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ORIGINAL ARTICLE

Comparative efficacy of solid nano-dispersions and conventional formulations of some insecticides against *Spodoptera littoralis*, (Boisd.) under laboratory and field conditions

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Abstract

Owing to the large quantity of pesticides utilized conventional pesticide formulations can have numerous negative environmental impacts such as side effects on human health and pest resistance development. Using nano-pesticide formulations can minimize the quantity of pesticides used, thereby lowering pest control costs, and environmental contamination. This work used self-emulsifying and solidification technology to convert chlorpyrifos, emamectin benzoate, and beta-cyfluthrin to solid nano-dispersions, all of which were examined for their properties and efficacy against the Egyptian cotton leafworm, *Spodoptera littoralis* (Boisd.). During the preparation of the formulation mixture, solid nano-dispersion particles with sizes ranging from 7 to 400 nm were developed. With the design of the nano-formulation, there were variations in the active ingredient, carrier, surfactant, and pesticide concentration types. The type of active ingredient, carrier, surfactant, and pesticide concentration varied with the nano-formulation design. The nano-formulation with 1 to 5% pesticides, 8% a combination of Nonyl phenol ethoxylated surfactant (Unitop 100) mixed with Geronol surfactant (FF4), and sucrose as a carrier indicated the best polydispersity index, Z-average, and biological activity. Moreover, the surfactant and solvent content in the solid nano-dispersion formulation was lower than in conventional pesticide formulations. Based on the LC_{50} values, chlorpyrifos, emamectin benzoate, and beta-cyfluthrin solid nano-dispersions were more toxic (LC_{50} values were 0.17 and 0.07 for emamectin benzoate, 4.61 and 3.61 for beta-cyfluthrin, and 10.06 and 6.74 mg/L for chlorpyrifos after 24 and 48 h of treatment, respectively) than their conventional formulations (LC_{50} values were 0.85 and 0.36 for emamectin benzoate nano-dispersion, 19.19 and 15.30 for beta--cyfluthrin nano-dispersion, and 27.01 and 26.17 mg/L for chlorpyrifos-nano-dispersion after 24 and 48 h of treatment, respectively) against *S. littorralis* under laboratory conditions. Under field conditions, chlorpyrifos, emamectin benzoate, and beta-cyfluthrin in nano-dispersion formulations were more effective against cotton leaf worms than the same insecticides in commercial formulation. Thus, nano-formulations could be recommended in pest control where they avoid organic solvents and reduce surfactants, control costs, and environmental pollution.

Keywords: adjuvants, fabrication, nanotechnology, pests, toxicity

Introduction

The indiscriminate and heavy use of broad-spectrum, conventional insecticides, primarily carbamates, organophosphates, and synthetic pyrethroids to eradicate the Egyptian cotton leafworm has resulted in its resistance development as well as serious negative effects on the environment's natural resources and beneficial insects (Aydin and Gurkan 2006). For example, in Egypt, approximately 70% of the total amount of insecticides, used for pest control in all crops combined, is used in cotton fields. Such applications had a negative impact of insecticides, seen as a sharp decline (about 58–80% reduction in the numbers of predatory species populations) in cotton fields post applications (El-Heneidy *et al.* 1987; El-Dewy *et al.* 2018), as well as in other crops like wheat, where there was a 26–72% decrease in the number of predatory and parasitic species (El-Heneidy *et al.* 1991; Awadalla *et al.* 2018).

To retain the bioactivity of active ingredients during spraying, suitable adjuvants must be used in the formulation of most pesticides. These adjuvants must also be able to improve efficiency, safety, and practicality of the active ingredient. The formulations of conventional pesticides such as wettable powders (WP), have many disadvantages in their formulations (Chen *et al.* 2003; Sekhon 2014). For instance, in the emulsifiable concentrates (EC) formulation, large amounts of organic solvents like toluene and xylene are used as main components which are toxic, inflammable, and explosive (Nai-Zhen 2007). As a rule, ionic emulsifiers like calcium dodecylbenzenesulfonate, nonionic surfactants like dibenzyl phenol polyoxyethylene ether, and nonylphenol ether make up the emulsifiers in traditional formulation compositions. In conventional pesticide formulations, the amount of surfactants is often equal to or greater than 8% of the total weight (Nai-Zhen 2007; Li 2010). Along with carriers and other additions, wetting agents such as alcohol ethoxylate, sodium dodecyl sulfate, and alkylphenol ethoxylates are constantly required to maintain the stability and dispersibility of WPs and SCs (Zhang and Sun 2000). According to Yang (2009) and Sekhon (2014) most pesticide ingredients are not very soluble in aqueous media, which restricts the creation of effective and environmentally friendly formulations. However, only particles of a size in the nano range can improve the solubility of pesticide ingredients in aqueous media (Sasson *et al.* 2007). The Ostwald-Freundlich equation, which investigates the relation between the solubility of pesticides and particle size, states that when the particle size decreases, the solubility of the substance rises while all other variables are held constant (Feng *et al.* 2016a). Therefore, reducing a pesticide's particle size might effectively improve their solubility (Mihranyan and Strømme 2007; Dizaj *et al.* 2015; Murdande *et al.* 2015); however, obvious change appears only when the particle size is in the nanoscale. In this situation, nanotechnology may represent a fresh approach for creating nano-pesticides to enhance the solubility of ineffective pesticides (Mihranyan and Strømme 2007; Yang 2009).

As is well known, nanotechnology improves the solubility and efficiency of insoluble pesticides by greatly increasing their surface area as compared to traditional pesticides (Ishaaya *et al.* 2007; Sasson *et al.* 2007). Therefore, nano-pesticides may be more effective against hazardous target pests because the pest is more likely to bind and accumulate the active component (Saini *et al.* 2014). Both top-down and bottom-up methods are used to create nano-formulations, however, the in-process heat generation and the requirements for expensive equipment are their drawbacks, even though they are less complex. By joining together molecules or smaller particles, bottom-up methods like microprecipitation and supercritical fluid create nanoparticles (Du *et al.* 2015; Jallouli *et al.* 2015). However, the procedure parameters of the bottom-up process require precise controls. Self-emulsifying is a major technology for preparing microemulsion and nano-emulsion (Tian *et al.* 2016; Vithani *et al.* 2019; Farhadi *et al.* 2024).

