Nanomaterial-based Agrochemicals New Avenue for Sustainable Agriculture: A Short Review

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ABSTRACT

The current scenario of agriculture and food production is unsustainable. Therefore, nanotechnology has provided innovative and creative frontiers to agriculture *via* developing novel nano-agrochemicals. The nanomaterial-based agrochemicals have a significant impact on agriculture activities (i.e., crop growth and protection) to support the necessary increase in the global food production in a sustainable way. Nano-fertilizers offer a promising alternative to the conventional fertilizers. Nano-fertilizers provide a control release strategy for nutrients which increases the use efficiency. Nano-pesticides further increase the efficiency of pesticide crop protection programs. Nano-pesticides improve the pesticide efficacy by increasing water solubility, bioavailability, enhancing adhesion to the plant foliage, and protecting active ingredients (AIs) from environmental degradation.

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1. Introduction

By 2050, the global population is expected to be 9.2 billion; the population in the developing countries will be 8.0 billion, while it will be 1.2 billion in the developed countries. Therefore, it is assumed that agriculture production should be increased by 50% from the current levels to meet the increased food demand [1]. This challenge is further exacerbated by climate change as agriculture activities have inextricable links with climate. An abrupt change in climatic conditions at such a rapid pace has threatened food security on a global scale [2]. Consequently, fertilizers and plant protection products (pesticides) are the necessary elements in modern agriculture to maximize crop productivity and boost its quality [3]. During the past two decades, many pieces of research have been carried out on nanotechnology and its numerous applications in the agriculture sector. Nanotechnology can be applied in agriculture activity by producing nano-fertilizers, nano-pesticides, nano-herbicides, nano-fungicides, and nano-sensors (**Figure1**)[4-9].

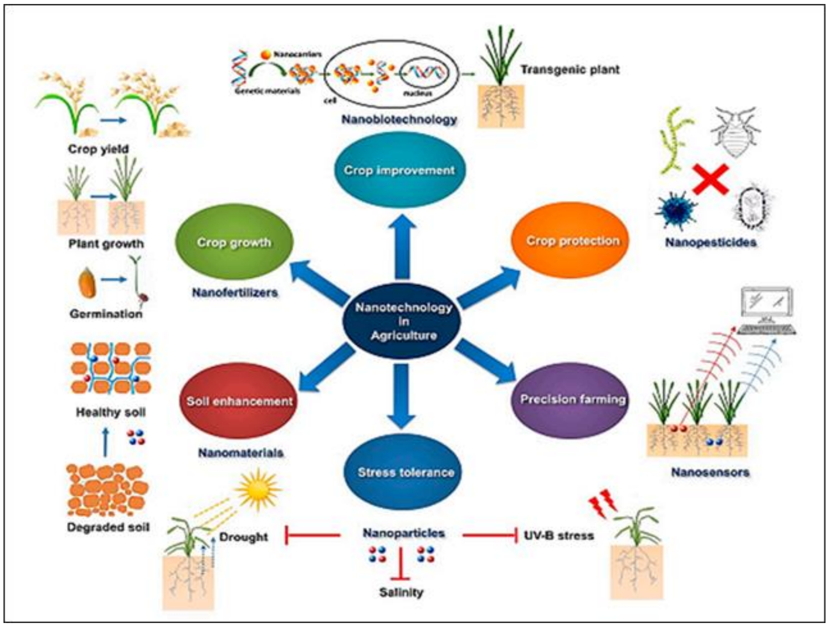

Figure 1. Applications of nanotechnology in agriculture [9]

2. Nano-fertilizers

Nano-fertilizers can be defined as encapsulated nutrients in which plant nutrients are coated with nanomaterials for the controlled delivery of plant imperative nutrient requirements (**Figure 2**) [10, 11]. The utilization of nanomaterials in fertilizer application increases the absorption and influence of nutritional elements and essential compounds for plants, as well [4]. Several factors are controlling the efficacy of nano-fertilizers such as the uptake, distribution, and accumulation of nano-fertilizers in crops. These factors strongly depend on both intrinsic and extrinsic factors; particle size and surface coating are the most important intrinsic factors. While the percent of organic matter, soil texture, and pH of the soil are significant extrinsic factors (**Figure 3**) [12, 13]. Foliar spray of calcium borate Nanoparticles (CaB_4O_7-NPs) was applied as a nano-fertilizer on *Lactuca sativa* and *Cucurbita pepo*, the application of CaB_4O_7-NPs promoted shoot and root biomass production of lettuce by 2.7 and 1.9-fold compared to the untreated plants, respectively

