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Ethology of Sunn-pest oviposition in interaction with deltamethrin loaded on mesoporous silica nanoparticles as a nanopesticide

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Abstract

Background: Wheat is one of the main food for around 2 billion people worldwide. Among the biological stressors, *Eurygaster integriceps* Puton is a damaging insect in wheat and barley fields, which harms them both quantitatively (by overwintered adults) and qualitatively (by instar nymphs). The ovipositional and the new generation's production control are pivotal approaches to control the severe damages of Sunn-pest.

Methods: In this study, to enhance the deltamethrin effectiveness while reducing its required dosage and also reducing the adverse health and environmental impacts, a novel MSN-based deltamethrin formulation was prepared and evaluated based on the laying-eggs number and oviposition behavior. To this, deltamethrin was loaded on KIT-6 mesoporous silica nanoparticles and characterized using SEM, TEM, and TGA analysis, and the insect potential of deltametrin@KIT6 was then evaluated.

Results: The results showed that there might be differences between the treatments (KIT-6, deltamethrin@KIT-6, deltamethrin commercial formulation, and water as a control) in terms of the insect control via the laying-egg and next-generation prevention. The results showed that KIT-6 and deltamethrin@KIT-6 could reduce the oviposition rate compared to water as the control. Deltamethrin@KIT-6 not only caused the less oviposition done but the eggs were scattered and the batch of eggs did not have a uniform-shape similar to the control mode. The deltamethrin@KIT-6 nanopesticide could increase the pesticide effectiveness by reducing the Sunn-pest's oviposition and nymphal population and subsequently decreasing the damage caused by them. So that the concentrations of 10, 25, and 125 mg L^{-1} of deltamethrin@KIT-6 reduced oviposition by 63.24%, 66.11%, and 67.62%, respectively, compared to the control group. On the other hand, descriptive observations showed that another possible tension is created through insect eggs deposition on the boundary layer of leaves.

Conclusion: The MSN-based nanoformulation could be effectively considered to control the next-generation population density of Sunn-pest.

Keywords: Deltamethrin, Mesoporous silica nanoparticle (MSN), Pesticide delivery system (PDS), Sunn-pest, Oviposition behavior, Wheat

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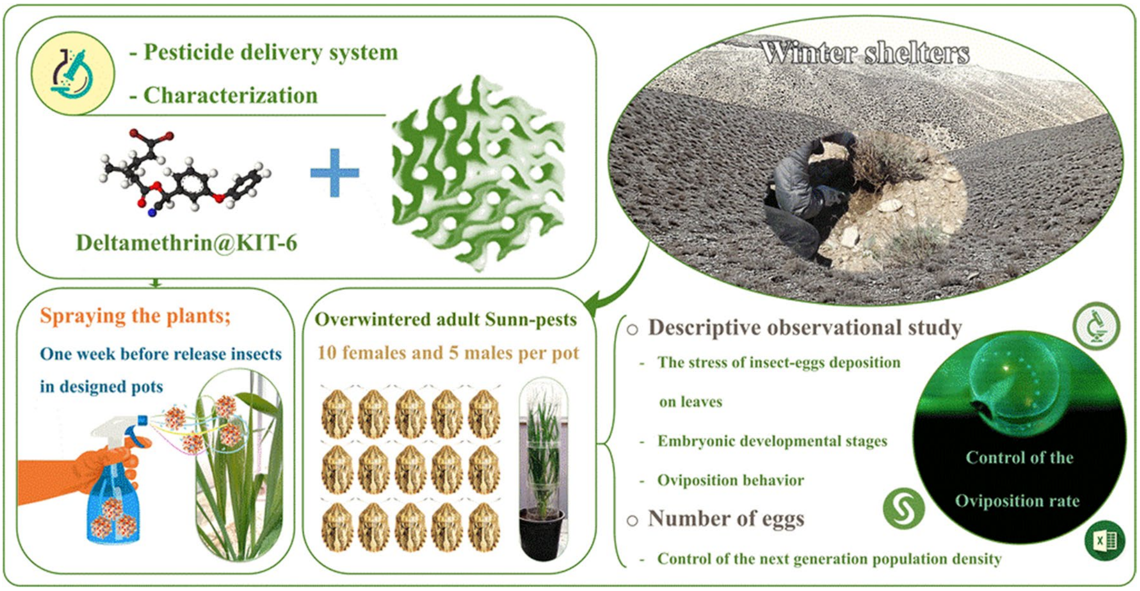
Graphical Abstract



Background

One of the socio-economic, political, and scientific challenges in ensuring global food security of the modern world is the continually growing human population estimated to reach 9 billion people by 2050. Therefore, the need to feed an increasing world population and respond adequately to climate change's effects must be urgently considered, and scientists must seriously rethink agriculture for the twenty-first century [1]. After the main turning points that existed in global food supply and increased productivity in agriculture (including the improvement of arable crops and chose good-quality plants with high yields, the introduction of chemical fertilizers, pesticides, and herbicides, "Green Revolution" [2] and obtaining the new varieties via traditional breeding, and finally the use of molecular biology and biotechnology-based tools [3]), it is anticipated that with the introduction of emerging technologies, such as agricultural nanotechnology industry [4], we will witness another milestone in this field.

A major grain food crop species grown on more than 200 million ha [5] and with a global production of about 765 million tons [6] is wheat whose domestication coincided with the start of agriculture history and development and has fed, and continues to feed a large part of the world's people directly over the centuries [7]. Therefore, it plays a very important role in ensuring universal food security program. Considering population growth and low productivity due to environmental biotic/abiotic tensions, by 2050, global wheat demand is predicted to increase by 60% [8]. Among the biotic stressors, insect pests are a significant constraint to wheat production globally. The point is that insect infestations' threat has increased due to irregularly rapid changes in temperature, unpredictable rainfall patterns, and increased CO_2 concentrations in the environment. These changes have altered insect biological behavior, making them invasive, more unpredictable, and bothersome to manage [9]. Given the importance of this issue, scientists have studied the mechanisms of insect immunity to pesticides and alternative methods as a strategy [10]. Not only do they have direct adverse effects on crop growth but they also threaten sustainable wheat production with their substantial impact on pest behavior and management. Sunn-pest, *Eurygaster integriceps* Puton (Hemiptera: Scutelleridae), is one of the chief biotic restrictions to wheat production in Central and West Asia, North Africa, and Eastern Europe. Its economic damage is about 42 million USD for the region, and this is just the cost of the chemical pesticides used to manage it [11]. Estimated damage to the wheat product caused by a high invasion of Sunn-pest is 20–30% in barley and 50–90% in wheat [12, 13]. This economic blow can reach 100% in the absence of pest control [14]. In Iran only, the qualitative and quantitative damage of Sunn-pest exceeds 9 million tons in wheat and barley [15].

