

## Application of nanotechnology in crop pest management- A review

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### Abstract

For materials with a size range of 1–100 nm, the term “nano” is typically employed. Still, given their smaller size, it is also typical for these materials to exhibit distinct characteristics from bulk materials. In this book, the traditional methods of managing insect pests were discussed, along with the prospective applications of nanomaterials as cutting-edge nanoscience and nanotechnology techniques. Increased efficacy, durability, and a reduction in the quantity of active chemicals needed are just a few benefits that nanopesticide solutions may offer. There are several formulation forms that have been suggested, such as nanoemulsions, nanocapsules, and goods that incorporate flawlessly produced nanoparticles such as metals, metal oxides, and nanoclays. Nanotechnological deliverables such as nanomaterials, encapsulated nanoscale plant production and protection inputs like fertilizers, pesticides, herbicides, plant growth regulators, and other formulations using surfactants, polymers, dendrimers, surface ionic attachments, and other related mechanisms can be used to achieve controlled release of agricultural and horticultural inputs. The use of nanoparticles offers the potential to transform the green revolution into an evergreen revolution and to effectively manage agricultural pests.

**Keywords:** Nanotechnology, insect control, nanopesticides, formulation

### Introduction

The main obstacles to greater productivity in horticultural and agricultural production systems are insect pests, which must be managed with frequent applications of insecticides. The 3Rs—resistance, resurgence, and residue—as well as environmental concerns were developed as a consequence of irregular pesticide applications for crop protection. By using nanotechnology, it is possible to strike a balance between crop protection and productivity. High electrical conductivity, remarkable strength, and chemical reactivity are just a few of the unique properties that nanoparticles frequently display. Nanotechnology will have a noteworthy effect on reducing non-targeted toxicity and improving the effectiveness on targeted organisms in smaller quantities. As a result, crop protection options are made safe and effective by nanotechnology (Kannan *et al.*, 2020a, b) [18, 19]. Throughout the past ten years, nanotechnology has become increasingly prevalent in horticulture and agriculture, developing unique input materials with a large number of uses to address unresolved pest issues.

### Principles of nanotechnology

The advantages of nanomaterials' small size, large surface area, and ease of attachment make them ideal for the efficient smart delivery of agrochemicals (Ghormade *et al.*, 2011) [11]. Unlike conventional pesticide formulations, where over 90% of the pesticides runoff within the surroundings and leave residue in agricultural goods during application, nanoparticles release the agrochemicals to plants through regulated delivery systems. For a necessary amount of time and at a predetermined pace of release, the control delivery systems enable the active ingredient to be released gradually at the target spot. According to Jha *et al.*, 2011 [16], targeted delivery improves the efficacy of pesticides against plants, insects, and pathogens; increases solubility; disperses fat-soluble chemicals in aqueous solution; decreases the amount of pesticides applied; increases treatment frequency by extending the validity period and improving bioefficacy; decreases the amount of chemicals applied to plants; resolves non-target toxicity; and

improves chemical stability for compounds that are light-sensitive by limiting photodegradation. Pesticide discharges that occur over time preserve ecological biodiversity.

### The utilisation of nanomaterials for pest management in agricultural and horticultural crops

According to Roy (2009) [41], a variety of insect pests may be managed with the use of nanomaterials such as carbon, titanium dioxide, zeolites, silver, silica, copper, and alumina. Nanomaterial-based plant protection solutions promise numerous advantages over traditional pesticide products while also changing the risk profile or functioning of current chemicals (also known as nano-enabled pesticides). According to Walker *et al.*, 2017 [47], these benefits could include enhanced environmental safety, reduced application rates, easier application, better insect species targeting, higher efficacy, and improved formulation features.

#### ■ Clay minerals

Among the larger class of minerals are the finely grained solids known as clays. The hydration of exchangeable cations and the presence of Si-OH clay mineral groups provide the surface of clay minerals its hydrophilic characteristics. The clay minerals exhibit a greater affinity for hydrophobic molecules in the absence of water. Thus, clay has the ability to absorb substances from insect bodies that are both hydrophilic and hydrophobic, leading to desiccation and ultimately death. An increased number of particles adhere to the insect's body surface thanks to its flat surfaces. These days, nanosilica is employed extensively in the fields of medicine, drug research, packaging, coating, and filtration. It has also grown in significance as a cutting-edge nano biopesticide (Barik *et al.*, 2008) [2]. Application of silica nanoparticles at 200 mg/kg in *Tribolium castaneum* and *Rhyzopertha dominica*, adults of the rice weevil *Sitophilus oryzae*, and adults and larvae of *Tribolium confusum* resulted in mortality after 7 days of exposure (Ziaee & Ganji, 2016) [52].

### ▪ Nanoscale silver

High surface area, extreme stability, and excellent dispersibility in aqueous solution characterize silver nanoparticles. Pesticides can be applied with fewer doses when coupled with metal-based nanoparticles. In a number of ornamental plants, Rouhani *et al.*, 2012<sup>[40]</sup> confirmed that silver nanoparticles showed greater insecticidal action against the oleander aphid, *Aphis nerii*. Ag<sup>+</sup> aqueous solution and more deaths were caused by gold nanoparticles based on pungam oil., according to Sahayaraj *et al.*, 2016<sup>[42]</sup>, whereas Ag<sup>+</sup>-AuNPs treatment aqueous solutions significantly increased food consumption and assimilation but decreased conversion and had an impact on *Olepa ricini* growth.