Early in the 1960s, mixtures of lipidic and hydrophilic excipients were used to solubilize drugs and insecticides that were weakly water soluble, giving rise to the idea of self-emulsifying (SE) processes (Hartley 1967). Self-emulsifying systems can be employed in the pharmaceutical industry as pesticide formulations as well as delivery systems for drugs as oral, rectal, and topical applications for therapeutic requirements. The phenomenon of self-emulsification has been extensively used commercially in the production of emulsifiable concentrates of insecticides and herbicides. In order to effectively transport extremely hydrophobic substances, crop spray concentrates must be diluted by the user, such as farmers or home gardeners. In contrast, self-emulsification delivery techniques for drugs (SMEDDS) have not been extensively used, and as a result, there is a limited understanding of their physicochemical principles. SMEDDS use excipients safe for consumption to humans (Gursoy and Benita 2004). This solid nano-dispersion is very efficient, eco-friendly, and significantly reduces surfactants. It has a wide range of applications in crop protection for enhancing pesticide efficacy and lowering residual pollution in agricultural goods and the environment (Feng *et al.* 2016b; Yang *et al.* 2017; Cui *et al.* 2018; Cui *et al.* 2020; Tengshe and Karande 2020). Studies have also shown that formulation bioavailability for pesticides applied to foliage correlated positively with wettability and negatively with surface tension and contact angle.

The development of innovative pesticide formulations can be guided by the relationship between formulation parameters and biological activity using a suitable target pest. The Egyptian cotton leafworm, *Spodoptera littoralis* (Boisd.) (Lepidoptera: Noctuidae), is a serious yield loss pest of economic crops such as cotton that is widely distributed and highly polyphagous; it originates in tropical and subtropical zones (Brown and Dewhurst 1975). It is also considered to be a model pest to evaluate the biological activity of insecticides and is available in Egypt throughout the whole year either in the laboratory or field.

Therefore, the objective of this study was to optimize chlorpyrifos (CP), emamectin benzoate (EB), and beta-cyfluthrin (BC) to solid nano-dispersions by self-emulsifying and solidification technology and to study their characteristics and toxicity to the *S. littoralis* (Boisd.) larval instars under laboratory and field conditions.

Materials and Methods

Chemicals

Technical grades of emamectin benzoate (90% w/w), chlorpyrifos (95% w/w), and beta-cyfluthrin (95% w/w) were obtained from Kafr El-Zayat Company for Pesticides and Chemicals, Kafr El-Zayat Egypt. The commercial chlorpyrifos (Tack, EC 48%) and Agral were obtained from the Star Chem Company for Pesticides and Chemicals, Egypt. Emamectin benzoate (Sulim, WDG 5.7%) was provided by Top Chemicals Agricultural Technology Co., Egypt. BC (Bulldock, 12.5% SC) was provided by the Bayer Crop Science Company, Egypt. A non-ionic surfactant based on a trisiloxane ethoxylate is called Agral (Silwet). El--Gomhouria Company for Chemicals & Pharmaceutical Appliances, Egypt, provided sodium benzoate, sucrose, and sorbitol (80%) as carriers as well as ethyl acetate as a solvent. Geronol FF4 or FF6 is a mixture of anionic and non-ionic surfactants. It was obtained from Rhodia-Home, Personal Care & Industrial Ingredients, Milan, Italy. A surfactant Unitop 100 (Nonyl phenol ethoxylated) with 9.5 moles of ethylene oxide was obtained from Unitop Chemicals Ltd., Mumbai, India.

An assay of the effects of surfactants

To assess the effects of surfactants on the quality of the solid nano-dispersion formulation of the active ingredient 5% of chlorpyrifos was dissolved in ethyl acetate. Various surfactant mixtures (Unitop 100 mixed with FF/4, Agral mixed with FF/4, FF/4 mixed with FF/6) at a ratio of 4:4g were incubated at 20°C for 24 hours using a water bath. The Zeta average and PDI for each mixture were measured to select the best mixture. The stability of each mixture at low (2°C) and high (54°C) temperatures was evaluated in order to select the most effective surfactants (Aly *et al.* 2023).

An assay of the effects of carriers

To assess the effects of carriers on the quality of the solid nano-dispersion formulation of the active ingredient 5% of chlorpyrifos, dissolved in ethyl acetate, mixed with the best surfactant mixture, various carriers (sucrose, sodium benzoate, and sorbitol) were used. The Zeta average and PDI for each mixture were measured to select the best carriers.

An assay of the effects of active ingredient percentage

To assess the effects of active ingredient percentages on the quality of the solid nano-dispersion formulation of chlorpyrifos dissolved in ethyl acetate mixed with the carrier and surfactant mixture, various active ingredient percentages (2, 5, 7.5, 10, 15, and 20%) were used. The Zeta average and PDI for each mixture were measured to select the best carriers.

The preparation of the final WP solid nano-dispersion formulation

To make the solid nano-dispersions, a self-emulsifying mixture, made with carrier solidification, was adopted from Feng *et al.* (2016b) and Cui *et al.* (2020) with some modifications. To obtain 5% chlorpyrifos, 3% EB and 4% BC solid nano-dispersion, 5.26 g of chlorpyrifos (a.i. 95%), 3.33 g of EB (a.i. 90%), and 4.21 g of BC (a.i. 95%) were used and dissolved in ethyl acetate. Then 8 g of the best surfactant mixture (1:1) were dissolved simultaneously. After that, with the appropriate carrier (sucrose), the solution was then finished to a weight of 100 g. The whole mixture was then evenly stirred with a glass rod to achieve the solid nano-dispersion. Lastly, the mixture was evaporated in the oven (SL SHEL LAB 1350 GX Sheldon Manufacturing, Inc.) for 3 h at 40°C. Based on the experimental design, different carriers, surfactants, and amounts of each component were used in the formulation development process. The stability of each final formulation was at low (2°C) and high (54°C) temperatures (Aly *et al.* 2023).

Particle size and polydispersity index of synthesized nanoparticles

Dynamic light scattering (Zetasizer Nano ZS90, Malvern Pananlytical Company, Malvern, UK) was used to estimate the polydispersity index (PDI), the average droplet size (d. nm) and viscosity (cP). To lessen the numerous scattering effects at room temperature, the formulations were diluted with deionized water. The average of three measurements was used to evaluate the suspension droplet size, which was displayed as an average diameter in nanometers.