Sunn-pest adults remain inactive in the high altitude overwintering sites for 9–10 months (summer, autumn, winter, and even part of the spring) in diapause and use the food stored in their bodies and then migrate back to the fields and become active in spring and begin to feed. Usually, after falling from winter shelters to farms, Sunn-pests produce one generation annually and peel five times during each generation (5th nymphal ages) to become a new generation of adult insects. Sunn-pest damage to wheat is quantitative and qualitative. Overwintered adults inflict only quantitative damage, while the damage of nymphs and new generation of adult insects includes both quantitative and qualitative aspects. The greatest amount of falling the overwintered adult pests in wheat fields is in the tillering stage. The amount of their feed in each year is related to the storage content of the previous year's nutrition. This phenomenon is very important that will play a fundamental and decisive role in the laying-eggs and producing the next generation of the pest. The longer period between the falling overwintered adults in wheat fields and the onset of oviposition will have an equal effect on the Sunn-pest population in the following year as well as on the pest ruin's ability in the new stage of infestation. Therefore, farmers may have to spray pesticides in the fields several times during this period to reduce Sunn-pest (adults, nymphs, and new-generation insects) damages [16, 17].

Using of chemo-insecticides has been the main approach for Sunn-pest management. Annually, about 4 million acres are sprayed in the Near East and West Asia at the cost of ~ $150 million [18–20]. Deltamethrin, lambda-cyhalothrin, fenitrothion, and trichlorfon are some of the major registered insecticides used against Sunn-pest in Iran [17, 21]. However, deltamethrin pyrethroid insecticide has recently shown the more desirable lethal effect and has a lower dose, and is cheaper than other formulations [21, 22], but it is a high-risk pesticide to human health and the environment [17, 23].

Recent progress in nanotechnology creates hope for a sustainable future in agriculture and food sciences [24]. Based on the background of nanoencapsulation techniques in the delivery of fertilizers and pesticides [25, 26], scientists expect to improve agro-systems to diminish losses caused by biotic and abiotic stresses and increase yield. Using nanomaterials has introduced a new generation of pesticides with the ability to slow-release while being environmentally compatible, having a more significant impact on yield production [4]. Silicon and its derivatives have been studied recently due to their biocompatibility, versatility, and chemical stability [27, 28]. Mesoporous silica nanoparticles (MSNs) that can be easily functionalized with molecules for effective loading and delivery are stable due to their Si–O bonds [29] and also have adjustable porosity and pore size [30] through an inexpensive and straightforward synthesis [31]. In the agricultural sector, silica nanoparticles were observed to be applied in UV-B stress [32], heavy metal detoxification [33], salinity stress [34], dehydration [35], etc., and MSNs seem to be promising for sustainable agriculture [36, 37]. Nanoparticles can be easily dispersed and are appropriate for impregnation in aqueous suspension. In the last few years, they have been used widely to encapsulate and release drugs and many chemicals in a controlled and predictable order. Various types of inorganic NPs have been employed to deliver DNA and genes [38, 39]. Since Mobil's discovery of MCM-41, research and development of MSNs has gained universal interest [40]. Mesoporous materials with diverse meso-structures have been designed and shown to be promising candidates in adsorption, immobilization, and drug delivery because of their unique properties, such as large surface area (~ 1000 m^2 g^{-1}), large pore volume (~ 1 cm^3 g^{-1}), controllable pore size (2–50 nm), very thin particle size distribution, and open-pore structures [41]. One of the early studies to use these nanomaterials in agriculture and pesticides was the effective loading of imidacloprid on porous silica nanoparticles to control termites [38]. Therefore, due to the severe damage of Sunn-pest, the pivotal role of oviposition in the damage of nymphs, and the next generation to yield, which will also lead to repeated sprayings, we used nanoencapsulation to help reduce this damage and examined the effects of only once spraying with deltamethrin loaded in the KIT-6 on the number of eggs and the oviposition behavior under the greenhouse conditions, 1 week before release of insects in designed pots.

Material and methods

Materials

Technical/analytical grade deltamethrin and deltamethrin emulsion EC 2.5% were provided from TAGROS (in India) and Mahan (in Iran) companies, respectively [42, 43]. Tetraethylortho silane (TEOS) and Ploronic P-123 were obtained from Sigma-Aldrich.

Characterizations of nanomaterials

The particle size distribution and surface charge of samples were achieved by a dynamic light scattering instrument (DLS, Brookhaven, USA) and nano-sizer (Zeta seizer, Nano ZS90, Malvern, UK), respectively. To this, a mixture of the solid nanomaterials in deionized water dispersed using an ultrasonic bath for 10 min was used. The morphology and size of nanomaterials were taken by scanning electron microscopy (SEM, Hitachi S-4800 II, Japan) and transmission electron microscopy (TEM, Hitachi H-7650, 80 kV, Japan). For preparation the TEM and SEM samples, the nanoparticles were simply dispersed on the grids using suitable solvents, such as ethanol, air-dried, and used for imaging. Nitrogen sorption isotherms of NPs were taken using a BELSORP mini-II (Microtrac Bel Corp Company, Japan) apparatus at liquid nitrogen temperature (77 K), as a volumetric adsorption measurement instrument. To measure the specific surface area, the Brunauer–Emmett–Teller (BET) method and, for calculating the pore-size distributions, the nitrogen isotherms by the Barrett–Joyner–Halenda (BJH) method were applied. The sample was placed under vacuum at room temperature for 24 h before surface analysis. The topological characteristics of materials were observed using atomic force microscopy (AFM, DME-Ds95-50, Denmark) in ambient conditions at room temperature. To this, a sonicated solid nanomaterials mixture in deionized water was dispersed on the grids. The measurements were performed using a UV–Vis double-beam spectrophotometer (UV-3100 PC, Shimadzu).

