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ORIGINAL RESEARCH ARTICLE

Control of *Tuta absoluta* (Lepidoptera: Gelechiidae) by the new trend of photosensitizer and nanocomposites and their effects on productivity and storability of tomato

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Abstract

Tomato leaf miner, *Tuta absoluta* (Lepidoptera: Gelechiidae), is a serious insect pest on tomato plants worldwide. Its larvae can cause up to 100% damage if not controlled. Furthermore, using of chemical pesticides is causing serious threat to environment and human health. The effect of two photosensitizers; magnesium and copper chlorophyllin (Mg-Chl and Cu-Chl) alone and two nanomaterials (GO and Ag) over their photosensitizers (Mg-Chl /Go, Mg-Chl /Ag, Cu-Chl/ Go, and Cu-Chl /Ag) on *T. absoluta* in tomato field at two seasons were studied. The tested concentrations of photosensitizer and nanocomposites were 10^{-3} (100 ml/L), 10^{-4} (10 ml/L) and 10^{-5} (1 ml/L). The effect of photosensitizer and nanocomposites on reduction % of *Tuta absoluta*, tomato plants growth, yield, and quality were studied. The number of tunnels was recorded, the reduction percentages for each treatment were calculated compared to control before and after 1, 5, and 7 days of spraying. Results showed that the reduction in the number of tunnels after one day of spraying with photosensitizers (Mg-Chl and Cu-Chl) at the highest concentration (10^{-3}) was 72.79 and 70.52% in the 1st season and 77.95 and 60.08% in the 2nd season. The reduction percentage increased gradually with the number of days after spraying and reached 100% after seven days in both seasons. The reduction percentage reached 100% in plants treated with all nanomaterial concentrations after five days of spraying in the 1st season and after one day of spraying in the second season. Photosensitizer and nanocomposites treatments at all concentrations positively affected all vegetative growth parameters of tomato plants compared with insecticides and control. The highest concentration of all treatments increased yield and enhanced the storability of tomato fruits. The yield after treatment with Mg-Chl was 28.67 tons/fed, which was more than the yield of those treated with Cu-Chl (24.8 tons/fed). Loading nano silver (Ag) over Mg-Chl achieved tomato yield (35.18 tons/fed) compared with the loading of nano graphene oxide (Go) (32.95 tons/fed). Therefore, treatment with these materials can be recommended in the IPM program to control *T. absoluta* in tomato fields.

Keywords Leafminer · Photosensitizers · Nanocomposites · Control · Tomato · Quality

Introduction

Tomato (*Solanum lycopersicum*) is globally the most important vegetable crop after potatoes. The tomato cultivation area in the world is about 5 million hectares, producing 186.821 million tons in 2020 (FAO 2022). Egypt is the fifth country worldwide in the production of tomatoes, producing about 8 million tons annually (Olaniyi et al. 2010). Tomato plants are attacked by many insect pests, especially the tomato leaf miner *Tuta absoluta* (Lepidoptera: Gelechiidae), which is considered the major pest in tomatoes. More than 87% of global tomato production is threatened by this pest (Desneux et al. 2011). This insect is an oligophagous pest that feeds on tomatoes and other plants related to the

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family Solanaceae. Females lay the eggs on the underside of leaves or stems. After hatching eggs, neonate larvae penetrate leaves and feed on mesophyll tissues of leaves at any stage of plant growth and create irregular mines that become necrotic over time, reducing the photosynthetic potential of infested leaves. Also, their larvae attack the fruits and excavate tunnels, reducing the quality of tomatoes and their market value (Biondi et al. 2018)., It has been reported that this pest can cause reductions in crop yield of up to 90%. (Cuthbertson et al 2013). Tomato crop loss can reach 100% unless management measures are taken. A significant reason for the spread of this insect is the popularity of tomatoes and their export to many countries without strict quarantine measures to monitor its presence in the producing countries and prevent its entry into the importing countries (Biondi et al. 2018).

The tomato borer, *Tuta absoluta* is a very challenging pest to control by chemicals due to its high reproduction rate and potential to develop resistance to insecticides. Many different chemical insecticides has been traditionally undertaken (including organophosphates, pyrethroids, thiocarbamates and acylurea growth regulators). However, these insecticides lead to insect resistance, as well as the side effects on beneficial organisms, human health problems, and environmental contamination. Pesticides are being applied at a higher rate than those recommended which is inviting serious risk. Most vegetables, especially tomatoes are grown by independent farmers who applied the insecticide to control of insect at a higher rate than those recommended and makes consumers at high risk of buying a significantly high amount of pesticide residues (Poudel et al. 2020). So, applying environmentally friendly tools instead of chemical applications is necessary for integrated pest management (Guedes et al. 2019). Nanotechnology has recently been used in the field of pesticides and pest management, and it has the potential to revolutionise contemporary agriculture. Among the various scientific advances, nanotechnology (NT) is seen as a rapidly developing area with the potential to transform agriculture and food systems. When used as a tool, in conjunction with other strategies, nanotechnology can attempt to address some of the most pressing sustainable development issues in the fields of water, health, energy, and the environment, agriculture, biodiversity, and ecosystem management (Karthick et al. 2018; Arvind and Karthick 2017).

In recent years, nanotechnology has become one of the most successive methods to control of some insect pests and decrease their damage. Because the nanoparticles have different physical, chemical, and biological properties associated with their atomic strength, this nanoparticles can be used against different insect pests (Jameel et al. 2023). Using photosensitizers and nanomaterials is considered a promising alternative to insecticides because of their smart delivery system. They are releasing pesticides in a timely and controlled manner which, increase life span, protect agrochemicals from breakdown and degradation and naturally control crops' insects, pathogens, and weeds (Ghormade et al. 2011; Kah et al. 2013).

The photosensitizer is a treatment involving the administration of a photoactive compound that selectively accumulates in the cell of the insect body and, following exposure to visible light, induces lethal photochemical reactions and death (Lukšienė et al. 2007). Nanoparticles represent a new generation of environmental remediation technologies that have provided a wide range of novel pesticide formulations. Toxicity mechanisms of nanoparticles may be reactive oxygen types, oxidative stress, membrane disruption, protein unfolding, and inflammation. (Saad et al. 2015; Jameel et al. 2020). However, few studies have discussed the effect of photosensitizers, and their combination with nanomaterials on insect pests, such as El-Tayeb et al. (2011) exposed the Hematoporphyrin IX photosensitizer on the flesh fly, *Parasarcophaga argyrostoma*. Also, Berni et al. (2009) tested Xanthene dyes as photoinsecticides against *Ceratitis capitata* larvae. Furthermore, Lukšienė et al. (2007) investigated hematoporphyrin dimethyl ether photosensitizer on *Liriomyza bryoniae* (Kaltenbach) (Diptera, Agromyzidae), and Merghany et al. (2019) controlling *Thrips tabaci* (Lindeman) using nanomaterials. In addition, applications of nanoparticles in agriculture may play an essential role in global food security by helping develop improved plant varieties with high productivity (Parisi et al. 2015). Also, some nanomaterials significantly increase plant growth, enhancing their ability to resist pest infestations (Siddiqui et al. 2015). Therefore, the aim of this study was to evaluate the efficiency of two photosensitizers (magnesium and copper chlorophyllin) and four nanocomposites (Mg-Chl/GO, Mg-Chl/Ag, Cu-Chl/GO, and Cu-Chl/Ag) against *T. absoluta* and their effects on plants growth, quality, and storability of tomato.

Materials and methods

Preparation of photosensitizers and nanocomposites

Both magnesium chlorophyllin (Mg-Chl) and copper chlorophyllin (Cu-Chl) were used as photosensitizers. *Stevia rebaudiana* leaves extract was used to form Cu-Chl, and fresh spinach leaves extract to create Mg-Chl using acetone solvent as described by Abbas et al. (2022). Two different types of nanomaterials (silver nanoparticles and graphene oxide nanosheets) were synthesized to be conjugated with natural photosensitizers (chlorophyllin derivatives) in order to achieve the targeted novel natural nanocomposite. Spherical silver nanoparticles were simply synthesized by the citrate reduction method. In brief, 50 mL of 10^{-4} M silver nitrate solution were heated to boiling point while stirring in a 100 mL beaker. Then, one ml of 1% (by weight) of trisodium citrate solution was quickly added to the silver solution. The color of the solution changed within several minutes to red or yellowish orange depending on the sizes of the nanoparticles. Graphene oxide compound was synthesized through the oxidation of graphite powder. The oxidation was performed using a modification of Hummer experimental procedure. After synthesis, the powder was fabricated into graphene oxide films through vacuum filtration and transfer to desired substrates. A mixture of concentrated H_2SO_4/H_3PO_4 (90:10 mL) was added to a mixture of graphite flakes (1.0 g) and $KMnO_4$ (6.0 g) producing an exothermic reaction. This mixture was then heated to 50 °C and stirred for 12 h. The mixture was then cooled overnight and poured onto ice (around 200 mL) with 30% H_2O_2 (1 mL). The resulting mixture was then centrifuged (4000 rpm for 1 h) and the supernatant decanted away. The remaining solid material was then washed with 100 mL of HCl followed by centrifugation (4000 rpm for 1 h) and the supernatant decanted away. Finally, the solid material was washed 3–6 times with 100 mL H_2O, then centrifuged at 4000 rpm for 30 min each time, and the supernatant decanted away. The material from the centrifuge tubes remaining after the multiple wash process was then dissolved into water, collected by vacuum filtration, and ground with a mortar and pestle. Both the powder and the films were then characterized using spectral methods of analysis. To prepare the natural extract prophyrin-based photosensitizer nanocomposite. Two types of photosensitizers, Sodium Magnesium Chlorophyllin (Mg-Chl) and Sodium Copper Chlorophyllin(Cu-Chl) were grafted with silver and grapheme nanomaterials. Electrostatic deposition method was used for grafting the two photosensitizers over the two nanomaterials to form the required nanocompsites (Mg-Chl / Ag nanocomposite, Mg-Chl/ GO nanocomposite, Cu-Chl/ Ag nanocomposite and Cu-Chl/ GO nanocomposite. The nanoparticles and nanocomposites were performed by means of a transmission electron microscope (TEM), using FEI Tecnia G2 High Resolution Transmission Electron Microscope operating at 200 kV. Histograms of size distribution were calculated from the TEM images by measuring the diameters of at least 50 particles. Also, Fourier Transform Infrared Spectroscopy (FTIR) measurements were carried out to detect the functional groups formed on the surface of nanomaterials, which play an important role in the effect on the insect. The FTIR measurements were carried out by using FT/IR-6600 JASCO device according to the Potassium bromide (KBr) method at the infrared spectrum in the 500 to 4000 wavelength numbers (cm-1) Ganesan and Deepak (2013),

Experimental design

This study was conducted at the Experimental Station of the Faculty of Agricultural, Cairo University, Giza, Egypt (30°01′32.5 "N & 31°11′33.0 "E) during the 2019 and 2020 seasons. The tomato cultivar Addora commonly planted in Egypt was chosen for field evaluation. The seedlings were planted on 22 September in the 2019 season and 2 October in the 2020 season. Tomato seedlings were planted in rows separated by a 70 cm distance. In both seasons, the experimental area of approximately 2.6 feddan was divided into 84 equal plots. Each plot consisted of 30 rows (6 m long and 70 cm wide/row). The experiments were carried out with a randomized complete block design with four replicates. All experimental plots received regular agricultural practices except for insecticide application. Two photosensitizers materials (magnesium and copper chlorophyllin) and four nanocomposite (Mg-Chl / Ag, Mg-Chl/ GO Cu-Chl/ Ag and Cu-Chl/ GO) were used in this experiment. Three concentrations [10^{-3} (100 ml/L), 10^{-4} (10 ml/L), and 10^{-5} (1 ml/L)] of each treatment were applied in a tomato field infested with *T. absoluta*. At the same time, two insecticides (Methomyl and Flupendiamide) were sprayed at the recommended dose (1 cm/L) as a reference in addition to the control group sprayed with water. The tomato seedlings were sprayed with photosensitizers and nanocomposites after three weeks post planting. Plant samples were investigated before and after the treatment on the 1st, 5th, and 7th days.