[14]. The treatment of the Blackeye bean plant with hybrid chitosan-calcium oxide nanoparticles increased the growth of the plant by 8 cm and 10.7 cm compared with 6 cm for the untreated plant [15]. Synthesized nano-siderite ($FeCO_3$-NPs) was applied on chickpea and displayed high effectiveness in preventing iron chlorosis by an excessive residual effect [16]. Utilization of zinc oxide NPs (ZnO-NPs) by foliar application on rice showed the reliable results to beat zinc deficiency. Furthermore, the application of ZnO-NPs also improved the growth and yield parameters and enhanced dehydrogenase, as well [17]. Nitrogen fertilizer coated with a nanoporous zeolite base has been utilized as a secondary approach contributing to the slow release of nitrogen which increases nitrogen use efficiency [18]. The urea-modified hydroxyapatite nanoparticles were encapsulated into cavities of the softwood of *Gliricidia sepium*, such nano-fertilizer composition exhibited a moderate and controlled delivery of nitrogen at three divergent pH values (4.2, 5.2, and 7) up to day 60 compared to the commercial fertilizer [19].

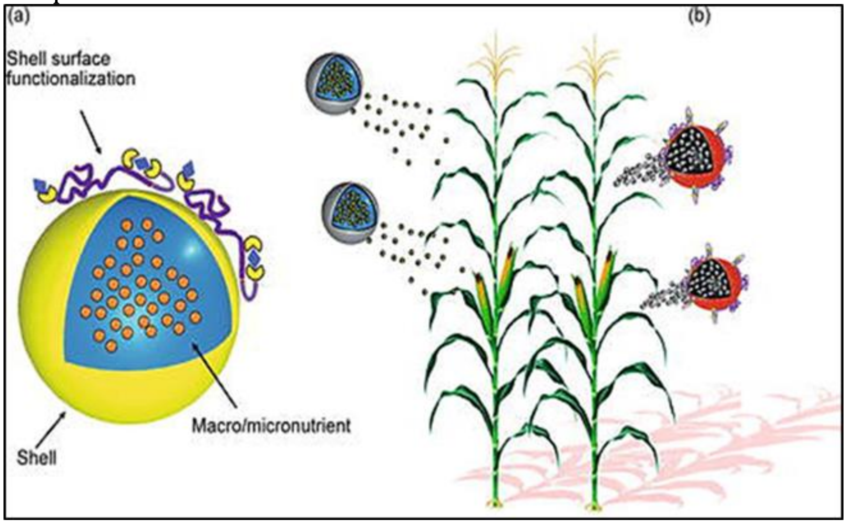

Figure 2. (a) Model of nanocapsule containing macro/microelements. Examples of opening strategies of nanocapsule: (b) release of nutrients as a function of time to avoid or limit nutrient losses or designed to occur when a molecular receptor binds to a specific chemical [11]

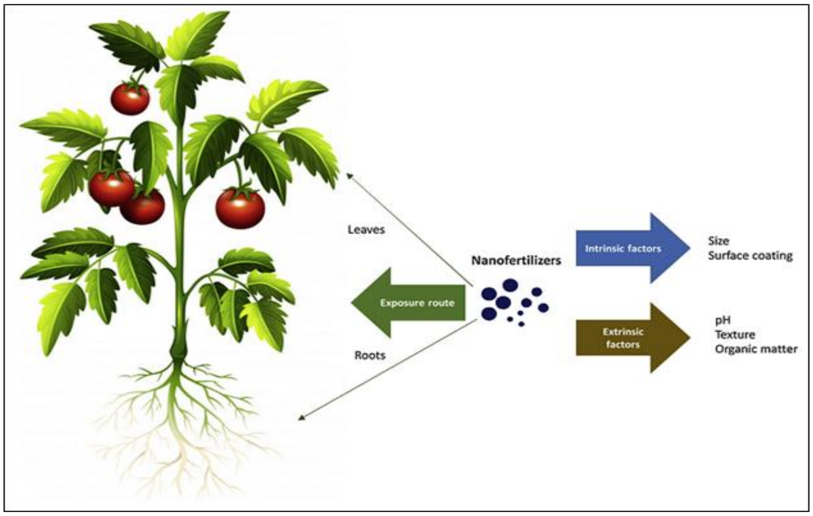

Figure 3. Factors that influence uptake, distribution, and accumulation of nano-fertilizers in crops [13]