Preparation of deltamethrin@KIT-6 and preparation of samples

The KIT-6 nanoparticles were prepared according to the previously reported method [44]. After that, a solution of 150 mg of deltamethrin in acetone was added to a mixture containing 500 mg of KIT-6 and deionized water (DW), and the later mixture was stirred overnight. The resulting solid was then centrifuged, washed thoroughly with DW and acetone, and dried in a vacuum oven to give deltamethrin-loaded KIT-6 mesoporous silica nanoparticles (deltamethrin@KIT-6). In the following, the amount of deltamethrin for deltamethrin@KIT-6 was determined 25 mg of deltamethrin per 100 mg of KIT-6 by elemental analysis. To prepare the deltamethrin nanopesticide samples for use, the required amounts of deltamethrin@KIT-6 were dispersed in a combination of water and tween 80 (100:0.5, respectively), and sonicated for 10 min. Water, KIT-6, and commercial deltamethrin EC2.5% were evaluated as negative, blank, and positive controls, respectively.

Wheat planting

Monotone seeds were planted to create a uniform condition in culture (same planting depth and growing media containing perlite and coco-peat equally) in seedling trays (along with an irrigation step with basic NPK fertilizer). Due to the growing season and better simultaneous control between morpho-physiological wheat development (here is the tillering stage) to interactive appraisements with the Sunn-pest, which in natural conditions is limited to a specific time, the Parsi spring cultivar (does not need to vernalization) was used. After emergence and growth, two-leaf seedlings with the same morpho-phenological appearance conditions were selected and transferred to steady dimensions (4 kg) pots with similar autoclaved sterile substrates containing farm soil and coco-peat in a ratio 2:1, and three plantlets per pot in the form of an equilateral triangle's vertices. The pots were also embedded with a transparent plexiglass cage that is adjusted to fit the height of the plant and has small air vents on each cage. About 40 mg kg^{-1} of phosphate fertilizer with triple-superphosphate (TSP) source was placed under and around the seedlings during transfer. Base fertilizer (NPK fertilizer in the ratio of 20:20:20, with a concentration of 2 g L^{-1}) was also used in the tillering stage with irrigation water in the same way for all treatments. The greenhouse was set with temperature conditions of 26 ± 3 °C (inside the chambers) and natural light (approximately March to June) conditions.

Collecting the overwintered adult insects and release in planted pots

In spring, with the increase of biological activity and breaking of Sunn-pest's diapause, they migrate from wintering habitats to the wheat fields. The time of this move to cereal fields differs according to climatic conditions and the type of rain-fed or irrigated system [45]. One of the distinct points among irrigated wheat cultivation areas regarding time, frequency, ecological and temperature conditions to start Sunn-pest's falls is the Ghara-Ghaj mountain [46] and its surrounding slopes, plains and fields, which is one of the primary Sunn-pest' summer/winter shelters. According to the statistics of the average daily temperature (12–15 °C) and investigating the trend of daily temperature increase (at least five days before) to reach the average migration temperature [45] and the onset of Sunn pest activity, the probable date of insects invasion was predicted. Therefore, based on assessing the daily humidity and rainfall condition in the region [47] as well as daily coordination with an on-site plant protection team, the appropriate time to dispatch the insects' collection team was selected. Overwintered adults of Sunn-pest were collected from the overwintering sites at Ghara-Ghaj Mountain, Varamin region, Tehran, Iran in January–February. The insects were gathered from under the Milkvetch (Astragalus spp.), Mugworts (Artemisia spp.), and Gramineae plant bushes and transferred to the laboratory in special boxes containing some moist soil and straw.

Experimental design for the study of oviposition–nanopesticide dual interaction

To assay and compare deltamethrin@KIT-6 with bulk analogs, the experiments were performed in a completely randomized design with three replications and four treatments, including the control (water), KIT-6 (blank), deltamethrin@KIT-6, and commercial deltamethrin formulation. Experimental treatments were used at three concentrations of 10, 25, and 125 mg L^{-1} of deltamethrin.

Before applying, the soil surfaces of the pots were covered with plastic insulation to prevent the contamination of pot soil and penetration of treatments into the plant root system. Then 60 mL of treatments (20 mL per plant; the required volume was assessed in a preliminary test) was sprayed on all shoot system parts of the plant, for each pot. In the control group, the same volume of water was sprayed on wheat bushes. After collecting Sunn-pests and with an initial weight selection for more excellent uniformity, 15 adult insects (10 females and 5 males) were assigned to each pot. One week after spraying the plants, the collected insects were released in each chamber, and 24 h after being exposed to the treated plants the insects were removed from the pots, and the laying-eggs behavior in interaction with the treatments, including the number of eggs and descriptive observations, were assayed.

Statistical analysis

Analysis of variance of the oviposition's data was performed in a completely randomized design and the Tukey statistical test at 5% was used to determine significance ranges. SAS 9.4 and Excel software were used to analyze the data and graphing, respectively.

Results

Nanoencapsulated pesticide characterization

Given the importance of active ingredient stability before and during pesticide use as well as during the pest control period on the leaves, herein, deltamethrin nanoformulation based on mesoporous nanocarriers as an acceptable approach was proposed. The prepared nanocarrier and deltamethrin@KIT-6 nanopesticide were characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), dynamic light scattering analysis (DLS), BET/BJH surface area and pore analysis, and Fourier transform infrared (FTIR) (Figs. 1, 2 and Table 1).

SEM and TEM images of KIT-6 and deltamethrin@KIT-6 are illustrated in Fig. 1a–d. These results showed that deltamethrin@KIT-6 particles had a regular three-dimensional porous structure network and they were spherical (Fig. 1). The AFM imaging of deltamethrin@KIT-6 and KIT-6 is demonstrated in Fig. 1e, f. The morphology of both nanomaterials has shown a uniform morphology with high dispersity. The average particle diameter of deltamethrin@KIT-6 was slightly larger than that of KIT-6 (300 nm vs 120 nm for KIT-6) determined using DLS in Fig. 1g, h.