Transmission Electron Microscopy (TEM)

Morphology of the pesticide solid nano-dispersion shape and size were analyzed by Transmission Electron Microscope (TEM) (JEM model-2100 plus, Japan, operated at 160 kv). Pesticide particles were created by drop coating them onto a carbon-coated grid. The nano-pesticide films were left in place for 10 minutes, after which any remaining solution was blotted away with paper towels. The grids were then given time to dry before being examined.

Insect colony and rearing

A susceptible strain of *S. littoralis* that had been reared for 10 years was obtained from the Cotton Leaf Worm Pesticides Testing Department, Plant Protection Research Institute, Sakha, Kafrelshiekh, Egypt in 2020. In 3-liter glass jars with gauze covering the jar mouth, susceptible egg strains were placed and incubated at 25°C until the eggs hatched. Then, newly hatched larvae started consuming the young leaves of a 1-year-old castor plant that was grown in the Cotton Pesticide Testing Department's greenhouses, Sakha, Kafrelshiekh, Egypt. Every day, the waste and residues of uneaten castor leaves were removed from these leaves by cleaning them with a brush. The freshly hatched larvae were reared until they developed into pupae, or sixth larval ages. Subsequently, the pupae were housed in wire cages, 45 cm in length and 50 cm in width, where they were fed a sugar solution that was applied on a piece of medical cotton, until they matured into adults (Eldefrawi *et al.* 1964). After mating, the moths laid their eggs on oleander plant leaves that had been put back into the jar. This strain was reared three generations before starting bioassay tests under controlled conditions of 25 ± 2°C, RH of 65% ± 5 and photo-period of 12 h light to 12 h dark. The first generation was adults and the 2nd and 3rd instar generation larvae were used for screening tests to get the appropriate pesticide concentration. In this study, recently molted 2nd and 4th instar larvae were selected.

Bioassay technique

According to El-Zahi *et al.* (2021) and Aydin and Gürkan (2006) the leaf-dip method was applied using a range of different concentrations of commercial and nano-dispersion formulations of the tested insecticides (0, 1, 10, 20, 50, 100, 1,000, 2,000, 5,000, and 10,000 mg a.i. $\cdot$ l^{-1}) prepared in pure water. The solution of each concentration was applied to castor leaves for 10 seconds, and they proceeded to dry for 45 minutes at room temperature. After that, one leaf was transferred to 500 ml clean plastic jar (Elgawhara Company, Tanta, Egypt). Then, 20 freshly molted *S. littoralis* of 2nd and 4th instar larvae were added to plastic plates in a separate experiment, and covered with muslin (Elnabarway Company, Tanta, Egypt) to simulate one replicate. Each treatment received four replications. The control treatment was carried out using pure water only. The controlled laboratory conditions used for the research were 25 ± 2°C, 65 ± 5% RH and photo-period of 12 h light to 12 h dark. The toxicity of the prepared insecticide formulation, apart from the active ingredient, on the larval stages under study was evaluated as a second control treatment. No mortality rates were recorded. Three different insecticides were used in this study that belonged to different chemical classes. Each had different modes of action to reduce the development of resistance. These compounds are also common in our region. The number of dead larvae was counted, and mortality percentages were computed, after the larvae had been eating the treated leaves for 24 and 48 h. Mortality was determined by the failure of larvae to move/turn upright/wriggle following prodding with a small paint brush.

Efficacy of the tested insecticides against cotton leaf worm under field conditions

The efficiency of the tested insecticides [Sulim 5.7% emamectin benzoate (EB-C), Buldok 12.5% beta--cylfurthrin (BC-C), Tack 48% chlorpyrifos (CP-C), Chlorpyrifos 5% solid nano-dispersion (CP-SND), emamectin benzoate 3% solid nano-dispersion (EB-SND) and beta-cylfuthrin 4% solid nano-dispersion (BC-SND)] on *S. littoralis* populations in cotton fields was evaluated through field experiments conducted at the Farm of Housht Aldawar, El Mahallah Al Koupra, Gharbia Governorate in 2021 and 2022. EB WDG, BC SC and CP EC as commercial formulations were used to compare the efficacy of solid nano-dispersion formulation of EB, CP, and BC because these formulations were recommended by the Egyptian Ministry of Agricultural and Land Reclamation. Also, these formulations were the only available formulation type in Egypt that contain the same active ingredient of the tested insecticides at the time of these experiments. *Gossypium barbadense* (Giza 86) cotton seeds were sown on April 1 in an area of 2000 m^2 divided into equal plots. The area had not received any insecticidal treatments prior to the experiment. Five treatments, including six insecticides and a control, were arranged in a completely randomized block design with four replications. The tested insecticides (both commercial and nano-dispersion types) were sprayed once on July 13 in both seasons according to the recommendations of the Egyptian Ministry of Agriculture and Land Reclamation using knapsack sprayer CP3 (Cooper Pegler Co. Ltd., Northumberland, England). The final volume of the spray solution was 470 l per hectare. A sampling method was employed to assess the impact of different treatments on *S. littoralis* in cotton fields. Twenty-five cotton leaves were randomly chosen from the bottom, middle, and top sections of the cotton plants in each plot. The upper and lower surfaces of the leaves were examined, and the *S. littoralis* were directly counted in the field using an 8X lens. The counting was conducted in the early morning before spraying and 1, 3, 7, and 10 days after spraying. Additionally, for sampling the *S. littoralis*, visual observations were made on 10 randomly selected plants from each plot at the same time as the insect sampling. Plant samples were chosen randomly from both diagonals of the inner square across the plot area. Reduction percentages of *S. littoralis* were calculated using the method developed by Henderson and Tilton (1955). The formula used to calculate the reduction percentage of *S. littoralis* was as follows:

$$\% \text{ Reduction} = [1 - (C \times T/C^{*} \times T^{*})] \times 100,$$

where: C – the number of insects in the control before treatment, T – the number of insects in the treatment before treatment, C^{*} – the number of insects in the control after treatment and T^{*} – the number of insects in the treatment after treatment.

Data analysis

Toxicity lines were made using concentrations of each insecticide and percentages of mortality. If there were any mortality in the control treatment, mortality percentages in different concentrations were corrected using the formula of Abbott (1925). Lethal concentration (LC_{50}) values were calculated from probit analysis with 95% confidence limits ($p \leq 0.05$) according to Finney (1971). All statistical analyses were carried out using the SPSS statistical software (version 18.0, SPSS Inc., Chicago, IL, USA). Statistically significant mean reduction values of treatments at each time were compared using one-way ANOVA tests followed by Tukey's HSD method ($p < 0.01$).

