest number of mite was related to the control treatment (49) and the lowest treatment was 5 (5.5 g / l nano capsule) with 1 mite. Treatments 4 and 3 were 4 and 8.7 at the next stages, which showed no significant difference together. Treatment 2 showed a significant difference with 18.7 mite with control.

According to the results, the use of copper nanocapsules has a significant effect on decreasing population of the pest. This can be different by change the concentration of nanocapsules.

CONCLUSION

The two-spotted spider mite (TTSM), is one of the most important bean pests. A new approach is imperative to be adapted to strengthen plant innate immunity to cope with mutating plant pathogens, reduce chemical use and alongside sustained plant growth. Cu-chitosan NPs have been proven as a promising plant protection and growth promotry agent in our past and recent studies. this research provided some evidence of the applicability of CuO nano capsule for controlling TTSM from red beans. The use of CuO nano capsule has a significant effect on decreasing population of the pest. This can be different by change the concentration of nanocapsules.

CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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