3. Nano-pesticides

Nano-pesticides are any pesticide formulations intentionally including nano-sized entities (up to 100 nm) and claiming new properties arising from size [20]. Due to their small size and high surface area to volume ratio, nano-pesticides are expected to exhibit unique advantageous features compared to the conventional pesticides [21]. Nano-formulations increase the solubility and dispersion of lipophilic pesticides in water; stable aqueous nano-dispersions of lipophilic pesticides can be prepared by using suitable surfactants. Nano-formulations increase the bioavailability of the pesticides and reduce the use of toxic organic solvents [22]. An assortment of different forms of nano-based pesticides, including nanoemulsions, nanocapsules, nanospheres, nanosuspensions, solid lipid nanoparticles, mesoporous metal oxide nanoparticles, and nanoclays have been developed (**Figure 4**) [23-26].

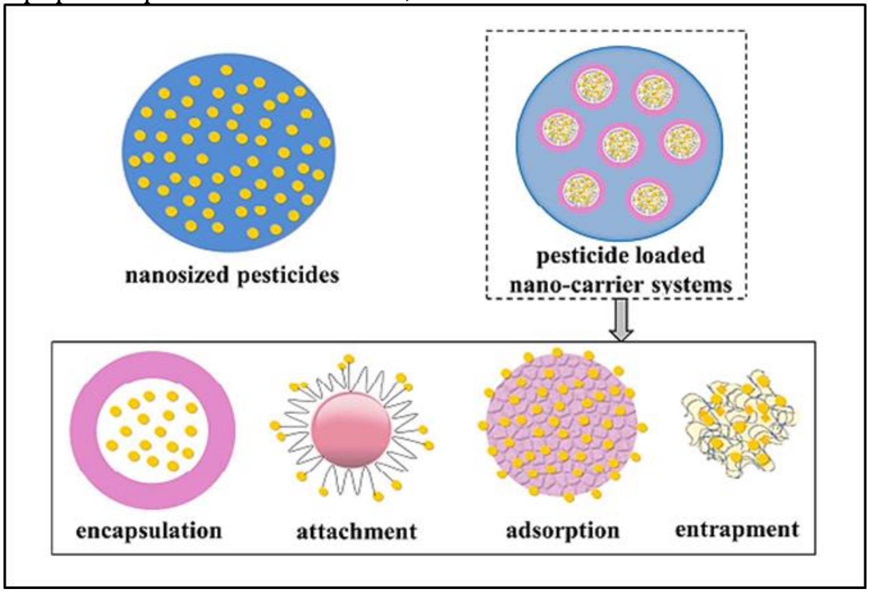

Figure 4. Schematic diagram of nano-based pesticide formulation [26]

3.1. Nano-emulsions

Nano-emulsions are heterogeneous systems composed of one immiscible liquid dispersed as droplets within another liquid. The droplets size of nano-emulsion is between 20 to 500 nm, the diameter and surface properties of the droplets possess a significant role in biological behaviour of the formulation [27]. Nanoemulsions consist of three main parts: oil, surfactant, and water, the two immiscible phases oil and water are present in a nano-emulsion system are separated by interfacial tension induced by surfactants (**Figure 5**) [28].

Abamectin-loaded nanoemulsion with a remarkable physical stability and application performance was obtained. The optimal formula was 2% abamectin and 5% castor oil polyoxyethylene (EL-40) dissolved in 7.5% hydrocarbon solvent (S-200) made up to 100% with deionized water. Abamectin nanoemulsion droplets exhibited the excellent wettability and diffusivity on cabbage leaves with a small dynamic contact angle. The insecticidal activity against the 3rd instar larva of *Plutella xylostella* explored the lowest LC_{50} value of 0.0686 mg/L [29].