Results

Evaluation of surfactant type effect

In this study, the chlorpyrifos solid nano-dispersions were prepared with the following surfactants: Unitop 100 mixed with FF4, Agral mixed with FF4 and FF4 mixed with FF6. As presented in Table 1, the Z-average of the nanoparticles using Unitop 100 mixed with FF4 as surfactant was 361.7 nm and PDI was the smallest of the three formulations (less than 0.119) as shown in Table 1. In contrast, the particle Z-averages were 366.5 and 503.6 nm with PDI of 1.0 using the surfactants which contained Agral mixed with FF4 and FF4 mixed with FF6, respectively. The composite surfactant of Unitop 100 mixed with FF4 showed the best nano properties of the tested surfactants in the self--emulsifying technique and provided good stability in the evaluated temperatures. Therefore, the mixture of these surfactants was chosen to create the solid nanodispersion of the three selected insecticides.

Evaluation of the carrier type effect

The effects of sucrose, sodium benzoate, and sorbitol as carriers on 5.0% (w/w) chlorpyrifos solid nano-dispersions were investigated and the results are shown in Table 2. The effect of sucrose, sodium benzoate, and sorbitol as carriers on 5.0% (w/w) chlorpyrifos solid nano-dispersions were investigated and the results are shown in Table 2. The Z-average of chlorpyrifos solid nano-dispersions using sucrose as a water soluble carrier was 312.3 nm with a PDI value less than 0.48. Among the three carriers, it was the smallest. On the other hand, the Z-average and PDI values of the sodium benzoate carrier were 602 and 0.84 while for the sorbitol carrier, it was 650.6, and 0.54 in chlorpyrifos solid nano-dispersions. Therefore, sucrose was selected as the best carrier and used in the final formulation. Their properties are shown in Table 2.

Table 1. The effects of surfactant mixtures on chlorpyrifos solid nano-dispersion formulation

Surfactants	Stability at various tempratures		Z-average [nm]	Polydispersity index [PDI]
	0 ± 2°C	54 ± 2°C		
Unitop 100 mixed with FF4	passed	passed	361.7	0.119
Argal mixed with FF4	crystallization	passed	366.5	1.0
FF4 mixed with FF6	passed	crystallization	503.6	1.0

Table 2 .The effects of sucrose, sodium benzoate and sorbitol as carriers on chlorpyrifos solid nano-dispersion formulation

Carrier name	Z-average [nm]	Polydispersity index [PDI]
Sucrose	312.3	0.48
Sodium benzoate	602	0.84
Sorbitol	650.6	0.54

Table 3. The effect of chlorpyrifos active ingredient percentage on its solid nano-dispersion formulation

Active ingredient percentage	Z-average [nm]	Polydispersity index [PDI]
2	50.3	0.312
5	102.7	0.371
7.5	361	0.549
10	503	1.0
15	574	0.84
20	650	1.0

Pesticide active ingredient optimization

The effect of 2, 5, 7.5, 10, 15, and 20% w/w active ingredient of chlorpyrifos on the particle size of fabricated solid nano-dispersions is shown in Table 3. When the pesticide loading was in the range of 2 to 5% (w/w), the particle sizes were between 50 and 102.7 nm. The particle size rapidly increased to 650 nm when the concentration of the chlorpyrifos active ingredient reached 20% because the active ingredient was simpler to combine during carrier adsorption. The results in Table 3 show that the increase of active ingredient percentage in the fabricated nano-formulation led to a significant increase of particle size.

Size and morphology of the final fabricated nano-formulation

The solid nano-dispersion containing 5% (w/w) chlorpyrifos, 3.0 (w/w) EB and 4.0% (w/w) BC characteristics are shown in Figsures 1, 2 and 3. The results revealed that the final fabricated nano-formulation of the three insecticides provided good stability under the evaluated temperatures (Tab. 4). The results also showed that the particle size of the chlorpyrifos solid nano-dispersion ranged from 7.34 to 43.68 nm (average particle size of 25.6 nm) in parallel with a z- average of 102.7 and PDI value of 0.371 (Fig. 1). As shown in Figure 2, the particle size of EB solid nano-dispersion ranged from 5.373 to 36.55 nm (average particle size of 20.96 nm) with a z-average of 124.6 and PDI value of 0.368. BC solid nano-dispersion size ranged between 7.232 and 38.96 nm (average particle size of 32.6 nm) with a z-average value of 188.3 and PDI value of 0.433 (Fig. 3). The intercept values for chlorpyrifos, emamectin benzoate and beta-cyfluthrin were 0.863, 0.873, and 0.873, respectively (Figs. 1–3).

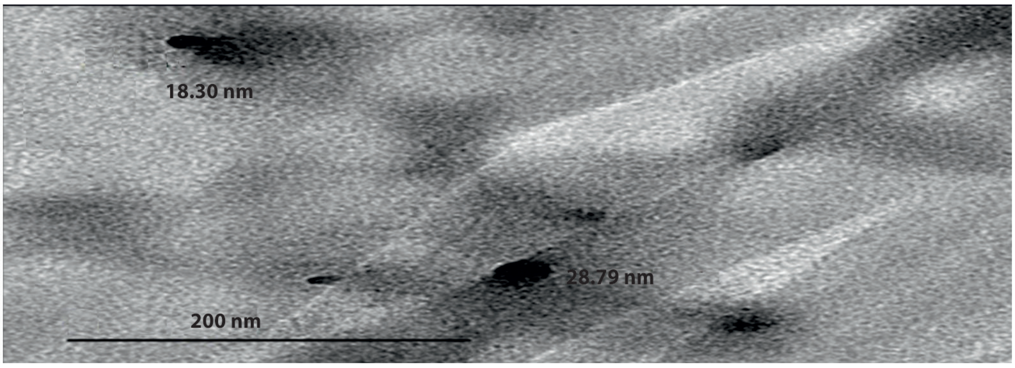
Toxicity of nano and commercial formulations of the tested insecticides to *Spodoptera littoralis*