### ▪ Nanoscale aluminosilicate

Chemical companies formulate effective nanoscale insecticides. Insect hairs readily absorb sprayed aluminium-silicate nanotubes from plant surfaces, and they aggressively groom and eat the nanotubes laced with pesticides. Pesticides using nanotubes are more environmentally friendly and biologically active. When the insecticidal action was tested on two stored grain insect pests, *S. oryzae* and *R. dominica*, it proved to be an effective and less expensive option to control the pests after causing mortality after three days of continuous exposure. (Source:-<https://doi.org/10.1007/978-981-19-0343-4>)

### ▪ Silica nanoparticles

One kind of special nanomaterial that was created from silica resources was silica nanoparticles, which were then applied as nanopesticides. In addition to animal ectoparasites of veterinary significance, nanosilica can be effectively utilized to manage a variety of agricultural insect pests via physisorption into the cuticular lipids, which results in the physical death of insects when applied to leaves or stem surfaces. Additionally capable of delivering chemicals and DNA into plants, mesoporous silica nanoparticles have created a potent new instrument for targeted distribution into plant cells and assistance with pest control (Barik *et al.*, 2008)<sup>[2]</sup>. Against *S. oryzae*, *R. dominica*, *Callosobruchus maculatus*, and *Lasioderma serricornis*, silica nanoparticles were very efficient at 2.5, 1.5, 1.0, and 0.5 g/kg of seeds, respectively (Borie *et al.*, 2014).

The natural sugarcane *Erianthus arundinaceus*, which yields

biologically generated nanosilica, has demonstrated insecticidal action against *Plutella xylostella* larvae, with an LC50 of 30.03 µg/mL. (source:-<https://doi.org/10.1007/978-981-19-0343-4>)

### ▪ Titanium dioxide

In comparison to ozone and chlorine, titanium dioxide (TiO<sub>2</sub>) is an extremely potent disinfectant and a common non-toxic white colour. As TiO<sub>2</sub> doesn't cause harm, it can be used in food products up to 1% of the total weight. Due to its high pathogen disinfection efficacy and lack of formation of hazardous or toxic chemicals, the TiO<sub>2</sub> photocatalyst technology holds tremendous promise for use in a variety of agricultural applications, including plant protection (Yao *et al.*, 2009)<sup>[50]</sup>. In the cotton leaf worm (*Spodoptera littoralis*; LC50 of 125 µg/mL) (Shaker *et al.*, 2017)<sup>[44]</sup> and the diamondback moth (*P. xylostella*) (LC50 of 37.57 µg/mL) in cauliflower (Preetha *et al.*, 2018)<sup>[27]</sup>, TiO<sub>2</sub> nanoparticles also shown their insecticidal properties.

### ▪ Carbon nanomaterials

Graphene, buckyballs, single-walled carbon nanotubes (CNT), multiwalled carbon, and other carbon-based nanomaterials are examples of manufactured nanomaterials that are heavily utilized in nano-biotechnology applications. The utilization of carbon-based nanomaterials functionalized with magnetic nanoparticles offers an advantage in that the internal space permits the filling of appropriate plant-protecting chemicals, while the magnetic nanoparticles allow external control of the nanocarriers' movement within the plant system. By using electronic devices that sense the harmful gases that insects generate, nanosensors-based monitoring utilizing carbon nanotube materials can be utilized to find hidden insects (Lee *et al.*, 2014)<sup>[23]</sup>.

### ▪ Polymer nanoparticles

In addition to being inexpensive and easily biodegradable, polymer nanoparticles also don't produce any harmful breakdown byproducts. There are various applications for biopolymers, or polymers that come from organic origins with favourable chemical and physical characteristics for moderate biodegradation to prevent environmental contamination. The common polymers (both natural and synthetic) included in controlled release formulations (CRFs) for the administration of insecticides are noted in Table 1.

**Table 1:** A list of common polymers used in the manufacturing of nanoparticles

Polymer	Active compound	Nanomaterial	References
Glyceryl ester of fatty acids	Carbaryl	Spheres	Quaglia <i>et al.</i> , 2001 <sup>[38]</sup>
Lignin-polyethylene glycol-ethylcellulose	Imidacloprid	Capsule	Flores Céspedes <i>et al.</i> , 2012 <sup>[8]</sup>
Polyethylene glycol	β-Cyfluthrin	Capsule	Loha <i>et al.</i> , 2012 <sup>[28]</sup>
Poly lactide	Chlorantraniliprole	Capsule	Liu <i>et al.</i> , 2017 <sup>[26]</sup>
Polyethylene	Piperonyl butoxide and deltamethrin	Capsule	Frandsen <i>et al.</i> , 2010
Polyamide	Pheromones	Fibre	Hellmann <i>et al.</i> , 2011 <sup>[14]</sup>
Lignin	Imidacloprid or cyromazine	Granule	Fernández-Pérez <i>et al.</i> , 2000
N-(octadecanol-1-glycidyl ether)-O-Sulfate chitosan octadecanol glycidyl ether	Rotenone	Micelle	Lao <i>et al.</i> , 2010 <sup>[22]</sup>
Carboxymethyl chitosan ricinoleic acid	Azadirachtin	Particle	Feng and Peng, 2012 <sup>[6]</sup>
Chitosan-poly(lactide)	Imidacloprid	Particle	Li <i>et al.</i> , 2011 <sup>[24]</sup>
Poly(methyl methacrylate)-poly (ethylene glycol) Polyvinylpyrrolidone	Carbofuran	Suspension	Chin <i>et al.</i> , 2011 <sup>[5]</sup>
Polyurethane	Carbosulfan	Capsule	Xu <i>et al.</i> , 2016 <sup>[48]</sup>
Soybean protein isolate (SPI) and carboxymethyl cellulose (CMC)	Avermectin	Conjugated particle	Liu <i>et al.</i> , 2019 <sup>[27]</sup>
Carboxymethyl chitosan	Emamectin benzoate	Spherical particle	Song <i>et al.</i> , 2019 <sup>[46]</sup>