Data recorded

Reduction percentage in tunnels of *T. absoluta*

The sample included 20 plants randomly selected from each plot and investigated for infested leaves. The number of tunnels was counted, and the reduction percentages corresponding to each treatment were calculated using the means of tunnels for each treatment compared with those tunnels in the untreated control group by the equation of Henderson and Tilton (1955).

Growth parameters

After 60 days of the transplanting date, ten plants were randomly selected from each plot area to determine plant length, the number of stem/plants, stem diameter, plant fresh weight, and chlorophyll content. The SPAD (502, Japan) was used to determine the leave chlorophyll content.

Fruits color

Twenty fruits at the maturity stage (80% red) were taken from each plot area to evaluate fruit color. Using a Minolta

Chroma Meter model CR-200, USA), the surface color of tomato fruits was measured for a* (from red to green), b* (from yellow to blue), and L* (lightness). Three readings were collected at three different points on each tomato fruit to gauge the surface color.

Fruit quality

For testing firmness, ten mature fruits were selected. A fruit pressure tester was used to gauge firmness (FT011, Wagner Instruments, Italy). The results are presented in Newton (N). A digital refractometer was used to measure the total soluble solids (TSS) in tomato fruit (model PR101, Co. Ltd., Japan). A drop of fluid was applied to the lens, and the reading in degrees Brix (Bx) and its representation of the percentage of soluble solids in the fruit. Fruit diameter, length, and weight were also measured.

Yield and storability

The total yield per plot was harvested during the season and then calculated as ton/fedden (0.4 hectares). Tomato fruits free from diseases and physiological disorders, and uniform size and ripe (80% red) were selected and transferred after harvest to the vegetable crop department, faculty of agriculture. The selected fruits were stored in carton boxes at 10 °C and 90% relative humidity for two weeks. Weight loss and decay percentages were recorded after 7 and 14 days. Shriveling rotted or infected fruit were weighed and calculated as decay%.

Statistical analysis

Data were statistically analyzed using an analysis of variance (ANOVA). The means throughout investigated days were separated using a Duncan F-test at $P < 0.05$ by SPSS computer program version 14 (Snedecor and Cochran 1967). Vegetative growth and yield data were statistically analyzed using MSTAT (version 2.1), and treatment means were compared using Duncan's multiple range test. Data were combined over the two growing seasons. The correlation study was done by using the SPSS program (14.0).

Results

Characterization of nanoparticles and nanocomposites

Data in Fig. 1 showed the size of nano silver and graphene nanoparticles alone as well as these nanoparticles after coated with Mg-Chl or Cu-Chl to prepare four natural extract nanocomposite. The size of the silver particles varies, and the mean diameter is 10 nm. (Fig. 1a). The size of the Mg-Chl/Ag nanocomposite was found to be 30 nm (Fig. 1b) compared to 35 nm of the Mg-Chl/Ag nanocomposite (Fig. 1c). On the other hand, the structure of the graphene oxide nanosheets was a clear mono-layer with high integrity (Fig. 1d). Both of Mg-Chl / GO nanocomposite (Fig. 1e) and Cu-Chl/ GO nanocomposite (Fig. 1f) show the formation of the chlorophyllin coating (grafting) over the surface of graphene oxide nanosheets forming the nonocomposite. Figure 2 showed that FTIR of all tested nanoparticles and nanocomposite. The data refer to the major change in the bending vibrations of all nanocomposites.

Effect of photosensitizers on the population of *Tuta absoluta*

The data in Tables 1 and 2 showed that all concentrations of photosensitizers of Magnesium or Copper chlorophyllin (10^{-3}, 10^{-4} and 10^{-5}) reduced the mean number of tunnels of *T. absoluta* after 1 and 5 days of spraying, and no newly found tunnels after seven days of spraying. The differences between the mean numbers of tunnels after five days and seven days of spraying were insignificant, but it was highly significant when compared with the mean number of tunnels before spraying and one day after spraying at all concentrations of photosensitizer materials. Furthermore, the reduction percentage in newly tunnels gradually increased when increased the concentration or days after spraying, which ranged between 27.08–100% in the 2019 season and between 53.45%–100% in the 2020 season, while for plants treated with insecticides in season 2019, the reduction ranged between 27.54–91.37% and ranged between 49.48–70.36% in season 2020.

Effect of graphene oxide nanocomposites on the population of *Tuta absoluta*

Three concentrations (10^{-3}, 10^{-4} and 10^{-5}) of two nanocomposites, including graphene oxide (MgGo and CuGo) were tested against *Tuta absoluta* in the tomato field in the 2019 and 2020 seasons, as shown in Tables 3 and 4. In the 2019 season, after one-day post spray, the highest concentration (10^{-3}) was the most effective in reduction % of tunnels which reached 89.3% at MgGo and 82.8% at CuGo. At the lowest concentration (10^{-5}), the reduction percentage of tunnels was 75.9% at MgGo and 74.5% at CuGo, which was higher than that of insecticides (47.3 and 43.0%). No significant difference was found between all the tested concentrations of nanocomposites. While there were significant differences between them and the control. After 5 and 7 days of spraying, the reduction percentages of tunnels reached 100% at 10^{-3} and 10^{-4} of MgGo and CuGo, while it was lower than 70% at the two tested insecticides. The

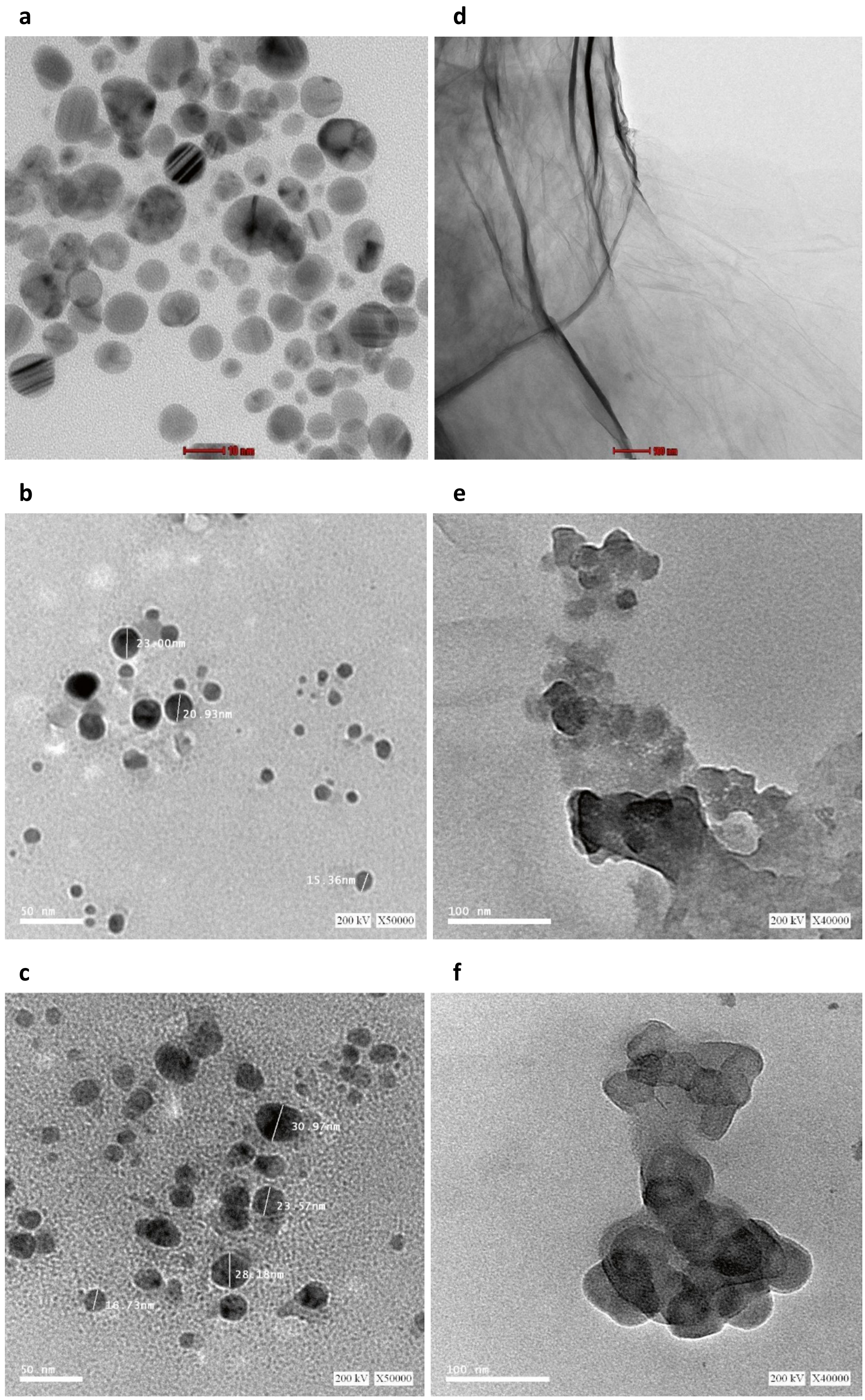

Fig. 1 TEM image of nanoparticles and nanocomposites. **a** Nano silver (Ag) alone **b** Mg-Chl/Ag **c** CU-Chl/Ag **d** Nano graphene oxide alone (GO) **e** Mg-Chl/GO **f** CU-Chl/GO

differences between nanocomposites at all tested concentrations were not significant except at the lowest concentration (10^{-5}) of MgGo after seven days of spraying, which was significant with other concentrations. A high significance was observed between the tested insecticides and the tested nanocomposites. The differences between the number of tunnels before and after spraying at each tested concentration of nanocomposites were highly significant (Table 3).