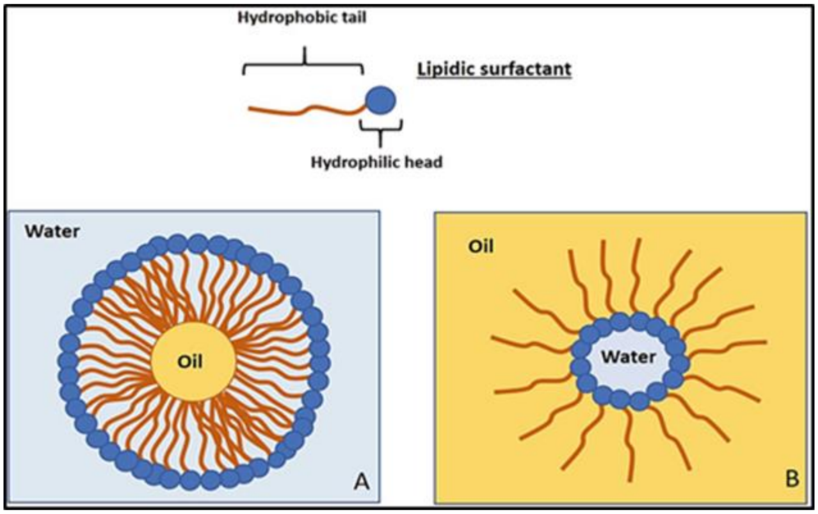

Figure 5. Schematic representation of Oil-in-water nanoemulsion (A) and water-in-oil nanoemulsion (B) [28]

3.2. Nano-capsules

Encapsulation technology provides a new strategy for improving the utilization rate of pesticides. Encapsulating pesticides into shell materials protects the active ingredients (AIs) from the degradation caused by environmental factors, reduces the loss of pesticides, achieves the sustainable release of AIs, and maintains the effective control over the extended periods of time [30]. A dual-function pesticide nanocapsule delivery system of two active ingredients (AIs) validamycin and thifluzamide was fabricated. The nanocapsule system was based on a water-oil–water double emulsion method combined with a high-pressure homogenization technology. The produced nanocapsules were monodisperse spheres with a mean particle size of ~260 nm. Compared with the commercial formulation, the nanocapsule delivery system demonstrated a synergistic effect, which enhanced the bioactivity against *Rhizoctonia solani* [25].

3.3. Nano-clays

Nano-clays are layered mineral silicates organized into several classes depending on chemical composition and morphology such as montmorillonite, halloysite, kaolinite, bentonite, and hectorite [31]. The chemical modification of commercial kaolin was performed *via* a simple hydrothermal method in the presence of NaOH and Na_2HPO_4 at 160 °C. Such type of modification changed the physical and chemical characteristics of kaolin in terms of morphology, surface area, and functionality which enhanced the insecticidal activity against *Spodoptera littoralis* The LC_{50} values for alkaline modified kaolin (AMK) in presence of NaOH were 403.19 mg/L and 98.11 mg/L for phosphate modified kaolin (PMK) in the presence of Na_2HPO_4 [24].

3.4. Solid lipid nanoparticles

Solid lipid nanoparticles (SLNs) are nano-sized carriers (50–1000 nm) developed in 1991 as a substitute colloidal drug delivery system parallel to liposomes, lipid emulsions, and polymeric nanoparticles. SLNs increase the biocompatibility, storage stability and prevent the degradation of the incorporated drug [32]. As a rule of thumb, SLN can be derived from the oil in water (O/W) nanoemulsions, however the oil droplets are replaced by a solid lipid or by a blend of a solid and a liquid lipid in which the active molecules can be incorporated with the solid lipophilic matrix (**Figure 6**) [33, 34]. The high shear homogenization and ultrasound methods were used for the fabrication of solid lipid nanoparticles loaded by essential oil *Ziziphora clinopodioides Lam* (SLN-EO). The lipid phase consisted of percirol ATO5 and campritol 888 (5% w/v), and Poloxamer 188 (2.5% w/v) was used as a surfactant. The fumigant toxicity of 2.5% SLN-EO with a particle size of 241.10 nm was evaluated against red flour beetle (*Tribolium castaneum*) and compared with the pure oil. The LC_{50} values of SLN-EO and pure oil were 30.602 and 68.303 (μL. L air-1), respectively. Further, the comparative assessment of persistence indicated that SLN-EO formulation remained effective until 14 days, while the pure oil lost its toxicity after the 8th day of application [35].