### ▪ **Magnetic nanoparticles**

Systemic plant protection compounds that affect only specific plant regions could be delivered to specific sites with the use of magnetic-based nanoparticles. External magnets with high power could be used to track the movement of internalized magnetic nanoparticles. Magnetic nanoparticles in social insects function as geomagnetic sensors, and insects are known to exhibit temperature-dependent ferromagnetic resonance.

(Source:

[https://www.researchgate.net/publication/313352305\\_Isnanotechnologypromising\\_field\\_for\\_insect\\_pest\\_control\\_in\\_IPM\\_programs](https://www.researchgate.net/publication/313352305_Isnanotechnologypromising_field_for_insect_pest_control_in_IPM_programs))

### **Types of nano-based pesticide formulations**

Nanotechnology has made it possible to create novel nano-based pesticide formulations, or nanopesticides. Emulsion, polymer, lipid, ceramics, proteins, and metals can all be used to create nanopesticides. Oil in water emulsion systems (microemulsion and nanoemulsion) are commonly used to prepare nanopesticides. The emulsion is then converted to organic nanoparticles through milling, solvent evaporation, coacervation, and precipitation techniques (Ragaei & Sabry, 2014; Nuruzzaman *et al.*, 2017) <sup>[39]</sup>. Another method for creating nanopesticides is to directly convert them into nanoparticles, or nanosized pesticides, or to load them onto nanocarriers in delivery systems. Pesticides are loaded into nanocarrier systems in the following ways: by being entrapped inside the polymeric matrix or by being encapsulated inside the nanoparticulate polymeric shell, which allows for absorption onto the nanoparticle surface and attachment on the nanoparticle core through ligands. Numerous forms of nanoformulations have been created, such as solid lipid nanoparticles, mesoporous nanoparticles, electrospun nanofibers, polymer nanoparticles, magnetic nanoparticles, nanogels, and dendrimers (Zhao *et al.*, 2017) <sup>[51]</sup>.

### ▪ **Nanospheres**

A polymeric matrix with a spherical form, nanospheres have diameters ranging from 10 to 200 nm. The medication is encapsulated, imprisoned, then dissolved. The mixture in which the polymeric matrix has a uniform distribution of the active component.

### ▪ **Nanocapsules**

Colloidal nanobubbles with a polymeric membrane around the centre and possessing unique features at the nanoscale are known as nanocapsules.

### ▪ **Micelles**

Micelles are amphiphilic compounds formed into nanoscale colloidal dispersions with a hydrophilic head and a hydrophobic tail. The aggregates developed when the concentration of amphiphile in water increased over a certain critical value, also referred to as the critical micelle concentration. (Source: <https://doi.org/10.1007/978-981-19-0343-4>)

### **Techniques used for CRFs preparations**

#### ▪ **Chemical bonding**

By attaching an active component to a monomer, a new polymer is produced using this approach. The chemical groups known as "active ingredients" include carboxylic acid, carbonyl group, and amines. These groups react with

reagents and attach themselves to the monomer unit or polymer as a whole. Particle size, medium pH, and degree of substitution all affect attachment. In order to develop polymeric formulations with halo aromatic structures, prior researchers (Muzammil *et al.*, 2017) <sup>[31]</sup> modified both linear and cross-linked poly (glycidyl methacrylate).

### ▪ **Microencapsulation**

This method entails coating tiny capsules—less than 1 micrometre in size as nanoparticles and more than 1000 micrometres in size as microcapsules. Insect growth regulators, weedicides, insect repellents, and microbiological inhibitors were among the emerging uses of nanoencapsulated polymers that Peteu *et al.*, 2010 <sup>[35]</sup> demonstrated. The stability of these nanoformulations at elevated temperatures was observed. Using urea formaldehyde polymer, Yang and Pan combined microencapsulated insecticide and obtained a patent for their technique. In their study, Brown *et al.*, 2003 <sup>[4]</sup> investigated the physical characteristics and thermal resistivity of urea-formaldehyde resins using various encapsulation techniques.

### ▪ **Matrix Capsulation**

The procedure of nanoencapsulation releases a chemical to a specific host for the purpose of controlling insect pests gradually but effectively. The most popular approach is this one. Mosurkal *et al.*, 2007 <sup>[30]</sup> investigated cyclic acetal molecules incorporated in a polyamide. The active component benzaldehyde was created by the gradual hydrolysis of acetal and was subsequently investigated utilizing spectroscopic methods. It is therefore possible to add a chemical moiety with insecticidal or antifungal activity for regulated release.