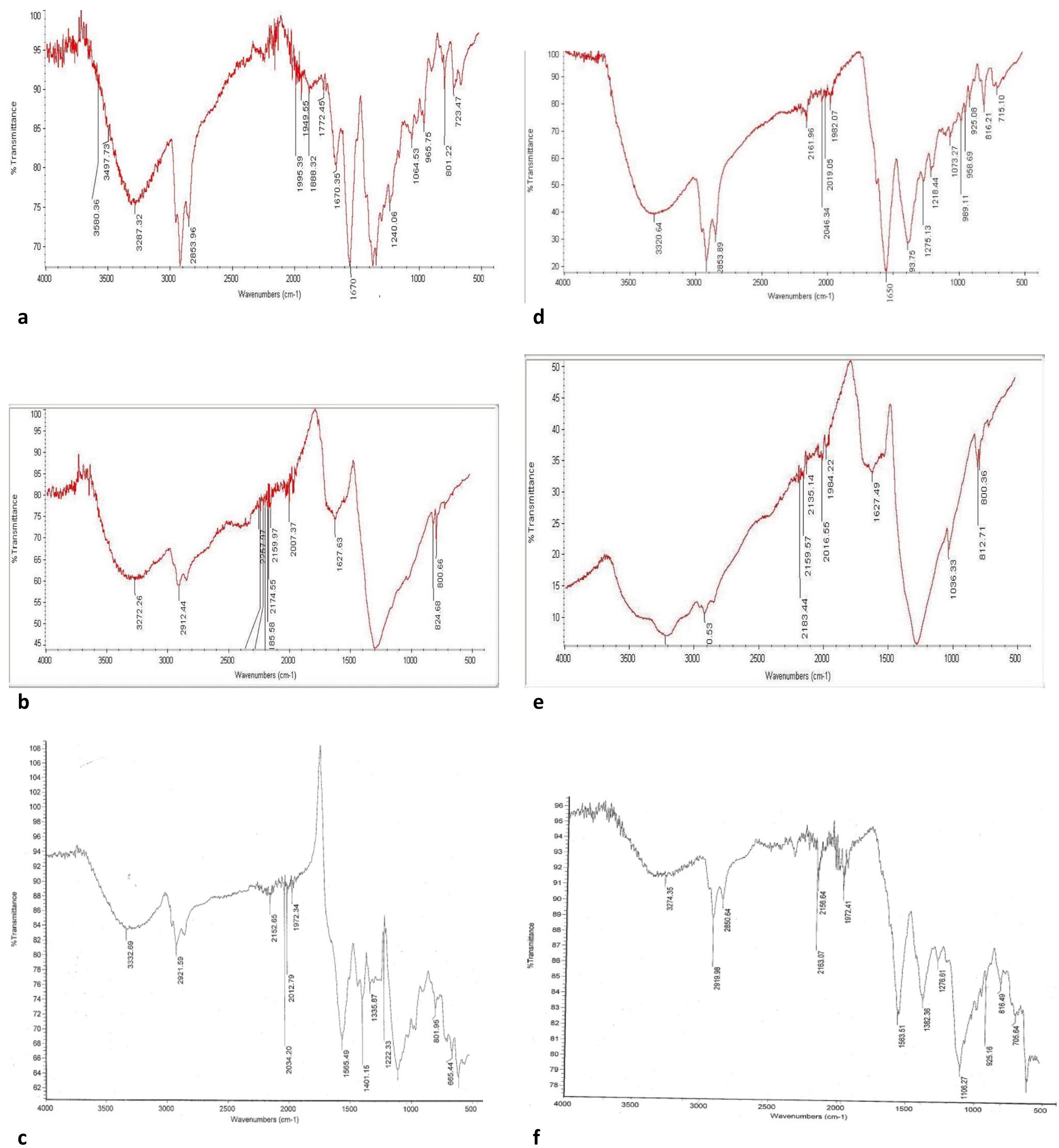

Fig. 2 FTIR of photosensitizers and nanocomposites. **a** Mg-Chl alone **b** Mg-Chl/Ag **c** Cu-Chl/Ag **d** Cu-Chl alone **e** Mg-Chl/GO **f** Cu-Chl/GO

In the 2020 season, a significant decline in the number of tunnels was observed at 1, 5, and 7 days post spraying with different concentrations of either MgGo or CuGo. All tested concentrations exhibited reduction percentages higher than insecticides and control. In general, the complete reduction percentages in the number of tunnels were found in all concentrations after seven days of spraying. No significant differences were observed between different concentrations of MgGo or CuGo, while significant differences were observed between their treatments and control. Significant differences between the examination of tunnels before and after spraying were observed (Table 4).

Table 1 Efficiency of some photosynthetizers against newly tunnels formed by leaf miner *Tuta absoluta* infesting tomato in the field in winter of 2019 season

Formulation	Rate (ml/l)	Mean number of newly-tunnels and reduction percentages							F value	P value
		Before spray	Day post spray							
			1		5		7			
			Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)		
Magnesium clorophline	10^{-3}	2.17 ± 0.37C	1.20 ± 0.30abcB	72.79	0.17 ± 0.07abA	94.43	0.00 ± 0.00aA	100	17.895	0.000
	10^{-4}	2.07 ± 0.37C	1.40 ± 0.29bcB	66.72	0.17 ± 0.07abA	94.16	0.00 ± 0.00aA	100	24.649	0.000
	10^{-5}	1.30 ± 0.24B	1.80 ± 0.34bcdB	31.86	0.03 ± 0.03aA	98.36	0.00 ± 0.00aA	100	19.144	0.000
Cuber clorophline	10^{-3}	2.17 ± 0.38C	1.30 ± 0.32bcB	70.52	0.47 ± 0.13bA	84.60	0.00 ± 0.00aA	100	13.795	0.000
	10^{-4}	1.43 ± 0.26B	0.97 ± 0.28abB	66.62	0.23 ± 0.09abA	88.56	0.00 ± 0.00aA	100	11.196	0.000
	10^{-5}	1.37 ± 0.18B	2.03 ± 0.34cdC	27.08	0.33 ± 0.11abA	82.87	0.00 ± 0.00aA	100	22.002	0.000
Methomyl	1	1.77 ± 0.26C	1.17 ± 0.24abcB	67.47	0.40 ± 0.13bA	83.93	0.17 ± 0.07aA	86.50	14.466	0.000
Flupendiamide	1	1.63 ± 0.27B	2.40 ± 0.36cdC	27.54	0.47 ± 0.12bA	79.50	0.10 ± 0.06aA	91.37	20.298	0.000
Control	0	1.87 ± 0.31	3.80 ± 0.33d		2.63 ± 0.21c		1.33 ± 0.19b		16.211	0.000
F value		1.083	9.616		45.301		38.316			
P value		IN	0.000		0.000		0.000			

Means within a column followed by the same letter are not significantly different using Duncan's Multiple Range Test. Capital letters indicate to the significant differences between days while small letters indicate to significant differences between treatments

N = 30

There is no new tunnels observed 10 days post spraying for all treatments

IN insignificant

Table 2 Efficiency of some photosynthetizers against newly tunnels formed by leaf miner *Tuta absiluta* infesting tomatoes in the field in winter of 2020 season

Formulation	Rate ml/l	Mean of tunnels and its reduction percentage							F value	P value
		Before spray	Day post spray							
			1		5		7			
			Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)		
Magnesium clorophline	10^{-3}	1.50 ± 0.27C	0.55 ± 0.11abB	77.95	0.13 ± 0.05aA	94.38	0.00 ± 0.00aA	100	21.786	0.000
	10^{-4}	0.95 ± 0.23C	0.48 ± 0.11aB	69.61	0.03 ± 0.03aA	97.95	0.00 ± 0.00aA	100	12.691	0.000
	10^{-5}	1.25 ± 0.26C	0.70 ± 0.15abAB	66.32	0.25 ± 0.07aA	87.03	0.03 ± 0.15aA	99.05	5.706	0.001
Cuber clorophline	10^{-3}	1.13 ± 0.24B	0.75 ± 0.14abB	60.08	0.30 ± 0.07aA	82.78	0.00 ± 0.00aA	100	11.743	0.000
	10^{-4}	1.15 ± 0.21B	0.89 ± 0.15abcB	53.45	0.33 ± 0.10aA	81.39	0.00 ± 0.00aA	100	14.303	0.000
	10^{-5}	0.93 ± 0.24B	0.70 ± 0.13abB	54.73	0.30 ± 0.08aA	79.08	0.00 ± 0.00aA	100	8.435	0.000
Methomyl	1	1.20 ± 0.28	1.05 ± 0.22bc	49.48	0.80 ± 0.13b	56.77	0.90 ± 0.23b	70.36	0.632	IN
Flupendiamide	1	0.95 ± 0.23	0.90 ± 0.18abc	52.52	0.73 ± 0.13b	50.17	0.90 ± 0.20b	62.56	0.291	IN
Control	0	0.83 ± 0.20	1.38 ± 0.26c		1.28 ± 0.25c		2.10 ± 0.24c		4.825	0.003
F value	-	0.752	2.645		11.637		27.848			
P value	-	IN	0.008		0.000		0.000			

Means within a column followed by the same letter are not significantly different using Duncan's Multiple Range Test. Capital letters indicate to the significant differences between days while small letters indicate to significant differences between treatments

N = 40

IN insignificant

Table 3 Efficiency of nanocomposites (graphene oxide nanosheets coupled with Mg-Chl and Cu-Chl) against newly tunnels formed by leaf miner *Tuta absoluta* infesting tomatoes in the field in winter of 2019 season

Formulation	Rate ml/l	Mean number of tunnels and its reduction percentage							*F* value	*P* value
		Before spray	Day post spray							
			1		5		7			
			Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)		
MgGo	10^{-3}	1.125 ± 0.26^{A}	0.20 ± 0.06^{Bd}	89.3	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	16.274	< 0.001
	10^{-4}	1.35 ± 0.24^{A}	0.40 ± 0.10^{Bd}	82. 2	0 ± 0.00^{Cc}	100	0 ± 0.00^{Cc}	100	24.175	0.000
	10^{-5}	1.25 ± 0.27^{A}	0.50 ± 0.13^{BCcd}	75.9	0.025 ± 0.025^{Cc}	98.7	0.075 ± 0.18^{Bb}	90.35	8.183	0.000
CuGo	10^{-3}	1.05 ± 0.23^{A}	0.30 ± 0.09^{Bd}	82.8	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	15.592	0.000
	10^{-4}	1.175 ± 0.24^{A}	0.475 ± 0.10^{Bcd}	75.7	0 ± 0.00^{Cc}	100	0 ± 0.00^{Cc}	100	17.868	0.000
	10^{-5}	1.30 ± 0.23^{A}	0.55 ± 0.12^{Bcd}	74.5	0 ± 0.00^{Cc}	100	0.025 ± 0.03^{Cc}	99.2	21.604	0.000
Methomyl	1	1.20 ± 0.28	1.05 ± 0.22^{ab}	47.3	0.80 ± 0.13^{b}	56.9	0.90 ± 0.23^{b}	70.5	0.632	IN
Flupendiamide	1	0.95 ± 0.23	0.90 ± 0.18^{bc}	43.0	0.725 ± 0.11^{b}	50.6	0.90 ± 0.20^{b}	62. 8	0.291	IN
Control	0	0.825 ± 0.20^{B}	1.375 ± 0.26^{Ba}		1.275 ± 0.25^{Ba}		2.10 ± 0.24^{Aa}		4.825	0.003
F value	-	0.487	6.234		23.007		25.504			
P value	-	0.865 (ns)	0.000		0.000		0.000			

Means within a column followed by the same letter are not significantly different using Duncan's Multiple Range Test. Capital letters indicate to the significant differences between days while small letters indicate to significant differences between treatments

IN insignificant

Table 4 Efficiency of nanocomposites (graphene oxide nanosheets coupled with Mg-Chl and Cu-Chl) against newly tunnels formed by leaf miner *Tuta absiluta* infesting tomatoes in the field in winter of 2020 season