The multiple-point Brunauer–Emmett–Teller (BET) technique was used to calculate the specific surface area. Based on the adsorption branch, the Barrett–Joyner–Halenda (BJH) technique was used to calculate the pore size distribution. The N_2 adsorption–desorption isotherm experiment indicated that the KIT-6 has a large pore volume and surface area. According to the results (Table 1), the surface area, pore volume, and pore size decreased after surface functionalization. The calcined KIT-6 has a BET surface area of 850.5 $m^2\ g^{-1}$ (BJH pore diameter: averaged 7.2 nm; total pore volume: 1.51 $cm^3\ g^{-1}$) [44]. The surface area, pore volume, and pore size of deltamethrin@KIT-6 sample decreased in comparison to the pristine KIT-6. These textural findings revealed that the deltamethrin was found inside of the pores of KIT-6 nanocarrier.

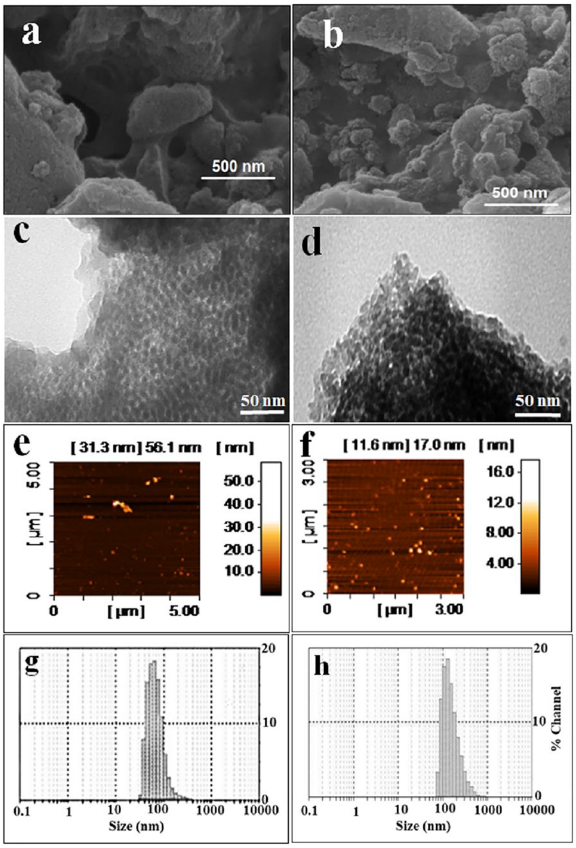


Fig. 1 SEM (**a**, **b**), TEM (**c**, **d**), AFM (**e**, **f**) images, and DLS (**g**, **h**) images of KIT-6 and deltamethrin@KIT-6, respectively

Based on the results of XRD of KIT-6 and deltamethrin@KIT-6 similar patterns were shown, including a strong diffraction peak and also two weaker diffraction peaks with Miller indices (211), (220), and (332), respectively, which are specific to nanoporous materials. Also in the FTIR results, strong peaks in the 1100 and 814 cm^{-1} regions are related to the asymmetric and symmetric Si–O–Si tensile. The band in the 476 cm^{-1} regions is related to the bending vibration of Si–O. The

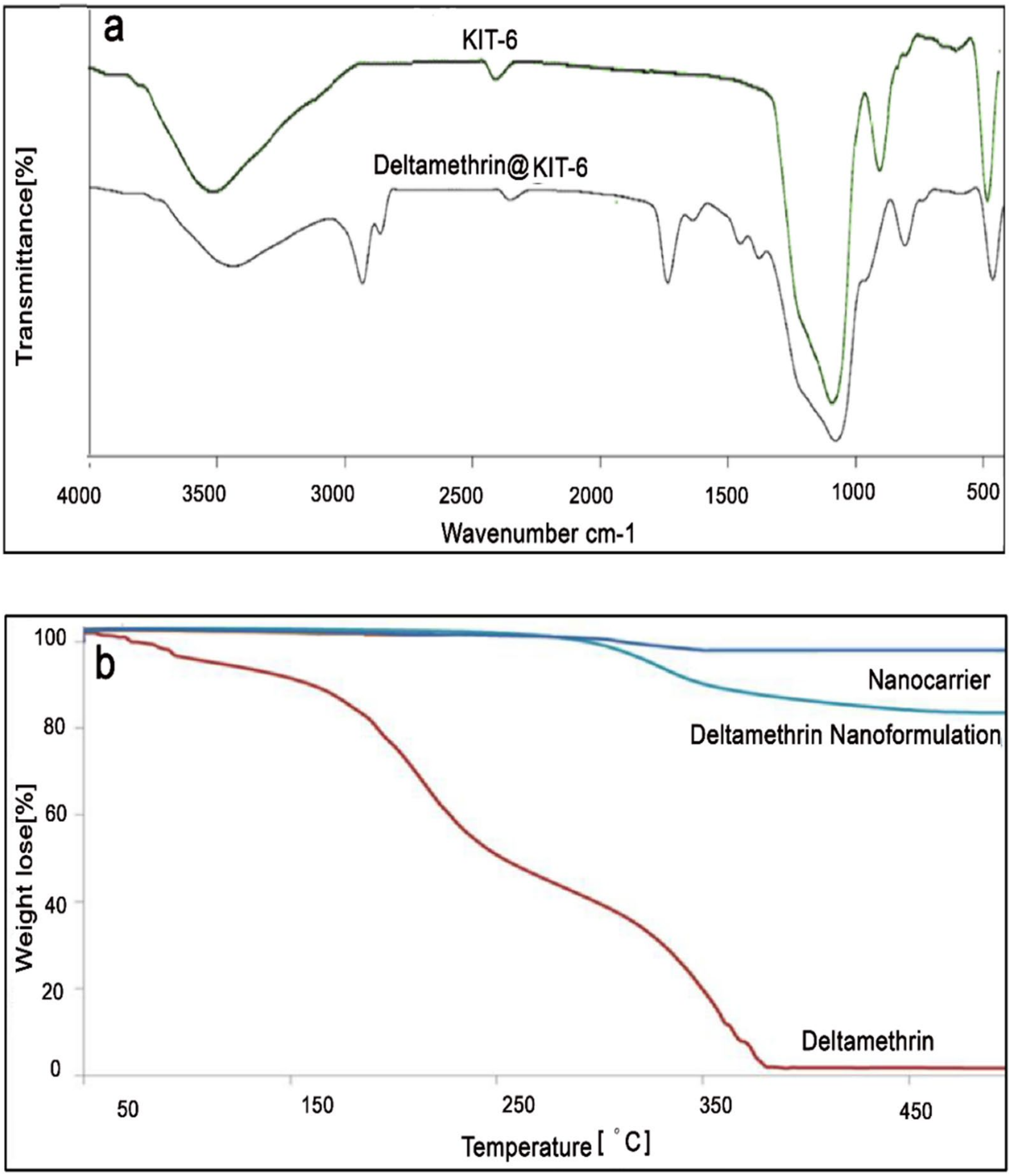


Fig. 2 FTIR spectrum (**a**) and TGA analysis (**b**) of materials

Table 1 The results of nitrogen adsorption/desorption for nanomaterials

NPs	S_{BET} (m^2g^{-1})	V_{total} ($cm^3\ g^{-1}$)	Pore diameter (nm, BJH)
KIT-6	850.5	1.65	6.5
Deltamethrin@KIT-6	525.6	0.689	3.5