### **Nanoencapsulation for precision pesticide application**

According to Hack *et al.*, 2012 <sup>[13]</sup>, nanoencapsulation is a subset of nanotechnology that offers a range of advantageous characteristics, such as decreased human exposure to active substances, controlled release, extended residual concentrations, removal of organic solvents, and enhanced efficacy. Since encapsulation of formulations allows for lower dosages of conventional pesticides to have maximal efficacy and more targeted action, it has revolutionized the administration of pesticides in the control of insect pests due to the advent of nanotechnology. With this technique, the pesticide's core substance is wrapped, or encased, in a shell or encapsulation material, causing the pesticide's size to drop to a nanoscale.

Insecticide is distributed efficiently and gradually by nanoencapsulation to manage insect pests. Only the designated environment receives the release of pesticide, such as in a specific pH (such as in the intestine or inside a cell), specific temperature, moisture, external ultrasound frequency, or in the presence of specific compounds. In this process, individual particles or droplets of solid or liquid core material are surrounded or covered by a continuous 6 film of polymeric material. Certain encapsulation techniques are applied so that the substance is absorbed into the surface of the plant and facilitates protract release which lasts for a longer time compared to conventional pesticides.



### Polymers-based nanoformulations for insect's control

Alginate, carboxymethyl cellulose, pectin, chitosan, and guar gum are examples of biodegradable polymers that are frequently combined with nanopesticides. The encapsulation technique was utilized to create imidacloprid CRFs [1-(6-chloro-3-pyridinyl methyl) -N-nitroimidazolidin 2-ylidene amine] using amphiphilic copolymers, which are synthesized from poly (ethylene glycols) and various aliphatic diacids and self-assemble into nano-micellar aggregates in aqueous media (Adak *et al.*, 2012) <sup>[1]</sup>. The CRFs required a duration of 2.32 to 9.31 days to release 50% of imidacloprid. Several crops can benefit from the effective pest management provided by the created CRFs. On the other hand, the CRFs required 2.32 to 9.31 days to release 50% of imidacloprid. The created CRFs can be applied to various crops for effective pest management. An intriguing way to prevent the use of petrochemical derivatives, which could be another source of environmental contamination, is to employ a variety of biopolymers, or polymers derived from natural sources that have good physical and chemical properties and mild biodegradation conditions. Depending on the characteristics of the polymer, the loading and solubility of the active component, and the diffusion or dissolution (erosion) of the ingredient, release processes can be regulated. Additionally, for a hydrophilic polymer matrix—a polymer matrix that is prone to swelling and dissolution—the thickness of the gel layer that forms will influence the diffusion paths, changing the release behaviour in the process (Kaunisto *et al.*, 2013) <sup>[21]</sup>. It is anticipated that the processes causing polymer breakdown would have a significant impact on the release of profiles. A phase of severe breaking down the polymer network occasionally results in the release of the remaining active component. Furthermore, fast desorption and diffusion from the surface may cause a burst of release of the active ingredients if the active ingredients are not uniformly distributed inside the polymer network.

### Nanoencapsulation process of insecticides

A nanopesticide is made up of either inorganic components, such as metal oxides in different forms, or organic components, such as polymers (e.g. particles and micelles). Increasing the apparent solubility of poorly soluble active ingredients, releasing them gradually or selectively, and/or shielding them from premature degradation are the goals of nanoformulations. Formulated pesticides in the pesticide market are a blend of active ingredients, solvents, surface active ingredients, stabilizers, etc. Among them, the active ingredients alone responsible for killing target pests and other materials like organic solvents, surface active ingredients (stickers or spreaders) and stabilizers help to maintain their solubility, stability and pesticide activity. Nanoencapsulated products facilitate appropriate assimilation of the active ingredients into the plants and protect them from abiotic degradation (Srinis & Lyons,

2007) <sup>[43]</sup>. Nanoencapsulates release the microencapsulation comprising nanosized particles of the active ingredients being sealed by a thin walled sac or shell (protective coating). Microcapsules generally measure 50–500 microns in size. Nanoencapsulation with nanoparticles in the form of pesticides, as opposed to bigger particles, permits appropriate chemical absorption into the plants, present in the conventional insecticide formulations.

### Nanoencapsulated pesticides used for crop pest's management

Through the method of nanoencapsulation, a chemical is released to a specific host for insect pest control slowly yet effectively. Materials with nanotechnological roots have better bioavailability of active compounds, lower toxicity, longer release times, greater solubility, increased stability, protection against early degradation, and lower dose requirements to kill the target organism (Smith *et al.*, 2008) <sup>[45]</sup>. Compared to commercial pesticides, nanoencapsulated formulations retain their pest control efficacy for a longer period of time because they enable the regulated release of active components. Numerous CRFs have been created through the use of broad nanoencapsulation techniques; the materials and enhanced properties of these materials have been extensively reported.