Formulation	Rate ml/l	Mean number of tunnels SE and its reduction percentage							*F* value	*P* value
		Before spray	Day post spray							
			1		5		7			
			Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)		
MgGo	10^{-3}	0.075 ± 0.04^{Ac}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bb}	100	3.162	0.026
	10^{-4}	0.075 ± 0.04^{Ac}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bb}	100	3.162	0.026
	10^{-5}	0.375 ± 0.04^{c}	0 ± 0.00^{c}	100	0 ± 0.00^{c}	100	0.10 ± 0.06^{b}	66.12	1.979	IN
CuGo	10^{-3}	0.375 ± 0.06^{Abc}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.025 ± 0.025^{Bb}	89.27	6.548	0.000
	10^{-4}	0.375 ± 0.08^{Abc}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.05 ± 0.03^{Bb}	78.55	18.073	0.000
	10^{-5}	0.475 ± 0.10^{Ab}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.10 ± 0.08^{Bb}	66.12	12.441	0.000
Methomyl	1	0.275 ± 0.08^{Abc}	0.33 ± 0.14^{Ab}	78.5	0.45 ± 0.08^{Ab}	-	0 ± 0.00^{Bb}	100	4.272	0.006
Flupendiamide	1	0.225 ± 0.07^{bc}	0.43 ± 0.16^{b}	-	0.60 ± 0.14^{b}	-	0.35 ± 0.16^{b}	-	1.306	IN
Control	0	1.775 ± 0.24^{a}	1.175 ± 0.21^{a}		1.15 ± 0.18^{a}		1.10 ± 0.30^{a}		1.798	IN
F value	-	28.276	15.263		25.533		9.050			
P value	-	0.000	0.000		0.000		0.000			

Means within a column followed by the same letter are not significantly different using Duncan's Multiple Range Test. Capital letters indicate to the significant differences between days while small letters indicate to significant differences between treatments

IN insignificant

Effect of silver nanocomposites on the population of *Tuta absoluta*

Three concentrations (10^{-3}, 10^{-4} and 10^{-5}) of two nanocomposites, including silver (MgAg and CuAg) were examined against the *Tuta absoluta* in the tomato field at two seasons (Tables 5 and 6). A significant decline in the number of tunnels was observed at 1, 5, and 7 days post spraying with 10^{-3}, 10^{-4}, and 10^{-5} of MgAg or CuAg. All tested concentrations exhibited reduction percentages higher than insecticides and control. In general, the complete reduction percentages in the number of tunnels were found in all concentrations of MgAg after 5 and 7 days of spraying. No significant differences were observed between different concentrations of MgAg or CuAg, while significant differences were observed between their treatments and control. The significant differences between examining tunnels before and after spraying were observed. In the 2019 season, after one day of spray, the high dose of MgAg (10^{-3}) was the most effective achieving a 95.1% reduction in the number of tunnels of *T. absoluta*. The remaining concentration of MgAg (10^{-4} and 10^{-5}) also showed a decrease in the number of *T. absoluta* tunnels higher than all doses of CuGo and the two insecticides, 83.1% and 84.4%, respectively. After 5 and 7 days of spraying, the reduction percentages of tunnels reached 100% at all concentrations of both nanocomposites. In the 2020 season, the reduction percentage in the *T. absoluta* tunnels was recorded after 1 and 5 days of spraying with both nanocomposites. The new tunnels appeared after seven days of spraying, and these new tunnels decreased with increased concentration.

Effect of photosensitizers on vegetative growth and yield

Tomato vegetative growth was significantly affected by the photosensitizers magnesium and copper chlorophyllin (Fig. 3). Plants treated with Cu/Ch (10^{-4}) and Mg/Ch(10^{-5}) recorded the highest plant length (108.5, 107.2 cm) with no significant difference with Mg/Ch^{-4} (106.5) and methomyl insecticide (101.8) (Fig. 3a). Data in Fig. 3b showed that photosensitizers of magnesium or copper chlorophyllin significantly achieved the number of stem/plants compared both insecticide and control treatment. In the case of stem diameter, the highest value was recorded in Cu/Ch(10^{-3}) (15.17) compared to all other treatments (Fig. 3c); stem diameter increased by increasing the concentration of Cu-Chl. Leaves chlorophyll content was significantly positively affected by photosensitizers of magnesium or copper chlorophyllin treatments compared to methomyl insecticide and control treatment (Fig. 3d). Plant treated with photosensitizers of magnesium or copper chlorophyllin had the highest plant fresh weight (Fig. 3e). The highest yield/feddan (28.7) was recorded from plants treated with Mg/Ch^{-3}, followed by Mg/Ch^{-4} (26.7) and Cu/Ch^{-3} (24.1), with no significant difference between them. The lowest yield was recorded in the control treatment (17.8), followed by Cu-Chl $^{-4}$ and Cu-Chl $^{-5}$ (Fig. 3 f).

Effect of photosensitizers on fruit quality and storability

The treatment with Cu-Chl^{-5} recorded the highest TSS (3.8), followed by Cu-Chl^{-4} (3.6) and flupendiamide insecticide (3.7) without any significant difference (Fig. 4a). All the concentrations of copper photosensitizers and Mg-Chl $^{-4}$ recorded the highest fruit firmness value compared to all other treatments (Fig. 4b). Flupendiamide insecticide treatment recorded the lowest L value (36.43) compared to all other treatments (Fig. 4c). Flupendiamide insecticide treatment recorded the highest values of A and color index (Fig. 4d–f). The treatments did not affect the weight loss% of fruit stored at 10 °C during the first week while, in the second week the weight loss percentage was significantly affected by treatment (Fig. 5a). Control treatment recorded the highest weight loss% (8.6) after two weeks of storage at 10 °C, while the lowest percentage was recorded in the highest concentration (10^{-3}, 10^{-4}). Treatments with photosensitizers of magnesium or copper chlorophyllin reduced the decay percentage of fruit during all storage periods compared to the control treatment. The decay % affected with photosensitizer treatments which gradually decreased by increasing the concentration of Mg-Chl and Cu-Chl. Control treatment recorded the highest decay percentage (26.1 and 54.14), followed by flupendiamide (23.8 and 47.5%) and methomyl (20.1 and 40.1%) insecticide after one and two weeks of storage (Fig. 5b).

Effect of graphene oxide nanocomposites on vegetative growth and yield

Data in Fig. 6 show that the plant vegetative growth parameters were affected by the graphene nanomaterials. All the tested concentrations of copper graphene oxide and methomyl insecticide recorded the highest plant length compared to all other treatments (Fig. 6a). Plant treated by all graphene oxide treatments except Mg-Ch/GO^{-3} recorded the highest number of stem/plant compared to control and insecticides treatments (Fig. 6b). Stem diameter was affected by nanomaterial treatments. The two concentrations of magnesium graphene oxide (10^{-4} and 10^{-5}) and methomyl insecticide treatment achieved the stem diameter compared to the other treatments (Fig. 6c). The highest leaves chlorophyll content was recorded in the treatments of Mg-Chl/GO – 5 (38.75), Cu-Chl/GO^{-4} (38.38) and flupendiamide insecticide (35.9) without any significant difference (Fig. 6d). Plant fresh

Table 5 Efficiency of nanocomposites (silver nanosheets coupled with Mg-Chl and Cu-Chl) against newly tunnels formed by leaf miner *Tuta absoluta* infesting tomatoes in the field in winter of 2019 season

Formulation	Rate ml/l	Mean number of tunnels and its reduction percentage							F value	P value
		Before spray	Day post spray							
			1		5		7			
			Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)		
MgAg	10^{-3}	0.925 ± 0.17^{A}	0.075 ± 0.04^{Bf}	95.1	0 ± 0.00^{Bc}	100	0.025 ± 0.025^{Bc}	100	24.668	0.000
	10^{-4}	0.80 ± 0.19^{A}	0.225 ± 0.07^{Babef}	83.1	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	14.046	0.000
	10^{-5}	1.45 ± 0.19^{A}	0.375 ± 0.09^{Bdef}	84.4	0 ± 0.00^{Cc}	100	0 ± 0.00^{Cc}	100	43.609	0.000
CuAg	10^{-3}	1.375 ± 0.25^{A}	0.525 ± 0.10^{Bcdef}	77.1	0 ± 0.00^{Cc}	100	0 ± 0.00^{Cc}	100	22.400	0.000
	10^{-4}	1.50 ± 0.30^{A}	0.625 ± 0.11^{Bbcde}	74.9	0 ± 0.00^{Cc}	100	0 ± 0.00^{Cc}	100	20.237	0.000
	10^{-5}	0.775 ± 0.21^{A}	0.70 ± 0.12^{Abcd}	45.6	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	12.724	0.000
Methomyl	1	1.20 ± 0.28	1.05 ± 0.22^{ab}	47.3	0.80 ± 0.13^{b}	56.9	0.90 ± 0.23^{b}	70.5	0.632	IN
Flupendiamide	1	0.95 ± 0.23	0.90 ± 0.18^{bc}	43.0	0.725 ± 0.11^{b}	50.6	0.90 ± 0.20^{b}	62. 8	0.291	IN
Control	0	0.825 ± 0.20^{B}	1.375 ± 0.26^{Ba}		1.275 ± 0.25^{Ba}		2.10 ± 0.24^{Aa}		4.825	0.003
F value	-	1.682	7.524		23.345		32.423			
P value	-	0.101 (ns)	0.000		0.000		0.000			

Means within a column followed by the same letter are not significantly different using Duncan's Multiple Range Test. Capital letters indicate to the significant differences between days while small letters indicate to significant differences between treatments

IN insignificant

Table 6 Efficiency of nanocomposites (silver nanosheets coupled with Mg-Chl and Cu-Chl) against newly tunnels formed by leaf miner *Tuta absiluta* infesting tomatoes in the field in winter of 2020 season

Formulation	Rate ml/l	Mean number of tunnels and its reduction percentage							F value	P value
		Before spray	Day post spray							
			1		5		7			
			Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)	Mean ± SE	Reduction (%)		
MgAg	10^{-3}	0.10 ± 0.04^{ABb}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.175 ± 0.08^{Ab}	100	3.378	0.020
	10^{-4}	0.35 ± 0.06^{Ab}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.075 ± 0.06^{ABb}	65.52	3.258	0.023
	10^{-5}	0.20 ± 0.06^{Ab}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.05 ± 0.03^{Bb}	59.77	6.735	0.000
CuAg	10^{-3}	0.45 ± 0.09^{Ab}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.025 ± 0.025^{Bb}	91.0	23.703	0.000
	10^{-4}	0.35 ± 0.12^{Ab}	0 ± 0.00^{Bc}	100	0 ± 0.00^{Bc}	100	0.125 ± 0.06^{Bb}	42.4	5.767	0.001
	10^{-5}	0.275 ± 0.08^{Ab}	0.025 ± 0.025^{Bc}	86.3	0 ± 0.00^{Bc}	100	0.125 ± 0.05^{Bb}	26.6	6.341	0.000
Methomyl	1	0.275 ± 0.08^{Ab}	0.325 ± 0.14^{Abc}	78.5	0.45 ± 0.08^{Ab}	-	0 ± 0.00^{Bb}	100	4.272	0.006
Flupendiamide	1	0.225 ± 0.07^{b}	0.425 ± 0.16^{b}	-	0.60 ± 0.14^{b}	-	0.35 ± 0.16^{b}	-	1.306	IN
Control	0	1.775 ± 0.24^{a}	1.175 ± 0.21^{a}		1.15 ± 0.18^{a}		1.10 ± 0.30^{a}		1.798	IN
F value		22.960	15.038		25.533		7.961			
P value	-	0.000	0.000		0.000		0.000			

Means within a column followed by the same letter are not significantly different using Duncan's Multiple Range Test. Capital letters indicate to the significant differences between days while small letters indicate to significant differences between treatments