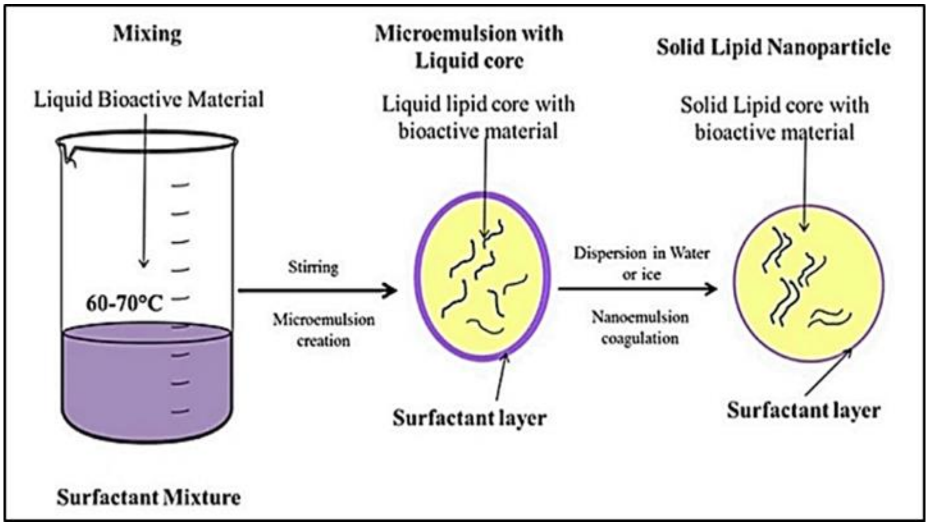

Figure 6. Schematic representation of SLN production by microemulsion technique [34]

3.5. Nano- Suspensions

Suspension concentrate (SC) is a new pesticide formulation used for water-insoluble pesticides. Dispersion of pesticides into the aqueous media can minimize the usage of organic solvents and soil pollution. SC is a thermodynamically unstable system in which pesticide particles are spontaneously deposited [36]. Pesticide nano-suspensions are nanocolloidal dispersions of pesticide active ingredient particles in crystalline or amorphous state stabilized by surfactants. The application of nano-suspension formulations in pest management programs not only increases the solubility rate of pesticides, but it improves the stability and enhances the efficacy, as well [32]. Nano-suspension of poorly water-soluble fungicide (azoxystrobin) was manufactured in the presence of 1-Dodecanesulfonic acid sodium salt (SDS) and polyvinylpyrrolidone K30 (PVP K30) by using the wet media milling method. The value of mean particle size, polydispersity index, and ζ potential of azoxystrobin nanosuspension was 238.1 ± 1.5 nm, 0.17 ± 0.02, and − 31.8 ± 0.3 mV, respectively. Compared to conventional fungicide formulations, the nanosuspension exhibited an increase in retention volume and reduced the contact angle which in turn enhanced the wettability and adhesion. Moreover, azoxystrobin nanosuspension indicated the highest anti-fungal activity against *Fusarium oxysporum* with LC_{50} = 1.4243 mg/L [37].