It has been observed that stored grain pests can be effectively controlled by using nanoencapsulated CRF insecticides and biopesticides (Table 2). In their study, Loha *et al.*, 2012 <sup>[28]</sup> evaluated the impact of nanoencapsulated CRFs of  $\beta$ -cyfluthrin with PEG and found that it resulted in increased *Callosobruchus maculatus* mortality compared to commercial formulation. The EC<sub>50</sub> values for the commercial and nano CRFs containing PEG  $\beta$ -cyfluthrin on the seventh were found to be 43.24 mg/L and 1.89 mg/L, in that order. Similar to how pirifluquinazon with polymeric chitosan on *Myzus persicae* (green peach aphid) and carbofuran against the root-knot nematode (*Meloidogyne incognita*) infecting tomato plants (Pankaj Shakil *et al.*, 2012) <sup>[34]</sup> demonstrated the usefulness of encapsulated pesticide formulation. Using polyethylene glycol and 1 aliphatic diacids, Adak *et al.*, 2012 <sup>[1]</sup> created nanoencapsulated imidacloprid CRFs. Testing the CRFs against *Bemisia tabaci* (whitefly) and *Melanagromyza sojae* (stem fly) in soybeans showed that they performed better than commercial formulations at lower doses without leaving residues in the soil and crops. *Spodoptera litura* exhibited a spinosad efficiency that was dependent on particle size. The low concentration (LC<sub>50</sub>) of the nanosuspension used on spider mites was 15 mg/L at 404 nm particle size. This further dropped to 11 mg/L at 372 nm, 7.6 mg/L at 332 nm, and 4 mg/L at 163 nm, and showed greater efficacy than as a commercial pesticide (Hwang *et al.*, 2011) <sup>[15]</sup>.

**Table 2:** Efficacy of nanoformulations

Type of formulation	Efficacy of the nanoformulation
Nanoemulsion: neem oil	LC <sub>50</sub> decreased with droplet size.
Permethrin	Greater efficacy than pure AI against larvae [LC <sub>50</sub> (24 h) 0.006 and 0.020 mg/L, respectively]. Reduced effects on nontarget organisms (soil bacteria and plants).
Polymer based on polyethylene glycol: $\beta$ -cyfluthrin	Greater efficacy than commercial formulation when evaluated over a long period (e.g. insect mortality bioassays, EC <sub>50</sub> (30 d) were 30–45 mg/L and 125 mg/L, resp.).
Carbofuran	Greater efficacy than commercial formulation.

Acephate	Greater efficacy than commercial formulation (biochemical assays, <i>in vitro</i> and field trials) Lower toxicity than Commercial formulation (mice acute oral toxicity and <i>in vitro</i> cytotoxicity).
Electrospun nanofibers thiamethoxam	Efficient at 50% of the recommended dosage (9 days glass House tests, whitefly).
Nano inorganic + organic AI chlorfenapyr	Insecticidal activity of silica nanoparticle formulation was twice as high as that of microparticles (laboratory and field tests).
Inorganic nano as active ingredient silica	Efficacy at similar rates than commercial diatomaceous earth for stored grains (0.5–2 g/kg) Effects of coating and size to be further investigated.
TiO <sub>2</sub>	Better or on par efficacy compared to standard treatment (greenhouse and field trials).

Source: (Kah and Haffman, 2014) <sup>[17]</sup>

### Nanoformulations of botanical biopesticides in insect control

Alternatives to synthetic chemical insecticides include plant-based botanicals and biopesticides. Tamil Nadu Agricultural University is using nanoparticles as an effective technique. A neem-based formulation (198 nm) has been produced and proven to be successful in eliminating mites, aphids, and thrips, as well as other sucking pests. The insecticidal effectiveness of garlic essential oil encapsulated in polyethylene glycol against adult *T. castaneum* showed 80% mortality, according to Yang *et al.*, 2009 <sup>[49]</sup>. According to González *et al.*, 2014 <sup>[12]</sup>, nanoparticles containing essential oils of bergamot or geranium also showed contact toxicity against *T. castaneum* and *R. dominica*. Regarding the nanoparticles encapsulated with neem extract, Forim *et al.*, 2013 <sup>[9]</sup> showed 100% mortality

of *Plutella xylostella*. When applied topically to the cowpea beetle, *C. maculatus*, nanoemulsions containing the essential oils of three local plants—*Ageratum conyzoides*, *Achillea fragrantissima*, and *Tagetes minuta*—exhibited ovicidal, adulticidal, and residual properties (Nenaah, 2014) <sup>[32]</sup>. In newly hatched *Pectinophora gossypiella* and *Earias insulana* larvae, a nanoemulsion of eucalyptus oil exhibited greater insecticidal and biological activities. When the sweet lag (*Acorus calamus*)-based botanical biopesticide was tested for comparative toxicity against the red flour beetle, *T. castaneum*, the results showed that lower doses (below 1%) of the nanoformulation were sufficient to kill 100% of the insects (Prabakaran *et al.*, 2017) <sup>[36]</sup>. Among the nanoparticles, silver nanoparticles are widely used accounting for more than 30% of nano-based commercial products in the world (Table 3).