IN insignificant

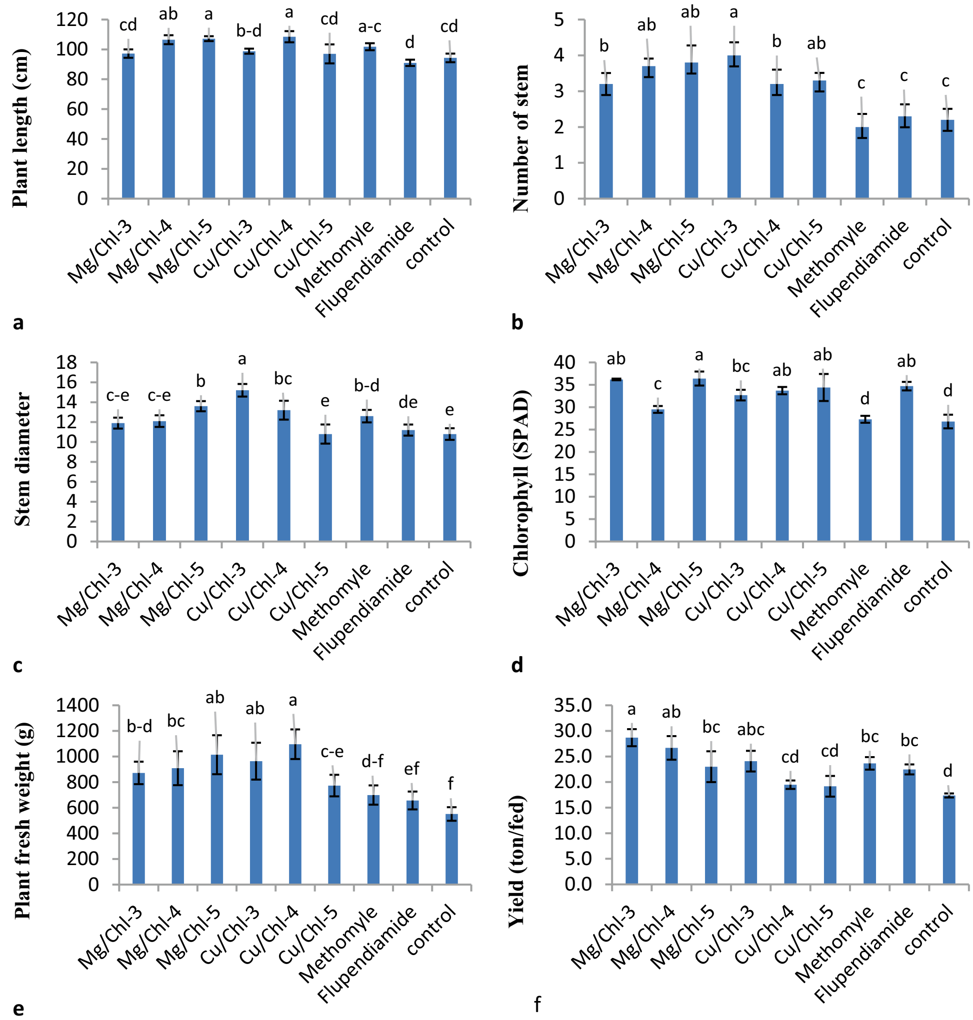

Fig. 3 Effect of photosensitizers of magnesium or copper chlorophylline on plant length (**a**), number of stem/ plant (**b**), stem diameter (**c**), leaves chlorophyll content (**d**), plant fresh weight (**e**) and total yield (**f**)

weight was affected by the treatments (Fig. 6e). Plant treated by all graphene oxide treatments except $MgGo^{-3}$ recorded the highest plant fresh weight. Plant treated with Cu-Chl/GO^{-3} achieved the highest yield/feddan (33.0 ton) compared to all other treatments (Fig. 6f); the total yield was positively affected by increasing the graphene nanosheets' concentration.

Effect of graphene oxide nanocomposites on fruit quality and storability

The graphene oxide treatments affected tomato fruit quality (Fig. 7). The treatments of Mg-Chl/GO^{-3} and flupendiamide insecticide recorded the highest fruit TSS (4.2 and 4.4%), while the treatment of Mg-Chl/GO^{-4} and Cu-Chl/GO^{-5} recorded the most increased fruit firmness (0.5, 0.5) compared to all other treatments (Fig. 7a and b). The lightness value of tomato fruit was not affected significantly by all the treatments of graphene oxide or insecticides except flupendiamide treatment which recorded the lowest value (36.2) (Fig. 7c). The color values (A & B) and color index were only affected by flupendiamide insecticide, which recorded the highest value compared to all other treatments (Fig. 7d–f). Control treatment, flupendiamide, and methomyl insecticide recorded the highest weight loss% (5.7, 5.5 and 5.3% respectively) after one week of storage at 10 °C. Also, Weight loss percentage increased by increasing the storage period in all tested treatments.Control treatment and flupendiamide insecticide recorded the highest weight loss percentage (8.8 and 8.6%) after two weeks of storage at 10 °C (Fig. 8a). The lowest weight loss percentage was recorded in Mg-Chl/Go^{-3} after one and two weeks of storage (3.2 and 6%). Magnesium or copper graphene oxide treatments reduced fruit decay percentage compared to the control treatment and both insecticide (flupendiamide and methomyl) (Fig. 8b). The lowest decay percentage (4.3 and 5%) was recorded in Mg-Chl/Go^{-3} and Mg-Chl/Go^{-4} after one week of storage while the highest decay percentage (54.1%) was recorded in control treatment after two weeks of storage.

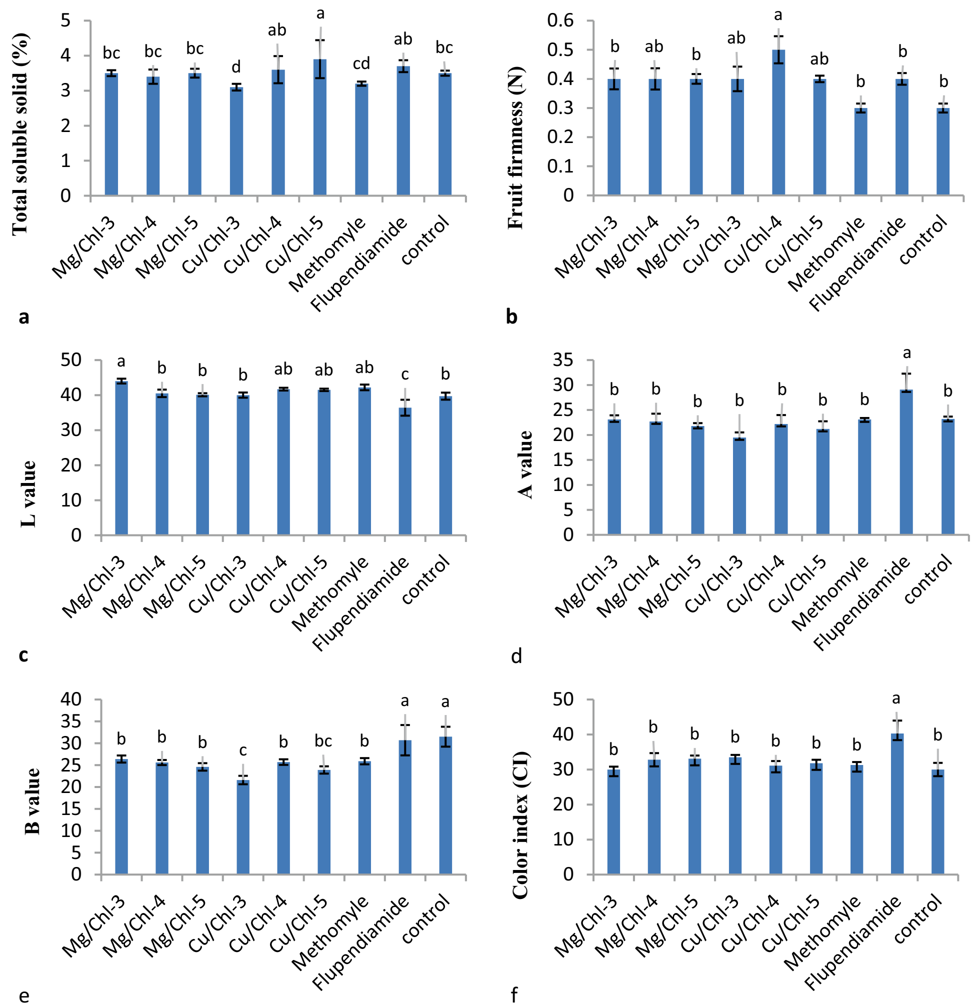

Fig. 4 Effect of photosensitizers of magnesium or copper chlorophylline on TSS (**a**), fruit firmness (**b**), L value (**c**), a value (**d**), B value (**e**) and color index (**f**)

Effect of silver nanocomposites on vegetative growth and yield

Plant length in Cu-Chl/Ag^{-5} treatment was consistently greater (110.8 cm) but not statistically different from those in Cu-Chl/Ag – 4 (106.7 cm), Mg-Chl/Ag^{-4} (106.2 cm) and methomylhomyl insecticide (105.8 cm) treatments (Fig. 9a). Cu-Chl/Ag^{-5} treatment recorded the highest No. of stem/plant (4.8) compared to all other treatments, followed by Mg-Chl/Ag^{-4} and Mg-Chl/Ag^{-5} (4.1 and 3.8) (Fig. 9b). All concentrations of Mg-Chl/Ag and Cu-Chl/Ag^{-5} achieved the highest stem diameter (Fig. 9c). Chlorophyll content was affected by both nonmaterial (Mg-Chl/Ag and Cu-Chl/Ag) and their concentrations. The lowest chlorophyll content (27.4 and 26.6) was recorded in methomyl insecticide and control treatment (Fig. 9d). Plant fresh weight was significantly greater in all the Mg-Chl/Ag treatment concentrations, with no significant difference with Cu-Chl/Ag^{-5} (Fig. 9e). Tomato yield was decreased gradually by decreasing the concentration of silver nanocomposites. Mg-Chl/Ag^{-3} and Mg-Chl/Ag^{-4} achieved the highest yield/feddan (35.2 and 34.5 ton) compared to all other treatments (Fig. 9f). The lowest yield was recorded in control (18.4 ton) treatments, followed by Flupendiamide (22.8 ton) and methomyl insecticide (24.1 ton).