The toxicity of the tested insecticides, either in commercial or nano-dispersion formulation against the 2nd and 4th instars of S. *littoralis,* is presented in Tables 5–6. Based on median lethal concentration (LC_{50}) values, EB was significantly more toxic than chlorpyrifos and BC against the 2nd instar larvae when used as solid nano-dispersion or commercial formulations. The median lethal concentration (LC_{50}) of the tested insecticides in nano-dispersion formulation was more toxic than the commercial ones against the 2nd instar larvae (Table 5). The LC_{50} values ranged from 0.07 to 0.36, 3.61 to 16.61, and 6.74 to 18.36 mg · l^{-1} for emamectin benzoate, BC, and chlorpyrifos against the 2nd instar larvae, respectively (Tab. 5). The LC_{50} values were 0.17 and 0.07 for EB-SND, 4.61 and 3.61 for BC-SND, and 10.06 and 6.74 mg · l^{-1} for CP-SND after 24 and 48 h of treatment, respectively. The toxicity of the tested insecticides against the 4th instar larvae of cotton leaf worm is presented in Table 6. Based on median lethal concentration (LC_{50}) values, emamectin benzoate was significantly more toxic than chlorpyrifos

Table 4. Composition and characterization of the final solid nano-dispersion pesticide formulations

Pesticides	Conc.	Active ingredient [g]	Surfactant Unitop100 [%, w/v]	Surfactant Genorol(FF4) [%, w/v]	Carrier [%, w/v]	Stability at various temperatures		Z-average [nm]	Polydispersity index [PDI]	Mean particle size [nm]	Viscosity [cP]
						0 ± 2°C	54 ± 2°C				
Chlorpyrifos	5%	5.26	4.0	4.0	86.73	pass	pass	102.7	0.371	25.6	0.8872
Emamectin benzoate	3%	3.33	4.0	4.0	88.66	pass	pass	124.6	0.368	20.96	0.8872
Beta--cyfluthrin	4%	4.21	4.0	4.0	87.79	pass	pass	50.3	0.312	32.6	0.8872

A



			Size [d.nm]:	% Volume:	St Dev [d.nm]:
Z-Average [d.nm]:	102.7	Peak 1:	43.68	6.0	11.12
PdI:	0.371	Peak 2	7.348	94.0	1.339
Intercept:	0.863	Peak 3:	0.000	0.0	0.000
Result quality:	Refer to quality report				

B

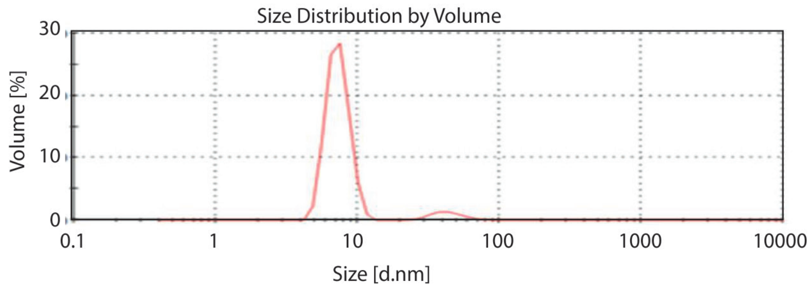
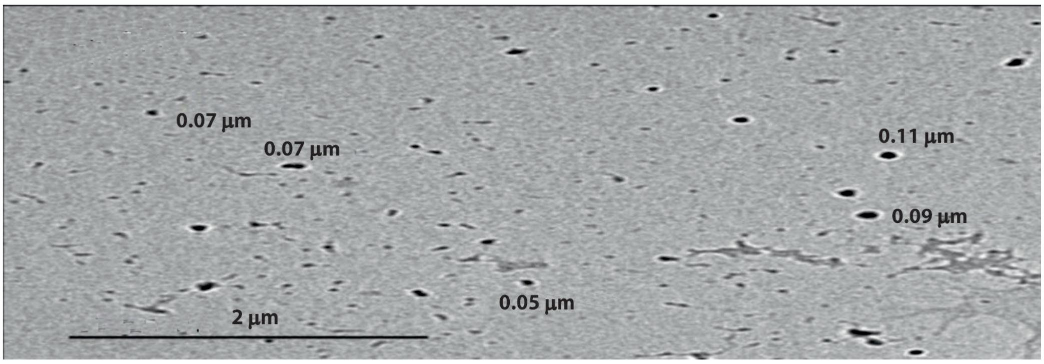


Fig. 1. TEM image – A and Z-average – B of the solid nano-dispersions containing 5% of chlorpyrifos

A



			Size [d.nm]:	% Volume:	St Dev [d.nm]:
Z-Average [d.nm]:	124.6	Peak 1:	36.55	5.1	9.951
PdI:	0.368	Peak 2	5.373	94.9	1.138
Intercept:	0.873	Peak 3:	0.000	0.0	0.000
Result quality:	Refer to quality report				

B

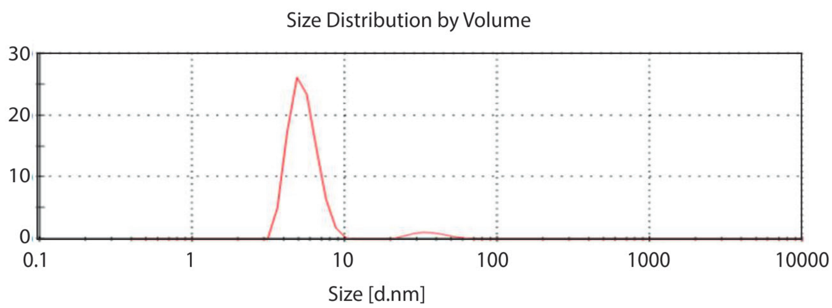
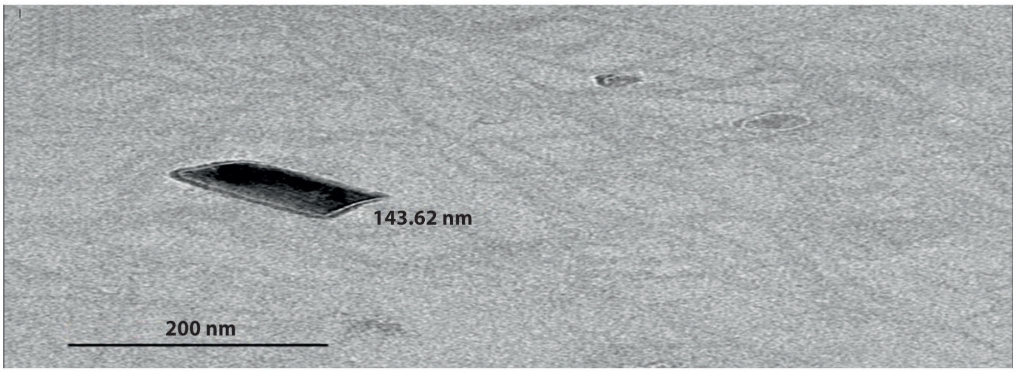