band of the 3500 cm^{-1} regions is related to the tensile bands of O–H groups related to free silanols (Fig. 2a).

In order to achieve the optimal loading conditions as well as to estimate the encapsulation efficiency (EE %), several experiments (in terms of reaction time and stirring speed) were performed (Table 2). After various experiments, the optimal conditions obtained, including 12 h and stirring at 500 rpm, the EE level was equal to 100%. The thermogravimetric analysis (TGA) curve shows the active substance deltamethrin, which has two failures (Fig. 2b): one at 195 °C, which is about 58.5% reduction in mass, and the other at 220 °C, about 42.5%

Table 2 The optimization of loading reaction condition at room temperature

Entry	Reaction time (h)	Stirring speed (rpm)	EE (%)
1	1	250	30
2	1	500	30
3	4	250	52
4	4	500	60
5	8	250	75
6	8	500	83
7	12	250	90
8[a]	12	500	100
9	16	250	100
10	16	500	100

[a] Based on these results, entry 8 was determined as the optimal condition. With this protocol including the reaction time of 12 hours and 500 rpm, EE% is equal to 100

of the mass of the material is lost. The thermal curve of the nanocarrier also shows only a 7% decrease. This means that in the nanoformulation curve, the amount of deltamethrin in the nanopesticide is 2.5 mg per 100 mg.

Oviposition behavior in interaction with the nanopesticide

Number of eggs

The highest amount of oviposition (an average of 197 eggs per pot; statistical group A) was in control (*i*), which indicated the existence of favorable conditions for mating and laying of insects compared to other treatments. However, the oviposition rate in the KIT-6 treatment at the lowest concentration (*ii*) was grouped with the control (*i*), but a considerable decrease was caused by an increase in the concentration, which may have been related to its silica-based nature. Also, the lowest amount of oviposition was observed at the highest concentration of commercial pesticide (*iv*) (Fig. 3). Well as comparing different concentrations of treatments in laying-control and consequently preventing damage of the Sunn-pest eggs, different ages of nymphs, and new-generation adult insects to wheat, it is shown that this deltamethrin@KIT-6 could reduce dose combined with the increase efficiency of deltamethrin as pesticide (the same results in different concentrations).

Descriptive observations

Descriptive observations to answer questions, such as "What," "Where," "When," and "How," play a fundamental role in the scientific view of biological phenomena and their behavioral discovery. Data/technology-driven studies are not merely alternatives to hypothesis-based researches in knowledge discovery, but are repetitive and complementary partners together [48–50]. During initial laboratory evaluations of insect behavior in pesticide bioassay, it was observed that in most oviposition, the insects deposited their eggs on the sidewall of dishes or places that were not in contact with pesticides, as opposed to normal, which was possible anywhere on plates (Fig. 4). Accordingly, the idea of

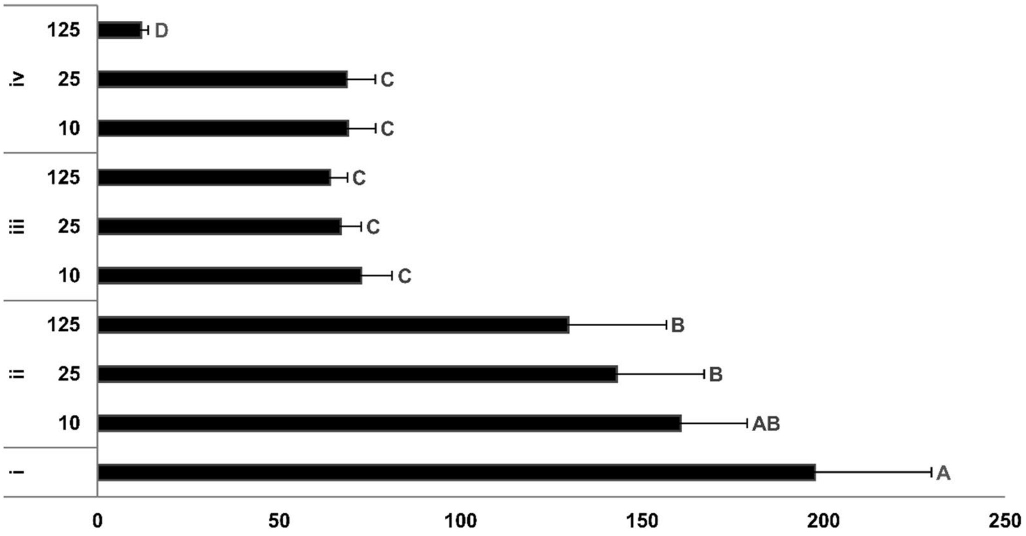


Fig. 3 Oviposition rate in different treatments—The vertical axis represents the different concentrations (10, 25, and 125 mg L^{-1}) of experimental treatments marked with Roman symbols: "**I**,""**ii**,""**iii**," and "**iv**" represent the treatments "control,""KIT-6,""deltamethrin@KIT-6," and "commercial deltamethrin formulation," respectively. The horizontal axis represents the average number of eggs (for ten females and five males in each pot) in different treatments. Values with the similar letters are not statistically significant (HSD = 0.05)