Effect of silver nanocomposites on fruit quality and storability

Flupendiamide insecticide recorded the highest fruit TSS (4.4%), followed by the control treatment (3.8%) (Fig. 10a). Cu-Chl/Ag^{-5} treatment recorded the lowest value of fruit firmness (0.28) with no significant difference with methomyl insecticide (0.31) and control treatment (0.30) (Fig. 10b). There is a little significant difference between the treatments on L value (Fig. 10c). The highest A and CI values were recorded in Flupendiamide insecticide (29.7 and 40) compared to all other treatments (Fig. 10d and f). The highest B value was recorded in Flupendiamide, methomyl, control, and Cu-Chl/Ag^{-5} treatments (Fig. 10e). All the magnesium or copper silver nanocomposites reduced the weight loss and decay% compared to all other treatments;

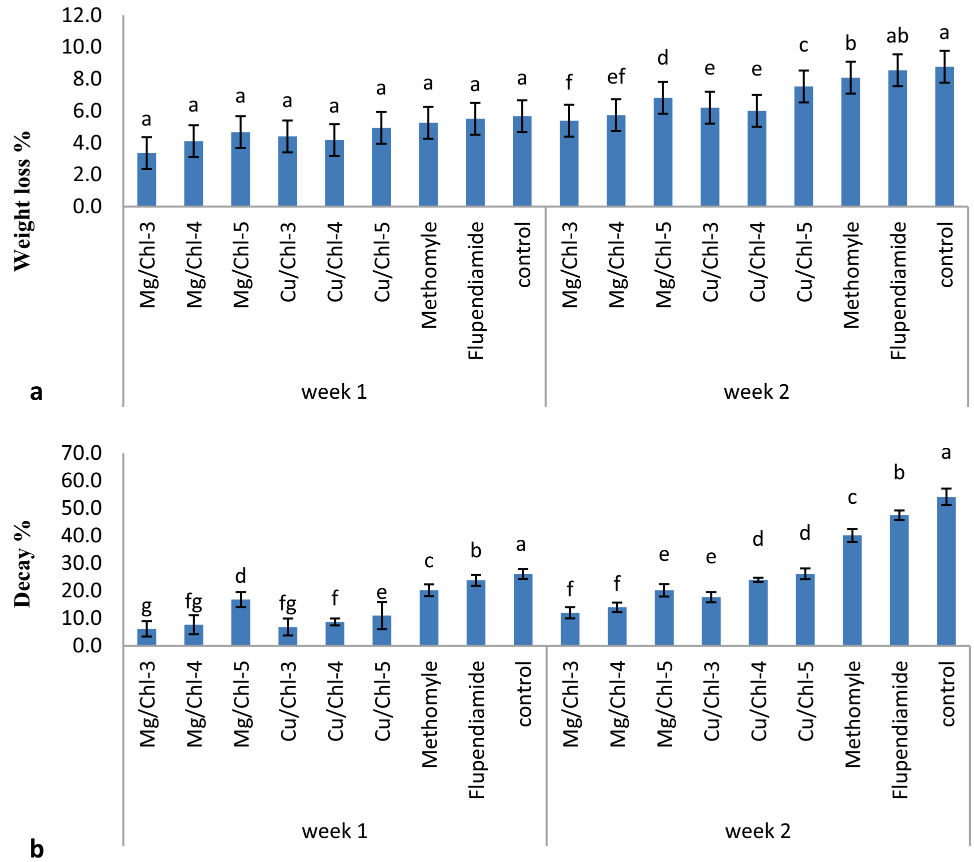

Fig. 5 Effect of photosensitizers of magnesium or copper chlorophylline on weight loss % (**a**) and decay % (**b**)

weight loss and decay% increased by increasing the storage period and decreased by increasing the concentrations of silver up to 10^{-3}. The lowest weight loss% (2.7 and 5.3%) was recorded in Mg-Chl/Ag – 3 after one and two weeks of storage (Fig. 11a). There were no symptoms of decay in fruit treated with Mg-Chl /Ag^{-3}, Mg-Chl /Ag^{-4}, and Cu-Chl/Ag^{-3} in the first week of storage (Fig. 11b). The treatment with Mg-Chl /Ag^{-3} maintains tomato fruit for two weeks without any decay%. Control achieved the highest decay% (26.1 and 54.1%) after one and two weeks of storage at 10 °C, followed by Flupendiamide insecticide (23.8 and 47.5%).

Correlation study

Data presented in Table 7 indicated a significant positive correlation between the reduction % of *Tuta absoluta* and plant length, No. of stem/plant, stem diameter, chlorophyll, plant fresh weight, and yield in photosensitizer treatments. In contrast, there was a significant negative correlation between reduction % and TSS, weight loss, and decay%. According to grapheme treatments, the reduction % correlated positively with No. of the stem, stem diameter, chlorophyll content, fruit firmness, and yield. In comparison, it correlated negatively with b value, weight loss, and decay%. In nano silver treatments, also reduction % correlated positively with plant length, No. of the stem, stem diameter, chlorophyll, fresh weight, and yield. On the other hand, there was a negative correlation between weight loss and decay %.

Discussion

The tomato leaf miner is a very dangerous insect on the tomato crop. Photosensitizers and nanocomposites were used in this study as new technological alternatives to pesticides that have high efficacy on insect pests and are less harmful to the environment (Ahmed et al. 2018). There are no previous studies on the effect of photosensitizers, as well as those loaded with nanomaterials (grapheme nanosheet and nano silver), on *T. absoluta*, but there have been few studies on some other insects such as *Spodoptera littoralis* (Ahmed et al. 2018; Awad 2018; Abd El-Naby 2019; Abd El-Rahman et al. 2019). In the present study, Mg-Chl or Cu-Chl photosensitizers significantly reduced the number of tunnels of *T. absoluta* after 1, 5, and 7 days of spraying. Treatment with Mg-Chl was better than Cu-Chl. The reduction in the number of tunnels reached 100% in the 2019 and 2020 seasons after seven days of spraying. In a similar study, Ahmed et al. (2018) used photosensitizers (Mg-Chl or Cu-Chl) against *S. littoralis* in the cotton field and found

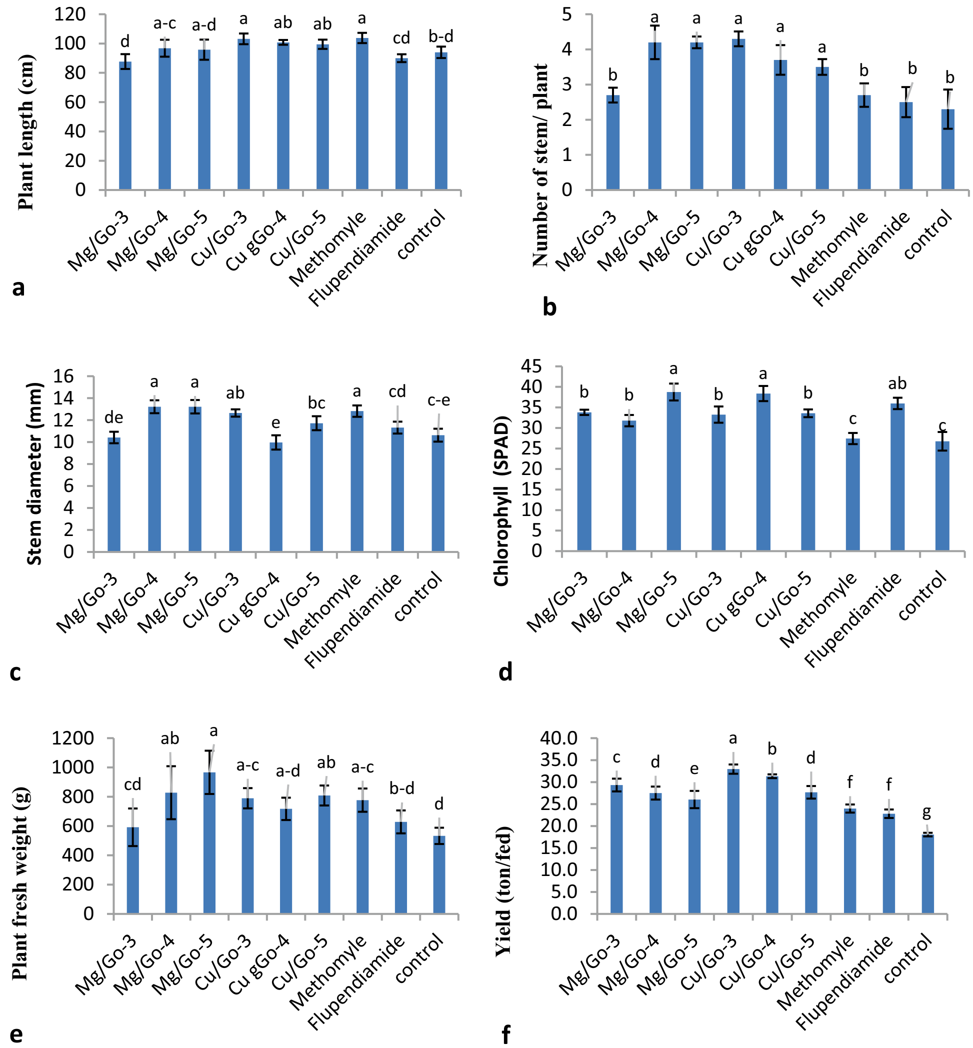

Fig. 6 Effect of nancomposites including graphene oxide (MgGo and CuGo) on plant length (**a**), number of stem/plant (**b**), stem diameter (**c**), leaves chlorophyll content (**d**), plant fresh weight (**e**) and total yield (**f**)

the reduction percentage in larvae ranged between 74.2% and 90.2% in the first season while, in the second season, it was ranged between 64.9% and 94.8% after 15 days of spraying. Lukšienė et al. (2007) evaluated the effects of several photosensitizers (acridine orange, aminolaevulinic acid, hematoporphyrin dimethyl ether "HPde," methylene blue) on the population of leafminer flies, *Liriomyza bryoniae* (Kaltenbach) (Diptera, Agromyzidae) and found that HPde was highly accumulated in the body of the insects resulting in the rapid death of *L. bryoniae* when exposed to visible light. The insect mortality after treatment with photosensitizer may be due to accumulated within the insect body and induces damage to the cuticle, Malpighian tubes, midgut wall, and feeding inhibition (Ben Amor et al. 1998). Four types of nanocomposites (MgGO, MgAg, CuGo, and CuAg) on *T. absoluta* were evaluated in our study, and no tunnels were found after five days of spraying in the first season and after one day of spraying in the second season. Few studies investigated the effect of different nanoparticles on *T. absoluta* in the tomato field, such as silica nanoparticles (El-Samahy et al. 2014; Derbalah et al. 2012 Abouelkassem et al. 2017). While the same nanocomposites were evaluated by Ahmed et al. (2018) against *S. littoralis* and recorded that MgGo was the most effective nanocomposite, which increased the reduction in the population of treated larvae to 88.54% after ten days of spraying at concentration of 10^{-3} m/L, while the decline was 96.51% after 15 days of spraying with MgAg. Our results indicated that, when loaded, nanomaterials over photosensitizers were more effective than photosensitizers alone. The reduction in the number of tunnels after treatments may be due to the effect of the photosensitizers and nanocomposites on eggs or the newly hatched larvae of *T. absoluta*, which leads to their death and thus their inability to make tunnels.