Table 3: Use of nanoparticles in insect pest management

Application	Nanoparticles
Avermectin	Porous hollow silica (15 nm)
Ethiprole/phenylpyrazole	Polycaprolactone (135 nm)
Gamma cyhalothrin	Solid lipid (300 nm)
Tebuconazole/chlothanal	Polyvinylpyridine and polyvinylpyridine co-styrene (100 nm)
Plant origin nanosilica for control of <i>Artemisia arborescens</i>	Nanosilica (3–5 nm)
Essential oil encapsulation	Solid lipid (200–294 nm)
Microorganisms <i>Lagenidium giganteum</i> cells in emulsion	Silica (7–14 nm)
Carbofuran/triazophos	Gold (40 nm)
Dimethoate	Iron oxide (30 nm)
Organophosphate	Zirconium oxide 50 nm
Pyrethroid	Iron oxide (22 nm)
Imidacloprid	Titanium oxide (30 nm)

(Source: Manjunatha *et al.*, 2016) <sup>[29]</sup>

### Beneficial insects in agricultural ecosystem safety

Recently, a wide range of nanomaterials and nanoformulations have been used to manage agricultural insect pests. The entire range of experiments on the effects of nanomaterials on growth, development, parasitism or predatory efficiency, emergence capability, and protection of beneficial insects remains unexplored. Even so, research conducted by Kannan *et al.*, 2020b <sup>[18, 19]</sup> on the effects of chemically modified silica nanomaterials against parasitoids (*Trichogramma*) and predators (green lacewing) showed no negative effects of the nanomaterials on their natural enemies. A 500-fold (20,000 ppm) increase in the LC<sub>50</sub> dose of host insect pests resulted in some observable damage. In contrast to nanomaterials, even at extremely low concentrations, manufactured chemical pesticides were poisonous and hindered the natural foes' ability to develop from host insects. Even less is known about the possible environmental implications of nanomaterial exposure than there is about the health effects on humans. As an alternative product for input delivery, the hexanal nanoemulsion is highly valued for its uniform surface

coverage, low viscosity, and extremely small droplet size of less than 100 nm, as well as its high kinetic stability and optical transparency. However, it has also been evaluated for its eco-safety in terms of beneficial biodiversity in the target ecosystem. This product has been thoroughly shown to be safe for honey bee workers as well as natural insect adversaries like *Trichogramma* (Karthika *et al.*, 2015) <sup>[20]</sup>.

### Safety of nano insecticides

Although the tendency of many nanoparticles to clump together or dissolve in water gives them a relatively short lifespan, the human body is equipped with a number of mechanisms for eliminating or filtering out these particles (Li *et al.*, 2007) <sup>[25]</sup>. However, there's a chance that exposure to artificial nanoparticles will have different consequences than that of naturally occurring nanoparticles. Further research is necessary to fully understand the health and environmental concerns associated with exposure to manufactured nanoparticles, as they may be more able to elude the body's defences due to their size or protective coatings (Li *et al.*, 2007) <sup>[25]</sup>. Thus, a great deal of research

is needed to comprehend the toxicity mechanism of nanomaterials and how they affect the natural environment. Walker *et al.*, 2017<sup>[47]</sup> have brought attention to several difficulties that regulators should be aware of, such as the differences in the ecological risk assessment between conventional plant protection products and nano-enabled pesticide products.

## Conclusion

Even though the field of plant protection has recently seen a rise in the usage of nanotechnology, pest control applications have already begun. Because nano-encapsulated pesticides release just on the targeted side, they can decrease the amount of insecticide lost to the environment. Nano-formulated pesticides can effectively control the target insect pest at a lower dose because of their comparatively higher surface area. It has not yet been investigated, but a variety of nanoparticles may have neurotoxic effects on the major insect pests now in use. In addition, the production of nanoparticles from biological agents like microorganisms and plants holds promise for the environmentally friendly control of insect pests. In general, insecticides based on nanotechnology have the potential to outperform traditional pesticides and lessen the amount of pesticides present in the ecosystem.