Fig. 2. TEM image – A and Z-average – B of the solid nano-dispersions containing 3% of EB

A



			Size [d.nm]:	% Volume:	St Dev [d.nm]:
Z-Average [d.nm]:	50.03	Peak 1:	51.75	8.4	20.50
PdI:	0.312	Peak 2	13.45	91.6	4.794
Intercept:	0.823	Peak 3:	0.000	0.0	0.000
Result quality:	Refer to quality report				

B

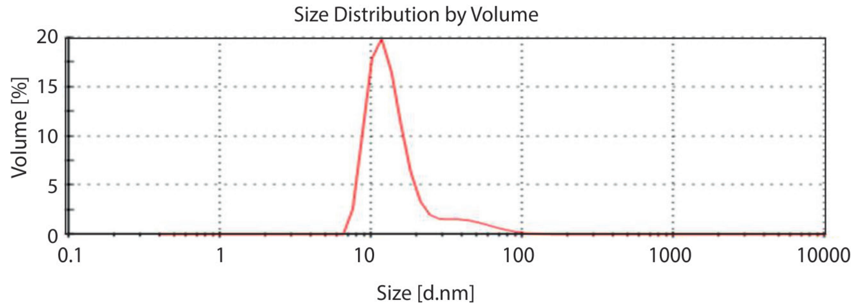


Fig. 3. TEM image – A and Z-average – B of the solid nano-dispersions containing 4% of BC

Table 5. Toxicity of commercial and nano formulations of some insecticides against 2nd instar larvae of *Spodoptera littoralis*

Insecticide	Formulation	Time post treatment	LC_{50} [mg a.i · l^{-1}] (95% Confidence limits)	LC_{90} [mg a.i · l^{-1}] (95% Confidence limits)	Slope ± SE	χ^2	DF
Chlorpyrifos (CP)	SND[a]	24 h	10.06 (8.69–11.65)	58.03 (45.41–79.9)	1.68 ± 0.11	5.76	4
		48 h	6.74 (5.63–8.05)	53.58 (38.24–84.54)	1.42 ± 0.12	8.34	4
	commercial (Tack 48%)	24 h	22.2 (19.89–24.72)	75.38(62.3–96.77)	2.41 ± 0.19	7.07	4
		48 h	18.38 (15.98–21.37)	21.37 (14.02–100.53)	1.85 ± 0.15	3.49	4
Emamectin benzoate (EB)	SND	24 h	0.17 (0.10–0.21)	0.49 (0.37–0.71)	2.06 ± 0.17	5.13	4
		48 h	0.07 (0.06–0.08)	0.29 (0.28–0.44)	2.00 ± 0.14	4.99	4
	commercial (Sulim 5.7%)	24 h	0.36 (0.30–0.44)	3.97 (2.81–6.25)	1.20 ± 0.09	10.21	4
		48 h	0.23 (0.19–0.27)	2.17 (1.52–3.43)	1.30 ± 0.09	6.78	4
Beta–cyfluthrin (BC)	SND	24 h	4.61 (3.93–5.41)	24.22 (18.33–35.34)	1.78 ± 0.157	7.43	3
		48 h	3.61 (2.96–4.33)	43.75 (29.19–78.43)	1.52 ± 0.15	1.56	3
	commercial (Boldouc12.5%)	24 h	16.61 (14.63–18.95)	69.12(54.03–95.5)	2.08 ± 0.16	7.5	3
		48 h	14.99 (13.09–17.19)	68.47 (54.32–92.65)	1.92 ± 0.15	8.37	3

[a]solid nano-dispersion

and BC against the 4th instar larvae when used either as solid nano-dispersion or commercial formulations. Furthermore, the median lethal concentration (LC_{50}) of the tested insecticides in nano-dispersion formulation was more toxic than the commercial ones against the 4th instar larvae. The LC_{50} values ranged from 0.20 to 0.85, 5.23 to 19.19, and 8.66 to 27.01 mg · l^{-1} for EB, BC, and CP, respectively, against the 4th instar larvae either in nano-dispersion or commercial formulation (Tab. 6).

Table 6. Toxicity of commercial and nano formulations of the tested insecticides against 4th instar larvae of *Spodoptera littoralis*

Insecticide	Formulation	Time post treatment	LC_{50} in mg a.i · l^{-1} (95% Confidence limits)	LC_{90} in mg a.i · l^{-1} (95% Confidence limits)	Slope ± SE	χ^2	DF
Chlorpyrifos (CP)	SND[a]	24 h	12.55 (11.06-14.25)	67.45 (49.80-100.17)	2.04 ± 0.13	6.84	6
		48 h	8.66 (7.49-10.03)	53.01 (43.16 - 68.53)	1.84 ± 0.14	0.86	4
	commercial (Tack 48%)	24h	27.01 (24.8-29.33)	80.8 (67.04-103.5)	3.46 ± 0.3	7.75	3
		48 h	26.17 (23.65-29.04)	63.32 (55.06-76.4)	2.61 ± 0.21	8.84	4
Emamectin benzoate (EB)	SND	24 h	0.72 (0.60-0.88)	7.4 (5.25-11.31)	1.27 ± 0.08	11.71	4
		48 h	0.20 (0.17-0.23)	0.94 (0.77-1.2)	1.90 ± 0.11	2.42	4
	commercial	24h	0.85 (0.73- 1.02)	6.9 (5.04-10.45)	1.40 ± 0.09	4.90	4
		48 h	0.36 (0.21- 0.44)	4.01 (2.8-6.2)	1.20 ± 0.09	7.13	4
Beta-cyfluthrin (BC)	SND	24 h	5.59 (4.60-6.65)	49.07 (32.61-92.91)	1.74 ± 0.21	0.64	2
		48 h	5.23 (4.54-6.16)	31.40 (23.49-46.2)	1.64 + 00.11	1.64	3
	commercial (Boldouc 12.5%)	24h	19.19 (17.11-21.11)	68.67 (56.89-87.45)	2.38 ± 0.18	9.05	4
		48 h	15.30 (13.61-17.04)	66.59 (55.41-84.34)	2.52 ± 0.18	6.47	4

[a]solid nano-dispersion

Efficiency of the tested insecticides against *Spodoptera littoralis* under field conditions

The data presented in Tables 7 and 8 showed the efficacy of the tested insecticides either in nano-dispersion or commercial formulations against cotton leafworm in the 2021 and 2022 growing seasons. Based on the reduction rates of the insect population with time and the mean reduction over time, the EB insecticide was the most effective against *S. littoralis*, recording the highest reduction rate in the insect population in 2021 and 2022, followed by CP and BC, respectively, either in commercial or nano-formulations (Tables 7 and 8). The results also showed that EB, BC, and CP in nano-dispersion formulations were more effective against cotton leaf worms than the same insecticides in commercial formulations based on the reduction rates of the insect population with time and the mean reduction over time in both growing seasons. Furthermore, the mean reduction in the insect population over time in 2022 for all treatments was higher than in 2021.