In contrast, GOAg acts as a carrier to enhance a photosensitizer's penetration and utilization efficiency, which leads to fast mortality of *T. absoluta* in addition to their toxicity. The effect of graphene oxide nanoparticles in insects may

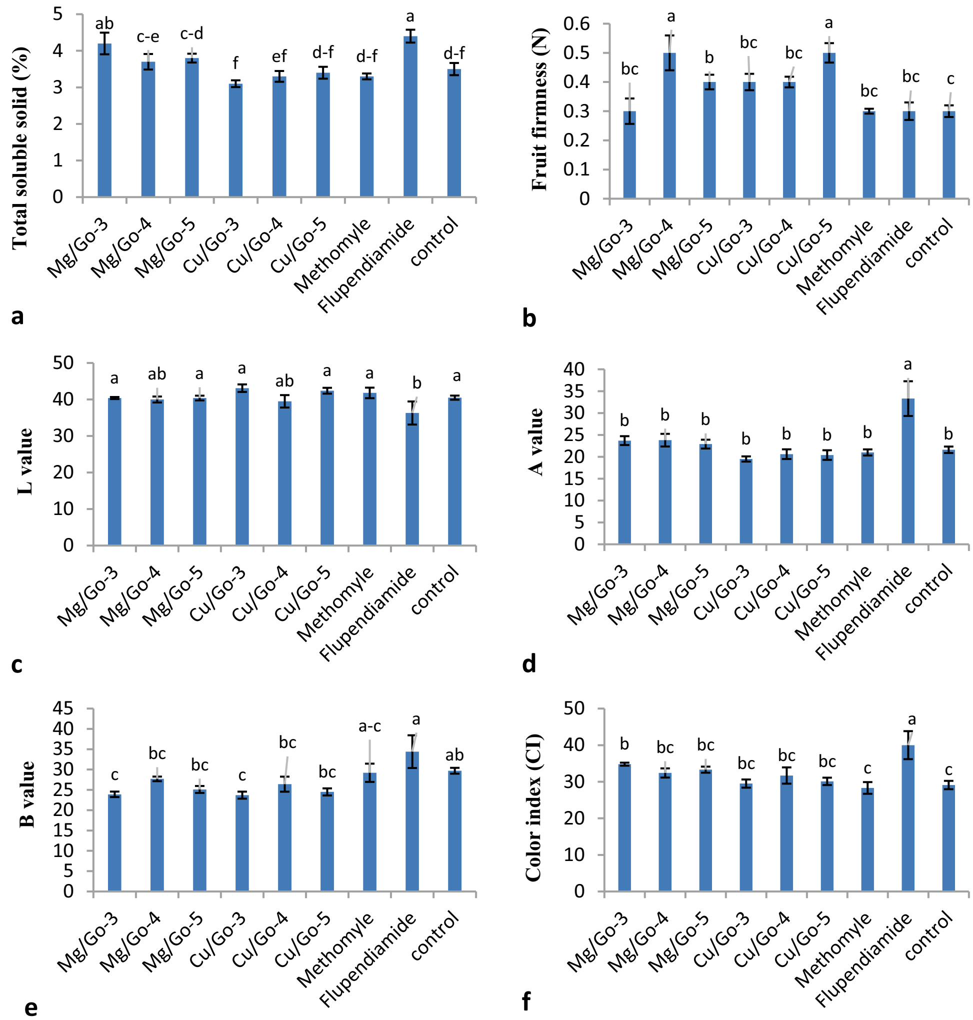

Fig. 7 Effect of nancomposites including graphene oxide (MgGo and CuGo) on TSS (**a**), fruit firmness (**b**), L value (**c**), a value (**d**), B value (**e**) and color index (**f**)

be due to their physical damage to the insect cement layer and rapid water loss. Also, GO increased catalase and glutathione peroxidases activity, heat shock in protein (HSP 70) and total antioxidants, leading to oxidative stress and cell death (Dziewięcka et al. 2015). While silver nanoparticles reduced acetylcholinesterase activity, protein synthesis, and gonadotrophin release, leading to developmental damages and reproductive failure (Benelli 2018).

Photosensitizers and nanoparticles have an important role in improving plant growth and botanical characteristics such as leaf area, stem height, chlorophyll content, germination, leaf numbers, and increasing production of plants (Amer and El- Emary 2018; Merghany et al. 2019). In the present study, tomatoes' vegetative growth parameters and chlorophyll content were increased significantly in both photosensitizers (magnesium and copper chlorophyllin) treatments compared with the control treatment and both insecticides. Increasing the vegetative growth parameters of tomato plants after treatments with photosensitizers and nanoparticles is due to the reduction of infestation by *Tuta absoluta.* Also, it could be attributed to less feeding of larvae on different plant parts (leaves, stem, and fruits), which reduces stress on plants, make them healthier (Mahlangu et al. 2022). According to Neves et al. (2006) unhealthy leaves cause a stressed and damaged photosynthesis system due to a lower intake of the photosynthesis active flux.These results agreed with Merghany et al. (2019), who found that magnesium and copper chlorophyllin positively affected chlorophyll content and the total yield of cucumber and onion plantsZinc, manganese and magnesium are essential micronutrient that improves enzyme reactions, and it can enhance the effectiveness of photosynthesis and improve the antioxidant activity of tomato plants (Faizan and Hayat 2019). Additionally, Zn helps plants produce auxin, develop cell walls, and reproduce more cells when combined with boron (Patil et al. 2008). Tomato yield was increased by a foliar application of nano zinc due to its defined surface area, potential surface energy and highly solubilty, which increased its uptake (Ahmed et al. 2021).Yield enhancement in the

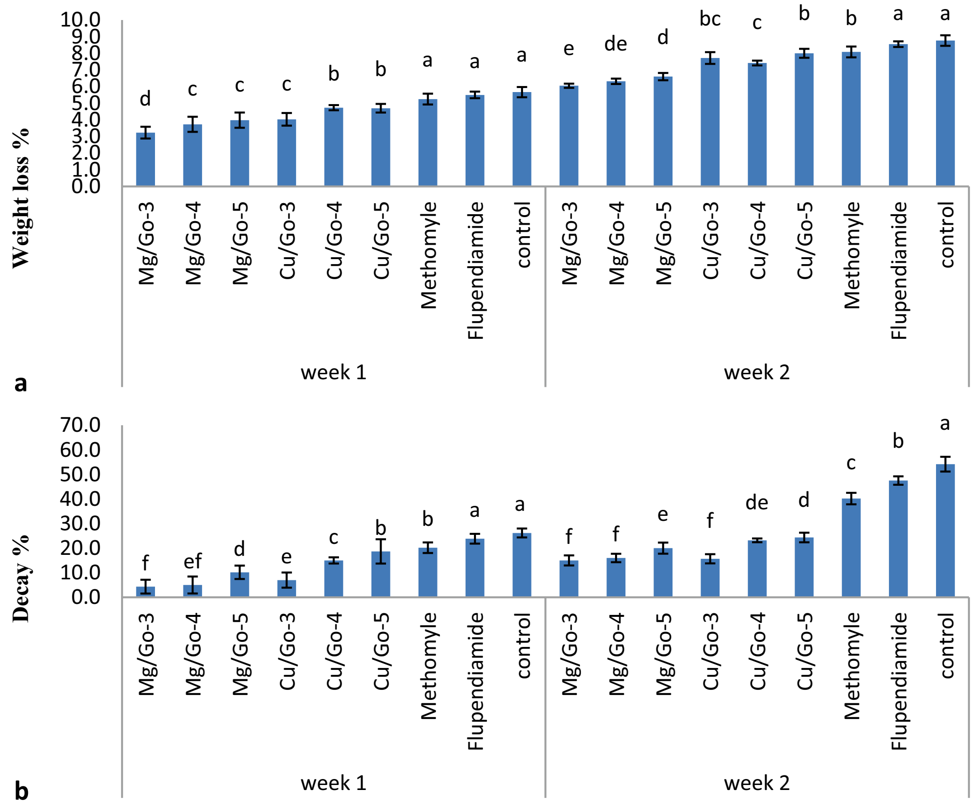

Fig. 8 Effect of nancomposites including graphene oxide (MgGo and CuGo) on weight loss % (**a**) and decay% (**b**)

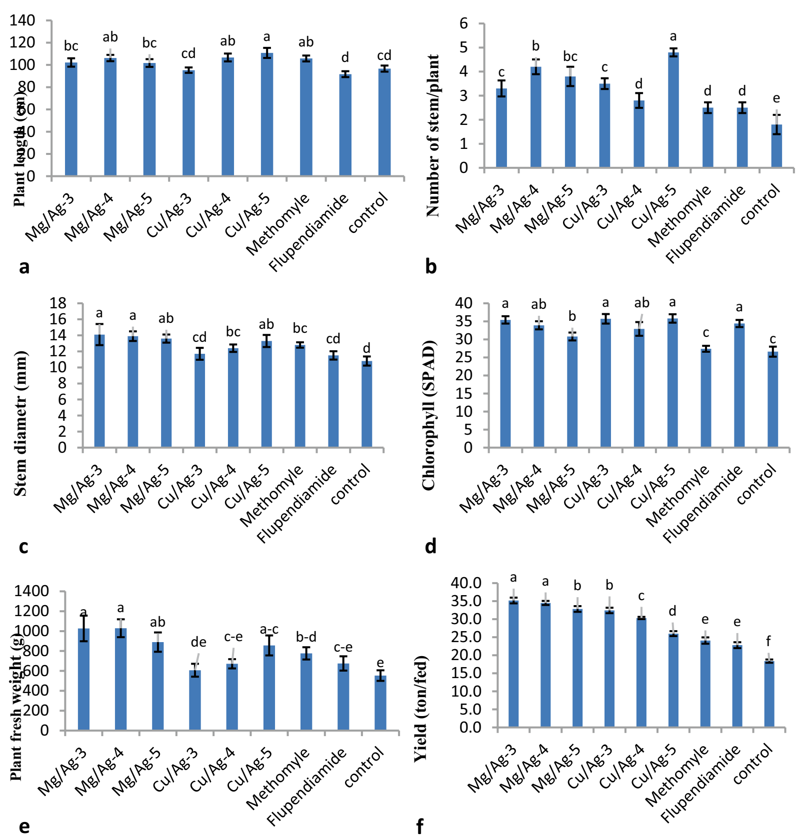

Fig. 9 Effect of nancomposites including silver (MgAg and CuAg) on plant length (**a**), number of stem/ plant (**b**), stem diameter (**c**), leaves chlorophyll content (**d**), plant fresh weight (**e**) and total yield (**f**)

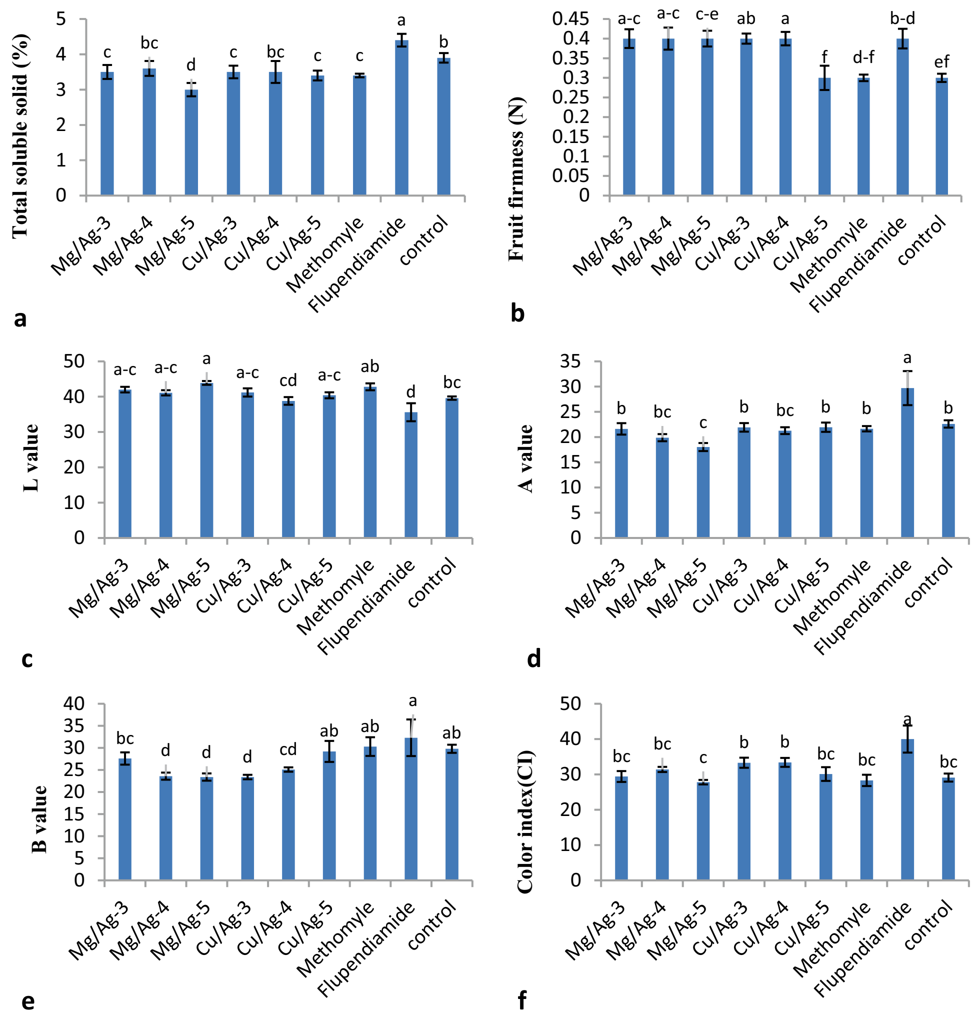

Fig. 10 Effect of nancomposites including silver (MgAg and CuAg) on TSS (**a**), fruit firmness (**b**), L value (**c**), a value (**d**), B value (**e**) and color index (**f**)