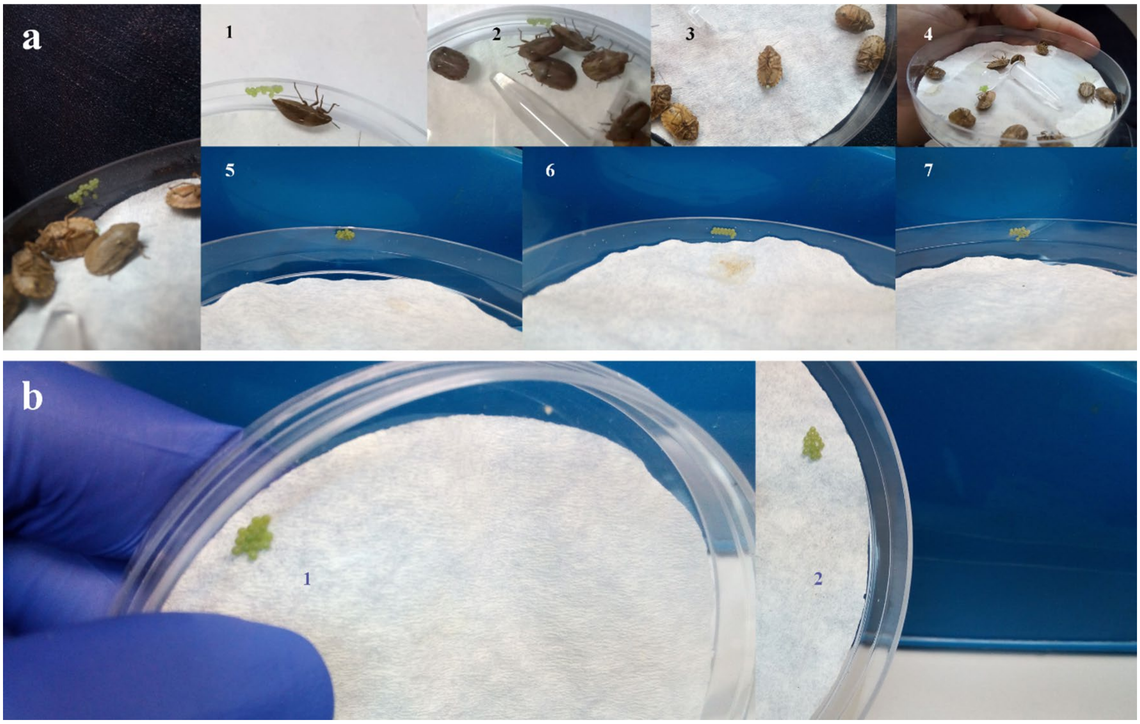


Fig. 4 Oviposition sites in the plates: in cases where the papers were contaminated with the treatments, laying-eggs was usually done on the wall, lid of a micro-tube or anywhere that was not in contact with the toxic materials ("**A**" items); under control conditions, oviposition was also observed on the bottom of the plates ("**B**" items)

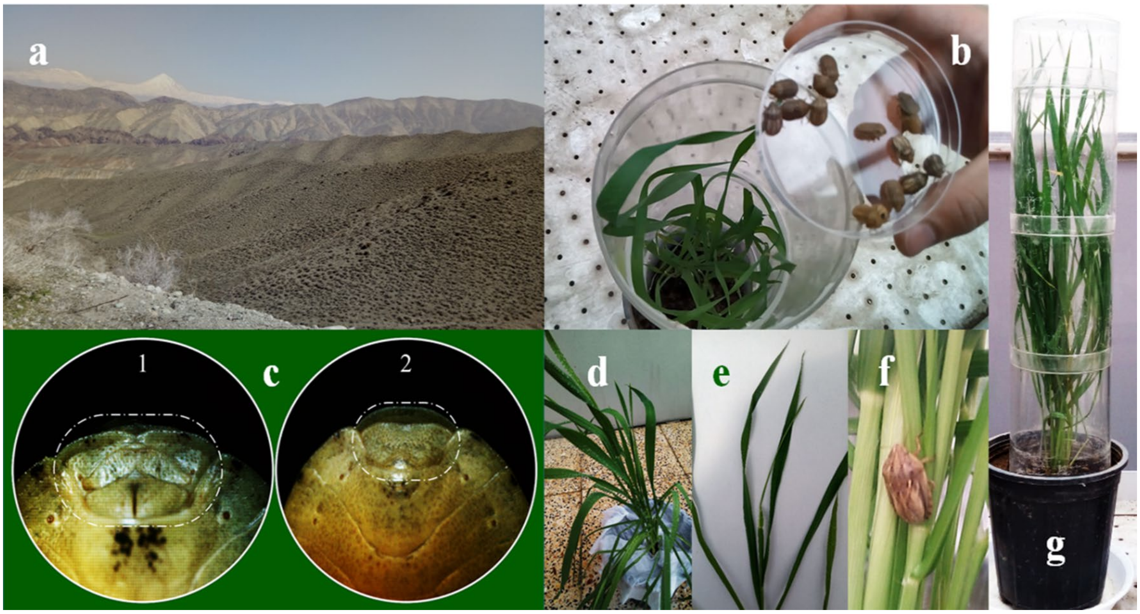


Fig. 5 Insects collecting and designing of the pots: slopes of the Ghara-Ghaj mountain (**A**), 15 insects (10 females and 5 males) per pot/plexiglass cage (**B**), Sunn-pest's abdominal morphology (**C**): 1 and 2 for female and male, respectively; a waterproof insulator was installed for the soil surfaces of the pots and then the necessary volume of treatments was sprayed to soak all surfaces of bushes (**D**), feeding insects from fresh leaves and stems (**E** and **F**), and designed pots (**G**)