Discussion

Surfactant content, particularly in self-emulsified microemulsions, is crucial for stabilizing nanoparticles (Zhu *et al.* 2006). Moreover, it is essential for lowering interfacial tension, stabilizing emulsions that have developed and preventing particle aggregation, which reduces particle size (Cui *et al.* 2018). In this study the composite surfactant of Unitop 100 mixed with FFT4 could improve the nano properties of the tested

Table 7. Efficacy of different insecticides against *Spodoptera littoralis* on cotton under field conditions in 2021

Treatments	Application r.ate g ai/hectare	Reduction percentage in *S. littoralis* number					Mean reduction
		Pre-spray No. of insects	Days after application				
			1	3	7	10	
EB-SND	10.85 g	75.75 ± 3.82	94.16 a	94.08 a	91.74 a	94.79 a	92.85 a
CP-SND	114.24 g	57.00 ± 2.58	64.18 b	80.33 c	87.26 b	91.43 a	81.64 b
BC-SND	18.78 g	59.25 ± 3.07	35.24 d	72.37 d	56.08 c	66.81 b	57.62 d
EB-C	10.85 g	52.75 ± 3.33	63.63 b	88.10 b	91.20 a	90.86 a	83.45 b
CP-C	114.24 g	73.00 ± 3.81	40.70 c	67.74 e	94.20 a	94.15 a	74.20 c
BC-C	18.78	47.00 ± 3.63	33.54 d	42.74 f	42.06 d	50.67 c	42.25 e
Control	–	76.25 ± 2.81	–	–	–	–	–

Values shown are the means of four replicates. Different lowercase letters refer to significant differences (Tukey's HSD test, $p < 0.01$). EB-SND –emamection benzoate solid nano-dispersion, EB-C – emamectin benzoate commercial, BC-SND – beta-cylfuthrin solid nano-dispersion, BC-C – beta cyfluthrin commercial, CP-SND – chlorpyrifos solid nano-dispersion, CP-C – chlorpyrifos commerical

Table 8. Efficacy of different insecticides against *Spodoptera littoralis* on cotton under field conditions in 2022

Treatments	Application rate g ai/hectare	Reduction percentage in *S. littoralis* number					Mean reduction
		Pre-spray No. of insects	Days after application				
			1	3	7	10	
EB-SND	10.85 g	82.00 ± 2.48	96.79 a	95.70 a	94.94 a	92.87 b	95.08 a
CP-SND	114.24 g	63.25 ± 4.09	73.34 b	82.59 b	92.66ab	97.41 a	85.39 b
BC-SND	18.78	49.00 ± 4.64	34.40 d	62.69 c	82.33 c	76.47 c	63.97 d
EB-C	10.85 g	45.50 ± 2.50	72.20 b	86.44 b	92.47ab	92.86 b	85.99 b
CP-C	114.24 g	56.50 ± 3.88	56.16 c	64.91 c	89.73 b	95.89 ab	77.79 c
BC-C	18.78	53.50 ± 8.17	18.74 e	41.94 d	77.09 d	76.65 c	53.61 e
Control	–	53.50 ± 2.14	–	–	–	–	–

Values shown are the means of four replicates. Different lowercase letters refer to significant differences (Tukey's HSD test, $p < 0.01$). EB-SND – emamection benzoate solid nano-dispersion, EB-C – emamectin benzoate commercial, BC-SND – beta-cylfuthrin solid nano-dispersion, BC-C – beta cyfluthrin commercial, CP-SND – chlorpyrifos solid nano-dispersion, CP-C – chlorpyrifos commerical

pesticides in the self-emulsifying technique. The mixture of these surfactants was chosen in previous research to create the insecticides' solid nano-dispersion (Pratap and Bhowmick 2008).

Surfactants commonly found in conventional formulation compositions include mixed, amphoteric, nonionic, and noncationic surfactants as well as anionic and cationic surfactants (Cserháti and Forgács 1997; Zheng *et al.* 2011; Seebunrueng *et al.* 2012; Vichapong and Burakham 2012; Yang and Yang 2013). The surfactants used in this study were selected to be a mixture of anionic and non-anionic. This may be due to the fact that electrical charges from the anionic surfactants could be enough to increase the electrostatic repulsion of the particles while through the formation of an adsorptive layer on the particle surface, a non––ionic surfactant can reinforce the steric stability (Shao *et al.* 2018). Because they are less affected by ionic strength and variations in solution pH and are typically regarded as biocompatible and harmless to non-target organisms, non-ionic surfactants are frequently utilized for the screening of surfactants (Butani *et al.* 2014). The use of Unitop 100 mixed with FF4 in this study showed PDI less than 0.5 which improved the system stability.

The concentrations of the surfactants used in this study were higher than the active ingredient of the examined pesticides. This is in agreement with previous research in which it has been reported that even in the presence of co-solvents, the surfactant amounts in aqueous microemulsions are typically twice as large as that of the active component to obtain a good self-emulsifying formula (Wang *et al.* 2008; Zheng 2012; Feng *et al.* 2020). Furthermore, the solid nano-dispersion formulation in this study used little surfactants while the normal formulation such as of EB often contains 10–20 times as many surfactants and co-surfactants as the active component, and 10–30 times as much organic solvents and co-solvents (Jinghua 2006; Fan *et al.* 2009; Sun *et al.* 2010; Zheng 2012). This means that the normal formulation contains five times more surfactants than solid self-emulsifying formulations (Abdalla and Mäder 2007; Yi *et al.* 2008; Cho *et al.* 2013). Also, Feng *et al.* (2020) reported that the emamectin benzoate solid microemulsion's composition greatly reduced the amount of surfactant and showed considerable benefits in terms of manufacturing cost.