highest concentrations (10^{-3} and 10^{-4}) of magnesium chlorophyllin due to its important role in photosynthetic and enzyme activation (Hermans et al. 2013). Also, these concentrations recorded the highest reduction% of *Tuta absoluta* (Tables 2 and 3). There was a positive correlation between reduction percentage and plant length (0.405*), number of stem/plant (0.518**), stem diameter (0.473*), chlorophyll content (0.487*), plant fresh weight (0.418*), fruit TSS (0.411*), and yield (0.418*). Weight loss and decay % are the most important parameters of fruit storability. Magnesium and copper chlorophyllin treatments (10^{-3} – 10^{-5}) recorded the lowest percentage of fruit weight loss and decay during the storage of two weeks at 10 °C. Chlorophyllins are porphyrins that are semi-synthetic and are made from chlorophyll. Porphyrin molecules are interesting because they are antimicrobial. The molecules produce singlet oxygen and free radicals that are harmful to the majority of living cells when triggered by visible light in the presence of air (Romanova et al. 2003). The positive effect of magnesium and copper chlorophyllin on reducing weight loss and decay rates is due to their action as coatings on the fruit surface and antimicrobial effect (López-Carballo et al. 2008).

In our results, graphene oxide (GO) treatments increased plant length, chlorophyll, TSS, stem diameter, number of stems, and fruit yield. These results were agreed with Younes et al. (2019) who studied the effect of graphene nanosheets (GNS) at 0.1, 0.2, and 0.3 GNS g L − 1 on agro-physiological traits of pepper and eggplants and the biosafety of leaf ultrastructure. They found that plants treated with all concentrations of GNS had increased plant length, fruit yield, and chlorophyll a, b without any cytotoxic effect on leaves. This increase may be due to GO acting as a cell growth factor capable of stimulating cell division and proliferation (Ruiz et al. 2011). Also, GO may impact photosynthesis in leaves by directly interacting with chloroplasts, which store sugar in cells and leaf pores that GO may pass through (Gao et al. 2020). The yield promotion in plants treated with graphene is due to the localization of graphene in the chloroplast, which enhances the photosynthesis process and leads to

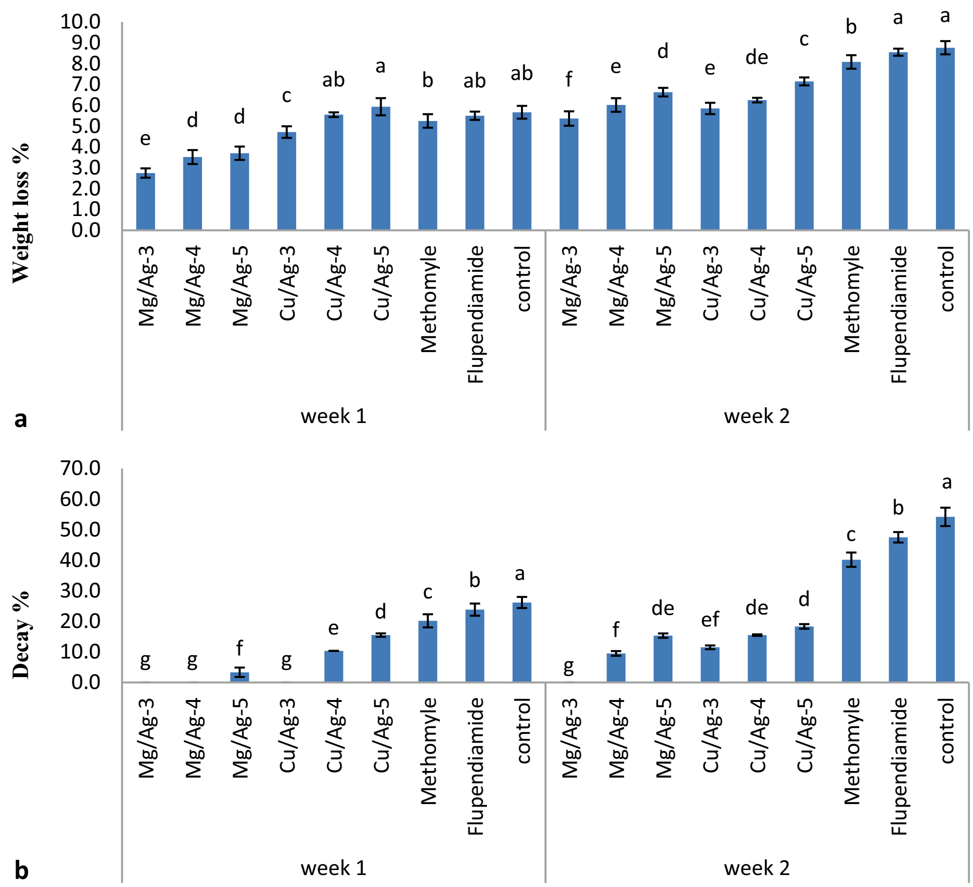

Fig. 11 Effect of nancomposites including silver (MgAg and CuAg) on weight loss% (**a**) and decay% (**b**)

increased growth and yield productivity (Koch 2004). Graphene treatments improve yield productivity by increasing the reduction % of *Tuta absoluta* in these plants. The yield of tomatoes was positively correlated (0.886**) with the reduction %. Fruit color index and A value were not affected by graphene treatments compared to control treatment. Tomato is a perishable fruit and fast decay. Fresh product water loss results in undesirable metabolic changes in cells, which activate enzymes, speed up senses, and reduce the nutritional value of the fruit (Shehata et al. 2021). Grapheme treatments decrease tomato fruit's loss and decay percentage due to their impact as a potent antifungal (El-Abeid et al. 2020). The foliar application of either Cu-Ch/Ag or Mg-Ch/Ag at 10^{-3}, 10^{-4}, and 10^{-5} enhanced growth parameters compared to the control treatment. These results were in agreement with Guzman-Baez et al. (2021) stated that the length and number of roots in tomato seedlings increased when plants were treated with silver nanoparticles. Salachna et al. (2019) and Casillas-Figueroa et al. (2020) also reported that silver nanoparticles are a stimulator of plant growth and metabolism. In many crops, nanoparticles greatly improved seed and yield, chlorophyll content, grain yield, and nitrogen use efficiency by increasing the absorption and transportation of NPK (Jhanzab et al. 2015). Tomato seedlings treated with 20 ppm of silver nanoparticles enhanced plant length, number of branches, number of leaves, root length, and weight

Table 7 Correlation coefficients amongst reduction percentage of *Tuta absoluta* and vegetative growth parameters, yield and storability

Parameters	Photosensitizers	Silver nanomaterials	Graphene oxide nanomaterials
Plant length	0.405*	443*	-
Number of stem/ plant	0.518**	685**	741**
Stem diameter	0.473*	636**	456*
Chlorophyll content	0.487*	645**	563**
Plant fresh weight	0.418*	562**	-
Total soluble solids	-0.411*	-	-
Fruit firmness	-	-	453*
Total yield(tone)	418*	842**	886**
Weight loss% (week1)	-448*	-533**	-723**
Weight loss% (week2)	-531**	-751**	-682**
Decay % (week1)	-553**	-764**	-705**
Decay % (week2)	-546**	-842**	-870**

* correlation is significant at 0.05 level

** corrlation is significant at 0.01 level of fruit yield (Abbas 2020). The effects of nanoparticles can vary according to the size, shape, and concentration of the nanoparticles, as well as age and species of plants (Rico et al. 2011). Metwally et al. (2021) sprayed maize plants with different concentrations of silver nanoparticles and found that leaf chlorophyll content was increased by increasing concentration. The increase in plant growth was mediated by plant growth regulators such as gibberellin and cytokinin, which are involved in cell division and elongation (Stampoulis et al. 2009; Stepanova et al. 2007). The use of nanoparticles (NPs) in the agricultural sector might benefit the field in terms of diseases and developing resistance to diseases and insects, which lead to increase, yield (Mousavi and Rezaei 2011). The foliar application of silver increased tomato storability due to silver's inhibitory effect on the activity of ethylene, which reduces flower abscission and fruit ripening (Uthaichay et al. 2007). According to several authors, phytohormones like auxin (IAA), ethylene, and abscisic acid control the abscission process (ABA). The former triggers the abscission process by promoting the manufacture of ethylene, whereas auxin effectively delays the abscission process by decreasing the sensitivity of cells to ethylene (Mishra et al. 2008).

Conclusion

In this study two photosensitizers (Copper and Magnesium chlorophylline) and two nanocomposites over two photosensitizers (MgAg, MgGO, CuAg and CuGO) were firstly evaluated to reduce the population of *Tuta absoluta* in tomato fields compared to two commercial insecticides (flupendiamide, and methomyl). Aso, the effect of photosensitizers and nanocomposites on tomato growth, yield and storability was studied. Three concentrations (10^{-3}, 10^{-4}, and 10^{-5}) from each treatment were used. The results indicated that reduction percentage increased by increasing the concentrations. When loaded, nanomaterials over photosensitizers were more effective than photosensitizers alone. No newly found tunnels after seven days of spraying with all concentrations of two photosensitizers. While the complete reduction percentages in the number of tunnels were found in all concentrations of nanocomposites after 5 and 7 days of spraying. The positive correlation was found between reduction % and plant growth parameters, yield and storability (weight loss and decay%). Our results suggested that all treatments with photosensitizers and nanocomposites can be used effectively as alternative insecticides for controlling *Tuta absoluta.*

Author contribution Sayeda S. Ahmed: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Software, Writing – original draft, Writing – review & editing. Mahmoud H. Abdel Kader: Conceptualization, Funding acquisition, Project administration. Mahmoud A. M. Fahmy: Conceptualization, Data curation, Methodology & Writing. Karima F. Abdelgawad: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Software, Writing – original draft, Writing – review & editing.

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Data availability The data that support our results are available on request from the corresponding author.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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