3.6. Mesoporous metal oxide nanoparticles

Mesoporous metal oxide nanoparticles (MMOs) have received much attention due to their unique physicochemical properties in terms of the large surface areas, reduced densities, and hydrothermal stability in aqueous and organic solutions [38]. The applications of mesoporous metal oxide nanoparticles depend on their properties, so as several MMOs, they have been synthesized with controlled structures, compositions, and morphologies [39, 40]. The insecticidal activity of different structures of SiO_2-NPs on *Spodoptera littoralis* has been evaluated, and the results demonstrated that the entomotoxic effect is dominated by particle size. SiO_2-NPs with the smallest size (33 nm) exhibited the highest control efficacy with LC_{50} = 327.7 mg/L after 11 days post-treatment [40]. The poisoned food technique was utilized to evaluate the anti-fungal activity of MgO-NPs against three seed-borne fungi of rice, *Fusarium verticillioides, Bipolaris oryzae, Fusarium fujikuroi*. Sepioliteblended MgO nanocomposite (SE-MgO) exhibited a higher antifungal effect compared to the pure MgO-NPs. The treated seed with SE-MgO (250 mg/L MgO as an active ingredient) revealed 100% hyphal reduction [41]. The template free direct precipitation method has been used for the fabrication of a hierarchical microflower-like structure of copper oxide nanoparticles with an average size of 1.0 µm. CuO-NPs exhibit fast entomotoxic effect on *Spodoptera littoralis* with LC_{50} = 232.75 mg/L after 3 days post-treatment. CuO NPs caused severe damages to the insect exoskeleton through the damage of its cuticle water barrier mostly by abrasion, besides the effect of reactive oxygen species (ROS) that create a pore network on the cell membrane which in turn causes the leakage of intracellular contents (i.e., lipids) and deterioration of the protective wax layer [23]. *Ijaz et al.* [42], evaluated the antibacterial activity of green synthesized CaO-NPs using leaf extract of *Mentha piperita* against *Escherichia coli* bacteria. The well-diffusion method was utilized for estimating their antimicrobial index on *Escherichia coli*. The maximum zone of inhibition (up to 42 mm) was observed when 100 mg/L CaO-NPs loaded with 50 µl inoculum size of *Escherichia coli* at sunlight exposure of 5 hours. The antiviral activity of a uniform sphere of TiO_2 nanostructures has been investigated against broad bean strain virus in faba bean plants. The hollow sphere structure of TiO_2 has birdcage-like perforations which in turn significantly increased the exposed interaction area between the plant virus and TiO_2, and subsequently increased their antiviral activity. The results confirmed a significant reduction in disease severity for treated faba bean plants relative to the untreated [43]. The insecticidal activity of sea urchin-like calcium borate (CaB_2O_4) microspheres and its synergistic combination with cholinesterase-inhibiting insecticides are explored against *Spodoptera littoralis.* The synergistic combination with methomyl and chlorpyrifos increases the toxicity to 2.4 and 2.6-fold higher than the individuals. CaB_2O_4 microspheres cause physical damage to the external insect's cuticle layer, which consequently enhances the uptake of organic insecticides (**Figure 7**) [44].

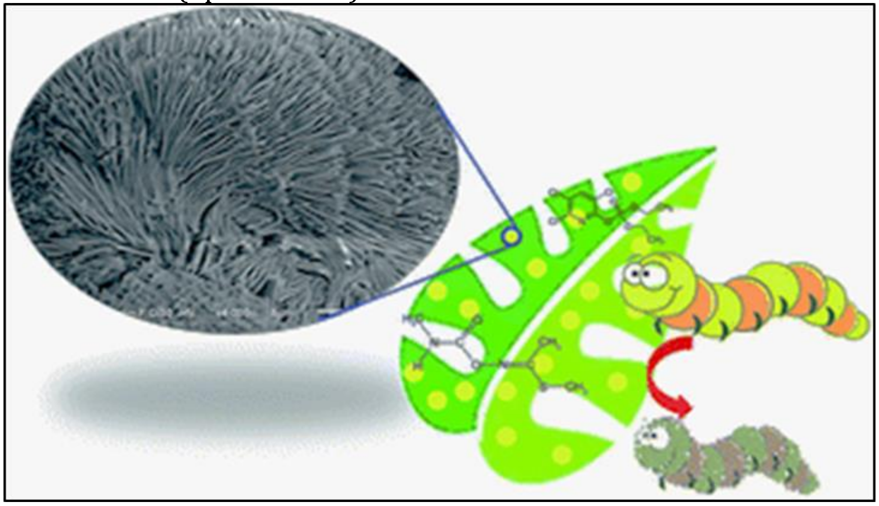

Figure 7. Synergistic combination of sea urchin-like calcium borate microspheres with methomyl and chlorpyrifos insecticides [44]

4. Conclusions

The urgent need for increasing agriculture production encourages the researchers to provide the efficient and sustainable strategies for food production. The engineering of nano-materials affords a prospective way for novel nano-agrochemicals by utilizing their efficacy and the environmental impacts. Nano-fertilizers increase the absorption and influence of nutritional elements and essential compounds for plants by encapsulating the nutrients with nanomaterials. These encapsulated nutrients provide a controlled delivery which in turn reflects on the crop's growth and productivity. Furthermore, nano-pesticides exhibit unique advantageous features compared to the conventional ones *via* increasing the bioavailability of the pesticides and reducing the use of toxic organic solvents. Besides, reducing environmental pollution through the mitigation of pesticide application rates and decreasing losses.

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Conflict of Interest

The authors declare no conflict of interest.

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