## References

- Adak T, Kumar J, Shakil NA, Walia S. Development of controlled release formulations of imidacloprid employing novel nano-ranged amphiphilic polymers. *J Environ Sci Health B*,2012;47(3):217-25.
- Barik TK, Sahu B, Swain V. Nanosilica—from medicine to pest control. *Parasitol Res*,2008;103:253-8.
- Borei HA, El-Samahy MFM, Galal OA, Thabet AF. The efficiency of silica nanoparticles in control cotton leafworm, *Spodoptera littoralis* Boisd. (Lepidoptera: Noctuidae) in soybean under laboratory conditions. *Glob J Agric Food Saf Sci*,2014;1(2):161-8.
- Brown EN, Kessler MR, Sottos NR, White SR. In situ poly (urea-formaldehyde) microencapsulation of dicyclopentadiene. *J Microencapsul*,2003;20(6):719-30.
- Chin CP, Wu HS, Wang SS. New approach to pesticide delivery using nanosuspensions: research and applications. *Ind Eng Chem Res*,2011;50(12):7637-43.
- Feng BH, Peng LF. Synthesis and characterization of carboxymethyl chitosan carrying ricinoleic functions as an emulsifier for azadirachtin. *Carbohydr Polym*,2012;88(2):576-82.
- Fernández-Pérez M, González-Pradas E, Villafranca-Sánchez M, Flores-Céspedes F. Mobility of isoproturon from an alginate–bentonite controlled release formulation in layered soil. *Chemosphere*,2000;41(9):1495-501.
- Flores-Céspedes F, Figueredo-Flores CI, Daza-Fernandez I, Vidal-Pena F, Villafranca-Sanchez M, Fernandez-Perez M. Preparation and characterization of imidacloprid lignin–polyethylene glycol matrices coated with ethylcellulose. *J Agric Food Chem*,2012;60(4):1042-51.
- Forim MR, Costa ES, Da Silva MFDG, Fernandes JB, Mondego JM, Boiça Junior AL. Development of a new method to prepare nano-/microparticles loaded with extracts of *Azadirachta indica*, their characterization and use in controlling *Plutella xylostella*. *J Agric Food Chem*,2013;61(38):9131-9.
- Frandsen MVV, Pedersen MS, Zellweger M, Gouin S, Roorda SD, Phan TQC. U.S. Patent Application No.13/057,773, 2011.
- Ghormade V, Deshpande MV, Paknikar KM. Perspectives for nano-biotechnology enabled protection and nutrition of plants. *Biotechnol Adv*,2011;29(6):792-803.
- González JOW, Gutiérrez MM, Ferrero AA, Band BF. Essential oils nanoformulations for stored-product pest control—Characterization and biological properties. *Chemosphere*,2014;100:130-8.
- Hack B, Egger H, Uhlemann J, Henriët M, Wirth W, Vermeer AW, *et al.* Advanced agrochemical formulations through encapsulation strategies?. *Chem Ing Tech*,2012;84(3):223-34.
- Hellmann C, Greiner A, Wendorff JH. Design of pheromone releasing nanofibers for plant protection. *Polym Adv Technol*,2011;22(4):407-13.
- Hwang IC, Kim TH, Bang SH, Kim KS, Kwon HR, Seo MJ, *et al.* Insecticidal effect of controlled release formulations of etofenprox based on nano-bio technique. *J Faculty Agric Kyushu Univ*,2011;56:33-40.
- Jha Z, Behar N, Sharma SN, Chandel G, Sharma DK, Pandey MP. Nanotechnology: prospects of agricultural advancement. *Nano Vision*,2011;1(2):88-100.
- Kah M, Hofmann T. Nanopesticide research: current trends and future priorities. *Environ Int*,2014;63:224-35.
- Kannan M, Elango K, Govindaraju K. Nanotechnological approaches in plant protection. In: *Nanotechnology in agriculture, energy and environment*,2020, 349-64.
- Kannan M, Elango K, Tamilnayagan T, Preetha S, Kasivelu G. Impact of nanomaterials on beneficial insects in agricultural ecosystems. In: *Nanotechnology for food, agriculture, and environment*,2020, 379-93.
- Karthika S, Kumar NN, Gunasekaran K, Subramanian KS. Biosafety of nanoemulsion of hexanal to honey bees and natural enemies. *Indian J Sci Technol*,2015;8(30):1-7.
- Kaunisto E, Tajarobi F, Abrahmsen-Alami S, Larsson A, Nilsson B, Axelsson A. Mechanistic modelling of drug release from a polymer matrix using magnetic resonance microimaging. *Eur J Pharm Sci*,2013;48(4-5):698-708.
- Lao SB, Zhang ZX, Xu HH, Jiang GB. Novel amphiphilic chitosan derivatives: synthesis, characterization and micellar solubilization of rotenone. *Carbohydr Polym*,2010;82(4):1136-42.
- Lee K, Park J, Lee MS, Kim J, Hyun BG, Kang DJ, *et al.* In-situ synthesis of carbon nanotube–graphite electronic devices and their integrations onto surfaces of live plants and insects. *Nano Lett*,2014;14(5):2647-54.
- Li M, Huang Q, Wu Y. A novel chitosan-poly (lactide) copolymer and its submicron particles as imidacloprid carriers. *Pest Manag Sci*,2011;67(7):831-6.
- Li ZZ, Chen JF, Liu F, Liu AQ, Wang Q, Sun HY, *et al.* Study of UV-shielding properties of novel porous hollow silica nanoparticle carriers for avermectin. *Pest Manag Sci*,2007;63(3):241-6.
- Liu B, Wang Y, Yang F, Cui H, Wu D. Development of a chlorantraniliprole microcapsule formulation with a high loading content and controlled-release property. *J Agric Food Chem*,2017;66(26):6561-8.