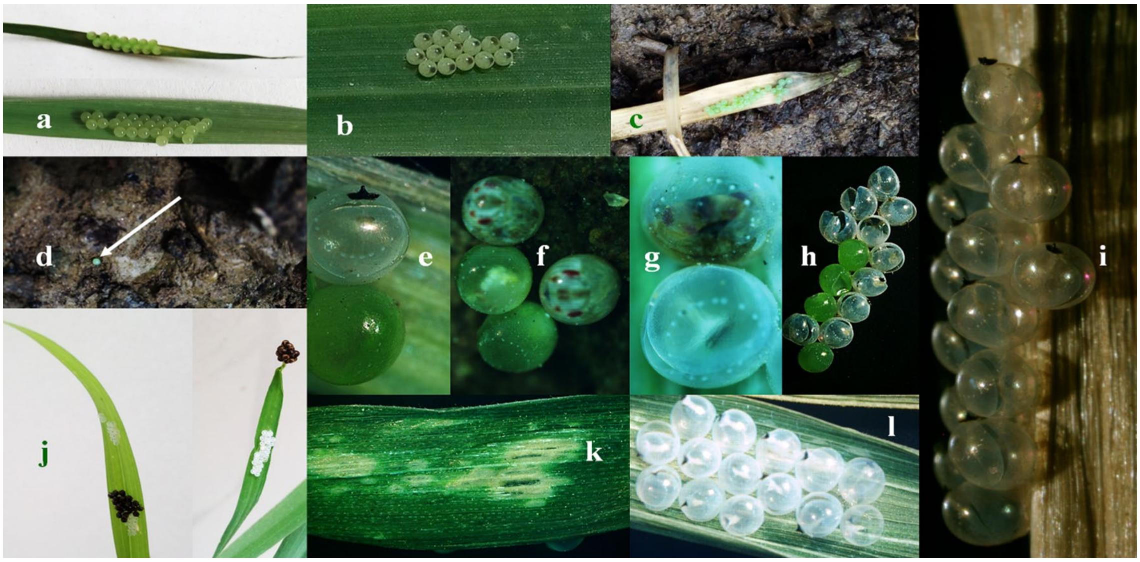


Fig. 6 Eggs in the pots: Uniform oviposition and simultaneously embryos development in control (**A**–**C**); uniform oviposition and simultaneously embryos development in control (**A**–**C**, **I**, **J**, **L**), and abnormality laying, uneven/inconsistent embryos development in pesticide treatments (**D**–**H**); eggs without embryos (**E**), uneven developmental stages of embryos (**F**), eggs with dead embryos (**G**); normal eggs hatching together in a bunch and accumulation of nymphs near the laying site (**I**, **J**); and egg deposition stress on the dorsal and upper surface of leaves (**I**, **K**, **L**)

conducting this study in greenhouse conditions was pursued. After collecting the Sunn-pests (Fig. 5A) and transferring them to the pots in the greenhouse under the designed conditions (Fig. 5B–G), the eggs were counted after 24 h of exposing the insects to the treated plants.

Laying-egg in the Sunn-pest begins immediately after mating (Fig. 5C). As we know, this insect typically lay fourteen eggs at a time, often in two parallel rows of seven and tangent together. In this study, uniform oviposition was observed in one bunch of sequences 14 or even 28 eggs on leaves (Fig. 6A–C), most often on fresh leaves or any position on control plants (Fig. 6J). Nevertheless, in other cases, especially those that had contained pesticide, oviposition was scattered form and heterogeneous in terms of number per bunch and different places on the plant, and sometimes just one egg was observed on the pot's soil and not on the plant (Figs. 4a_3 and 6D). This non-monotony was evident not only in the number but also in the lack of synchronization of egg embryonic developmental phases [51] in the pesticide and nanopesticide treatments. So that under normal conditions, the developmental stages were ostensible at the same time and one after the other (Fig. 6A–C); however, in the scattered eggs of other treatments, this developmental synchronicity did not exist, and different types of developmental stages were visible in a bunch of eggs. Even this lack of developmental uniformity may be associated with early fetal abnormalities in some eggs in a cluster, which may be due to either a defect in the mating pattern or a fault of embryo formation in response to the environmental conditions (Fig. 6E–H).

Another issue was the local change in the location of the nymphs-hatch from the eggs deposition site (on old leaf tissues); so that sometimes the first-instar nymphs, after embryo evolving and getting out of eggs shell, were socially located at or near the spot of the egg deposition site (usually at the tip of fresh-young leaves and stems tissue) (Figs. 5E, F and 6J). On the other hand, at the egg deposition sites on the plant and especially on the lower surfaces of the leaves (right behind the oviposition-site), the damage symptoms were observed, which is a kind of biological stress that it may reduce the photosynthesis and respiration or initiate/elicit defense response pathways in the wheat/pest. Following the oviposition places monitoring, it was observed that these leaves wither and dry earlier than the control (Fig. 6I, K, and L). These observations indicate the possibility of two direct and indirect plant defense pathways induced by insect laying-eggs as a separate biological stressor from the pest itself [52].

Discussion

In recent years, due to the increasing level of spraying against Sunn-pest (annually 2 million hectares in Iran) and the limited spraying equipment and time, it is necessary to use ULV (ultra-low volume) equipment, such as unmanned aerial vehicle (UAV)/drones or controlled droplet application (CDA) or micron-air, to find the most effective way to spraying [53] and or the less amount of pesticides and frequency of spraying (because of less phytotoxicity) and more targeted plant protection approaches. According to research on conventional foliar spraying, only 0.1% of the pesticide reaches the target and 99.9% of the solution enters the environment; this inefficiency of the spraying system can lead to water and environmental pollution, resistance to pests and diseases, and reduced species diversity due to the elimination of some soil biota [54, 55]. Today, there is plenty of emphasis on the introduction of the environmentally friendly agrochemical formulations based on non-toxic solvents, such as water. For example, the concentrated emulsion (EC) as one of the most common commercial deltamethrin formulations is xylene-based formulations and makes up more than 90% of the total EC formulation. Studies showed that xylene induces carcinogenicity, organismal, and environmental toxicity and also it should not be regarded as a safe carrier solvent with little biological activity [56–58]. This is while, according to the WHO, 7.4 million years of life annually are lost due to diseases caused by chemicals, such as pesticides [59].

The main advantage of nano-delivery systems in agriculture is that encapsulation dramatically reduces the amount of agrochemicals used (like pesticides, fertilizers, hormones, and growth regulators), by solubilizing them and providing a desirable release of these chemicals through nanoformulation [26].

Recent studies suggested that the silicon nanomaterials are useful in pesticide delivery [36, 60–64]. Some other reports have noted that the silica-based nanoformulations could be engineered in order to enhance the absorption and diffusion of different hydrophobic active compounds and present them as economically durable and biocompatible compounds [63].