The polydispersity index (PDI), which measures system stability, is also a concern while measuring the quality of nano-formulation fabrication procedure. Choosing a PDI value that is less than 0.5 is appropriate for agricultural usage and is regarded as having good particle diameter homogeneity (Díaz-Blancas *et al.* 2016). Only the sucrose in fabricated solid nano-dispersion formulation in our study had a narrow size distribution and a low particle density index (PDI) (0.48), indicating greater dispersibility and homogeneity in the pesticide formulation under study. This result is similar to Cui *et al.* (2020) who said that lambada-cyhalothrin with lactose, sucrose, and urea could disperse transparently in water, however, lambda-cyhalothrin with sodium benzoate settled.

Sucrose was selected as the best carrier in this study compared to sodium benzoate which has low solubility. Furthermore, the long-term storage experiment revealed that the formulation containing sucrose was less conducive to storage and more easily absorbed moisture than the others. As a result, sucrose was best suited for using in the solid nano-dispersion manufacturing process as a carrier in this study (Dege 1970; Shnidman and Sunier 2002; Tsavas *et al.* 2002; Li *et al.* 2016). Moreover, gravity separation, flocculation, and Ostwald ripening all contribute to the water-based formulations breaking down over time (Dickinson *et al.* 1997). So, after adding sucrose, the aqueous dispersion was freeze-dried into solid powder to increase the formulation's stability and extend its shelf life. Sucrose, a water-soluble antifreeze agent and carrier, may speed up the redispersion of the solid nano-dispersion while also protecting dispersion from freezing and desiccation impairment (Tanpradit *et al.* 2015). Additionally, by raising the viscosity of the re-dispersed dispersion, sucrose can enhance suspensibility and stability (Santiago *et al.* 2002).

In this investigation, the appropriate pesticide level ranged from 2% to 5% (w/w) depending on particle size and dispersion. However, when the number of pesticides in the active component rose, the amount of ethyl acetate used in the production process steadily increased as well. This led to a longer drying time (Feng *et al.* 2020). Consequently, considering energy usage, cost, and practical application, the 2% to 5% (w/w) active component concentration was selected. Feng *et al.* (2016b) stated that 2.8% EB solid microemulsion was the best for detailed characterization, where the amount of ethyl acetate dissolving pesticide increased with increasing active ingredient content of EB during the preparation of solid microemulsion.

The shapes and sizes of nano-dispersion were measured after 24 h of incubation using TEM analysis (Figs. 1, 2, and 3) The prepared nanoparticles of each pesticide in this study were spherical in shape with varying sizes, ranging from 50.3 to 124.6 nm which agree with the findings of Tengshe and Karande (2020). Cui *et al.* (2018) increased bioavailability by reducing particle size in the lambda-cyhalothrin nano-formulation system. The augmentation of the pesticide's biological activity was supported by the formulation's improved dispersibility, wettability, and photostability performance. With this very efficient nano-formulation, pesticide active ingredient dosage may be reduced, and organic solvent residue could be completely avoided, increasing its environmental friendliness by reducing their side effects on human health and non-target organisms.

Comparatively, the three insecticides were more toxic against the 2nd and 4th instars in their nanoform than in their commercial form. This could be due to the fact that nano-pesticides have more surface area per unit volume and solubility than bulk pesticides and conventional formulations, which could boost the pest's absorption and accumulation of the active ingredient (Anjali *et al.* 2012; Feng *et al.* 2016). This agrees with Badawy *et al.* (2017) who found that chlorpyrifos-methyl nano-emulsion was the most toxic to *S. littoralis* followed by EC formulation and active ingredients with LC_{50} values of 1.17, 12.93, and 25.69 mg · l^{-1}, respectively. In this scenario, nano-chlorpyrifos and nano-imidacloprid were also more toxic than chlorpyrifos and imidacloprid against larvae and adults of the red palm weevil, *Rhynchophorus ferrugineus* (Olivier) (Coleoptera Curculionidae) having LC_{50} values of 28.4, 52.0, 123.3, and 126.1 mg · l^{-1}, respectively (Abd El-Fattah *et al.* 2019). Additionally, with LC_{50} values between 49.26, and 436.48 mg · l^{-1}, the active component in cypermethrin, deltamethrin, and lambda-cyhalothrin demonstrated greater reduced toxicity than EC pesticide formulations (Massoud *et al.* 2014; Abou-Taleb *et al.* 2015; Saad *et al.* 2016; Abd Elnabi *et al.* 2021). Furthermore, Feng *et al.* (2016) found that the LC_{50} of emamectin benzoate solid microemulsion was low and was 1.3 times more toxic than the water dispensable granule formulation against diamondback moths (*Plutella xylostella* L.). The larvicidal action of EM was strengthened as pesticide droplet size decreased. These findings are in line with other research.

The nano-dispersion formulations of the tested insecticides showed higher mortality rates of *S. littoralis* under laboratory conditions than their commercial formulations. Moreover, the data in this study showed that the nano-dispersion of EB, CP and BC was more effective in reducing the population density of *S. littoralis* than their commercial ones at different times of spraying under field conditions indicating their efficacy in controlling the cotton leaf worm. This finding agrees with Feng *et al.* (2020) who demonstrated that nano-formulations exhibited superior insecticidal activity against the cotton leafworm compared to conventional formulations (Feng *et al.* 2020).

Conclusions

In this study, chlorpyrifos, EB, and BC active ingredients were prepared as solid nano-dispersions by self-emulsifying and solidification technology. The type of active ingredient, carrier, surfactant, and active ingredient amount varied with the nano-formulation design. The nano-formulation with 1 to 5% active ingredient of pesticides, 8% of surfactant Unitop 100 mixed with FF4 and sucrose as a carrier had the best poly-dispersibility index, Z- average and biological activity. Moreover, the surfactant and solvent content in the solid nano-dispersion formulation was lower than in the conventional liquid and solid pesticide formulations. Based on laboratory and field data, chlorpyrifos 5%, emamectin benzoate 3%, and beta-cyfluthrin 4% solid nano-dispersions were more toxic than their conventional formulations against *S. littorralis*. Hence, from this study, nano-formulations can be recommended in pest control since organic solvents were avoided and surfactants were obviously reduced, all of which reduces environmental pollution and control costs as well.

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