27. Liu G, Lin G, Tan M, Zhou H, Chen H, Xu H, *et al.* Hydrazone-linked soybean protein isolate-carboxymethyl cellulose conjugates for pH-responsive controlled release of pesticides. *Polym J*,2019;51(11):1211-22.
28. Loha KM, Shakil NA, Kumar J, Singh MK, Srivastava C. Bio-efficacy evaluation of nanoformulations of  $\beta$ -cyfluthrin against *Callosobruchus maculatus* (Coleoptera: Bruchidae). *J Environ Sci Health B*,2012;47(7):687-91.
29. Manjunatha SB, Biradar DP, Aladakatti YR. Nanotechnology and its applications in agriculture: A review. *J Farm Sci*,2016;29(1):1-13.
30. Mosurkal R, Kumar J, Parmar VS, Watterson AC. Controlled release of covalently bound organic molecules by slow hydrolysis for potential biocide applications. *J Macromol Sci A*,2007;44(12):1289-92.
31. Muzammil EM, Khan A, Stuparu MC. Post-polymerization modification reactions of poly (glycidyl methacrylates). *RSC Adv*,2017;7(88):55874-84.
32. Nenaah GE. Bioactivity of powders and essential oils of three Asteraceae plants as post-harvest grain protectants against three major coleopteran pests. *J Asia-Pac Entomol*,2014;17(4):701-9.
33. Nuruzzaman MD, Rahman MM, Liu Y, Naidu R. Nanoencapsulation, nano-guard for pesticides: a new window for safe application. *J Agric Food Chem*,2016;64(7):1447-83. <https://doi.org/10.1021/acs.jafc.5b05214>.
34. Pankaj, Shakil NA, Kumar J, Singh MK, Singh K. Bioefficacy evaluation of controlled release formulations based on amphiphilic nano-polymer of carbofuran against *Meloidogyne incognita* infecting tomato. *J Environ Sci Health B*,2012;47(6):520-8.
35. Peteu SF, Oancea F, Siciua OA, Constantinescu F, Dinu S. Responsive polymers for crop protection. *Polymers*,2010;2(3):229-51.
36. Prabakaran M, Sithanantham S, Subramanian KS, Vijayaprasad P, Punna Rao BV, Babu B. Silica application effect on sugarcane early shoot borer. In: Proceedings of International Symposium on "Sugarcane Research Since Co205: 100 Years and beyond " (SucroSym 2017),2017, 393-5.
37. Preetha S, Kannan M, Lokesh S, Gowtham V. Effect of neem oil based nanoemulsion on egg parasitoids, *Trichogramma chilonis* (Ishii) (Hymenoptera: Trichogrammatidae),2018;2(2):103-7.
38. Quaglia F, Barbato F, De Rosa G, Granata E, Miro A, La Rotonda MI. Reduction of the environmental impact of pesticides: waxy microspheres encapsulating the insecticide carbaryl. *J Agric Food Chem*,2001;49(10):4808-12.
39. Ragaei M, Sabry AKH. Nanotechnology for insect pest control. *Int J Sci Environ Technol*,2014;3(2):528-45.
40. Rouhani M, Samih MA, Kalantari S. Insecticide effect of silver and zinc nanoparticles against *Aphis nerii* Boyer De Fonscolombe (Hemiptera: Aphididae). *Chilean J Agric Res*,2012;72(4):590-4.
41. Roy SC. There's plenty of holes at the bottom: The other side of Nano. *Sci Cult*,2009;75(1-2):1-3.
42. Sahayaraj K, Madasamy M, Radhika SA. Insecticidal activity of bio-silver and gold nanoparticles against *Pericallia ricini* Fab. (Lepidoptera: Archidae). *J Biopestic*,2016;9(1):63-72.
43. Scrinis G, Lyons K. The emerging nano-corporate paradigm: nanotechnology and the transformation of nature, food and agri-food systems. *Int J Sociol Agric Food*,2007;15(2):22-44.
44. Shaker AM, Zaki AH, Abdel-Rahim EF, Khedr MH. TiO<sub>2</sub> nanoparticles as an effective nanopesticide for cotton leaf worm. *Agric Eng Int: CIGR J*, 2017, 19.
45. Smith K, Evans DA, El-Hiti GA. Role of modern chemistry in sustainable arable crop protection. *Philos Trans R Soc Lond B Biol Sci*,2008;363(1491):623-37.
46. Song S, Wang Y, Xie J, Sun B, Zhou N, Shen H, *et al.* Carboxymethyl chitosan modified carbon nanoparticle for controlled emamectin benzoate delivery: improved solubility, pH-responsive release, and sustainable pest control. *ACS Appl Mater Interfaces*,2019;11(37):34258-67.
47. Walker GW, Kookana RS, Smith NE, Kah M, Doolette CL, Reeves PT, *et al.* Ecological risk assessment of nano-enabled pesticides: a perspective on problem formulation. *J Agric Food Chem*,2017;66(26):6480-6.
48. Xu Y, Wang L, Tong Y, Xiang S, Guo X, Li J, *et al.* Study on the preparation, characterization, and release behaviour of carbosulfan/polyurethane microcapsules. *J Appl Polym Sci*,2016;133(35). <https://doi.org/10.1002/app.43844>.
49. Yang FL, Li XG, Zhu F, Lei CL. Structural characterization of nanoparticles loaded with garlic essential oil and their insecticidal activity against *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae). *J Agric Food Chem*,2009;57(21):10156-62.
50. Yao KS, Li SJ, Tzeng KC, Cheng TC, Chang CY, Chiu CY, *et al.* Fluorescence silica nanoprobe as a biomarker for rapid detection of plant pathogens. *Adv Mater Res*,2009;79:513-6.
51. Zhao X, Cui H, Wang Y, Sun C, Cui B, Zeng Z. Development strategies and prospects of nano-based smart pesticide formulation. *J Agric Food Chem*,2017;66(26):6504-12. <http://pubs.acs.org>.
52. Ziaee M, Ganji Z. Insecticidal efficacy of silica nanoparticles against *Rhyzopertha dominica* F. and *Tribolium confusum* Jacquelin du Val. *J Stored Prod Res*,2016;37:153-64.