Recent studies suggest two approaches to how silicon nanomaterials are useful in pesticides [36]: (1) Some reports have stated that the use of these particles themselves, per se, plays (by physisorption into the cuticular lipids) a role as nanopesticides to kill insects and larvae [60–64]. (2) On the other hand, silica-based nanoformulations are designed to enhance the slow absorption and diffusion of natural or hydrophobic active compounds and other purposes that are economically durable and biocompatible. The use of these materials improves the slow release rate by 25–75% and reduces the soil surface's leaching rate by up to 15%. Several reports have shown that MSNs increased commercial pesticides' currency period and their efficiency [63, 65–68]. For example, porous hollow silica nanoparticles extended the duration of abamectin against *Plutella xylostella* and significantly reduced cytotoxicity; so, MSNs are expected to significantly improve the pesticide delivery systems (PDSs) in the future [69]. Previous studies just have suggested that substances, such as silica, which may have inhibitory effects on Sunn-pest nutrition, should be examined [70]. But so far, based on our search of all, English and Persian literature, there has been no probing on the evaluation of laying-egg control of insects, especially the Sunn-pest using nanotechnology or MSN-based encapsulation, and our study is the first report in this area.

Natural selection probably influenced these two sights––the processing laying-eggs manner and the estimation of best time and place for oviposition––in different ways, leading to a contrasting scale in the former and variety of the latter. This decision-making process requires a complex neuronal control that begins with mating-derived signs and reinforces oviposition behaviors (including how, when, and the suitable site of egg-laying) immediately and lasting [71]. During this process, many known and unknown events happen, such as a post-mating switch, modulation of proteins/receptors signals [72–74] and abrupt modification of gene expression [75], sensing the mated state (mechanosensation and chemosensation), circadian and seasonal adjustment of the oviposition time that affecting factors, such as photoperiod, temperature, and food availability [76], localization of the egg-laying sites remotely via olfaction, vision [77] and finally, contact-based sensing (gustation), also detection the olfactory cues that inhibit oviposition and which are produced by various threats (i.e., salinity, fungal toxicants, phenol produced by pathogenic microorganisms, semiochemicals emitted by parasitoid wasps, and chemo/bio-pesticides) [78–84], chemical components detection of the egg deposition substrates with different organs [84–87], and other such phenomena. In Sunn-pest if the weather conditions are unfavorable after mating, laying-eggs will not occur, or if it has started, it will stop. In such cases, less than fourteen eggs are found in each batch. In one study, if the Sunn-pest was well fed, each female could lay up to 200 eggs; but in the water source alone, each female laid an average of 17 eggs. This indicates that food plays an essential and significant role in the number of eggs each female lays [45]. Regarding the Sunn-pest laying-eggs, the question is whether it may not be able to mate in nature? And if so, will the female insects be able to lay eggs or not? The point that has attracted the least attention of researchers is that throughout Sunn-pest's laying period in irrigated and rainfed crops, we encounter clusters of eggs without embryos that result from the laying of female insects without mating. These eggs always remain green, lose their water after a while, and disappear after shrinking (Fig. 6H).

In this study, we saw that females continue to scattered deposit eggs in several stages at a distance from each other; or if no suitable position is stock, they pause oviposition and ultimately eliminate the development of embryos or the depositioning of eggs. One thinkable exegesis for such events is that females, by modulating different parameters (for example, to be exposed to more light) and considering the "neighborhood effect," behaviorally prefer to lay their eggs near the food sources of the nymphs rather than precisely on it (likely to predict security sophistications against damages caused by food competitors, microorganisms, egg parasites, and because of the issues raised earlier, such as impregnation of leaf surface with pesticides) (Fig. 6J) [71, 88]. Moreover, perhaps this−−worrying about the offspring's future, before to engender−−is one of the forward-looking motherhood emotions that can be observed even in insects' behavior. However, from a plant perspective, exposure to herbivory/oviposition-induced plant volatiles and insect sex pheromones has been shown to launch a plant's anti-herbivore defense mechanisms [89]. Since it is known that herbivorous insects before feeding [90] and eggs deposition prior to the damage of nymph's feeding [91, 92] trigger the plant defense/resistance signaling pathways against the feeding stages of insects [89]; future studies must examine more closely why wheat bushes that were more exposed to the bio-stress of Sunn-pests or their eggs, underwent faster/earlier maturation and drying changes. For example in this study; it was observed that high concentrations of commercial deltamethrin formulation (iv), caused phytotoxicity despite further inhibition of laying-egg. Therefore, phytotoxic studies should be considered so as not to destroy the plant for preventing insect damage (Fig. 3). It is also still a matter of debate whether pesticide or nanomaterials used in this study affect the behaviors of males, females, or both before (on components and sexual cells of either gender, oviposition-stimulating semiochemicals, etc.) or during the mating phase.

Conclusions

It was observed that the PDS approach could increase the pesticide effectiveness (only by once spraying) by eliminating the Sunn-pest's oviposition, reducing the nymphal population, and damage caused by them (which are the most critical reason for qualitative damage to wheat). Therefore, nanotechnology and specifically pesticide delivery systems could be a precursor to future studies and efficient alternatives for managing agricultural pests without harming nature. Further works are expected on the relationship between the time-release effects of delivery systems and pest egg-laying behavior.

Abbreviations

AFM: Atomic force microscopy; BET: Brunauer–Emmett–Teller; BJH: Barrett–Joyner–Halenda; CDA: Controlled droplet application; DLS: Dynamic light scattering; EE: Encapsulation efficiency; EC: Concentrated emulsion; FTIR: Fourier transform infrared; MSN: Mesoporous silica nanoparticle; PDS: Pesticide delivery system; SEM: Scanning electron microscopy; TEM: Transmission electron microscopy; TEOS: Tetraethylortho silane; TSP: Triple-superphosphate; TGA: Thermogravimetric analysis; ULV: Ultra-low volume; UAV: Unmanned aerial vehicle.

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Author contributions

MA contributed to conceptualization, data curation and analysis, investigation, methodology, Laboratory and greenhouse tests (entomology and plant), validation, visualization, wrote the first draft of the manuscript, and designed graphical abstract. ASG was involved in methodology, laboratory and greenhouse tests (entomology and plant), validation, project management, data curation and analysis, and editing the final manuscript. LM and AB were involved in methodology, laboratory and greenhouse tests (nano and plant), validation, project management, data curation and analysis, and editing the final manuscript. GHS performed validation. All authors read and approved the final manuscript.

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Availability of data and materials

All data generated or analyzed during this study are included in this published article. The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no competing interests.

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