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Nano-pesticides in pest management

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Abstract
Pesticides are the basis to defend against major biological disaster in agriculture and important to ensure national food security. Biocompatible, biodegradable and responsive material is currently an emerging area of interest in eco-friendly green pesticide formulations. Nanotechnology plays a vital role in designing and preparation of target-oriented and controlled release pesticides which act environmentally safe. This can be achieved through chemical modification and this new technology has great potential in creating novel formulations. In this review, special attention has been paid towards pesticides with precise controlled release modes and responds to micro ecological changes such as light sensitivity, thermo sensitivity, humidity sensitivity, soil, pH, and enzyme activity. Moreover, establishing intelligent and controlled pesticide release technologies using nanomaterials are reported. The technologies could increase pesticide loading, improve the dispersibility and stability of active ingredient, and promote target ability.

Keywords: Nano-pesticides, control release, thermo sensitivity, humid sensitivity, and target release

Introduction
Pesticides are inevitable in agriculture to enhance crop yield. More than 90 percent of insecticides used are lost due to drift, leaching in soil, degradation process (Photolysis, hydrolysis), and microbial activities (Sabarwal *et al*., 2018) [31]. The only small amount of pesticides reach the targetsite (1%) which necessitates the repeated application of pesticides and resulted in increased cost and pollutes the ecosystem. Every year farmers in the United States spent $200 billion for pollination as discriminative usage of neonicotinoids caused honey bee colony collapse disorder. In India, 28 percent of the available pesticides are emulsifiable concentrates and oil in water emulsion which are poorly soluble in water due to the non-polar nature. A higher amount of organic solvents like xylene and surfactant are added to increase their solubility. But organic solvents are costly, flammable, and dermal toxicant and heavy metals present in surfactants accumulate in the soil which creates abiotic stress in plants (Rice *et al*., 2001) [28]. Repeated use of certain pesticides like malathion created genotoxicity to humans. Every year, nearly 20,000 human deaths are recorded due to pesticide consumption through food. The pesticides interact with the microbiome present in the human gastrointestinal tract and cause digestion problems, lung cancer, and hormonal imbalance. Premature degradation of the active ingredient in the pesticide formulations through soil bacteria also reduces the efficiency of pesticides (Anderson *et al*., 2016) [1].
Nanopesticides are the best alternative to increase solubility, dispersion, bioavailability, to protect against premature degradation and for the targeted release of active ingredients are Controlled release based on light, pH, humidity, and the temperature is possible through nano pesticides. In nature, essential oils with an insecticidal property are extremely volatile, sensitive to UV rays, and degrade when exposed to sunlight. Loading of these essential oils into nanoparticles will mitigate such problems and convert these essential oils as good pesticidal candidates.
The term nano is derived from the Greek word it's meaning dwarf 10^{-9} almost 1 to 100nm. The term nanotechnology is given by Norio Taniguchi. Nanotechnology is a newly emerging technology in which the structure of the matter is controlled at the nanoscale to produce a material having unique properties or nanotechnology is the art and science of manipulating matter at the nanoscale. The term nanomaterial generally refers to a material with an external dimension (or) internal structure that is on the nanoscale (ISO and organization for economic cooperation and development).

The term nano pesticides are used to describe any pesticide formulation that intentionally includes entities in the nanometer size range (European standardization committee).

Materials and Methods

The nanomaterial prepared through two basic methods according to the Royal Society and the Royal Academy of Engineering.

1. Top-down system (depending on size reduction from bulk material)
2. The bottom-up system whereas the material is synthesized from the atomic level.

Nanoparticle characteristics are identified through the Scanning Electron Microscope (SEM) which gives a three-dimension image, Transmission Electron Microscope (TEM) which gives a two-dimension image of a particle, Dynamic Light Scattering (DLS), Scanning Tunnelling Microscope (STM) and Atomic Force Microscope (AFM).

The entry of nanoparticle into plant

The uptake, translocation, and accumulation of nanoparticles depend on plant species, age, growth, and environmental condition. They enter into cells by a diffusion process. Zno^{2+}, Cu^{2+}, Al^{2+}, and Au^{2+} are translocated through the root system, and Fe_3O_4 enters into foliar part of the plant. Plant cell walls act as a barrier for entry of any external agent including nanoparticle into the plant system. Cell plasma membrane allows less than 5 to 20 nm nanoparticles (Behzadi *et al.*, 2017) [6]. There is a chance for enlargement of pore or induction of new cell wall pore. The nanoparticle enters into cells by endocytosis with help of cavity-like structure that forms around the nanoparticle by the plasma membrane. They may also cross the membrane using embedded transport carrier protein or through ion channels. When nanoparticles are applied on the leaf surface, they enter through stomatal opening and then translocated to various tissue (Nair *et al.*, 2010) [28]. Organic acids (or) phenolic substances from the root exudates broken down the chemical bond of nanoparticle once the nanoparticles enter into the root. Metal-based nanoparticles like ZnO increase permeability and create a new hole in the plant cell (Sattelmacher, 2001) [35]

Mode of entry in insect

Nanoparticles enter into insects through physical contact, ingestion, and inhalation. In physical contact nanoparticles penetrate the exoskeleton, binding the nanomaterials to sulfur from protein or phosphorus from DNA in intracellular space, leading to denature of organelles and enzyme resulted in cellular fraction and cell death (Abd-Elsalam *et al*., 2018) [1].

Nano specks of dust are commonly used for control of stored grain pests and the mechanism relies on physical disruption. The nanoparticles dehydrate the insect body by attaching to their cuticle wax layer. Nanoclay, nano alumina, and nano-silica are attached to insect cuticles and absorb the water from the insect body. Hydrophobic behavior of nanosilver particles cause splits and scratches on the insect body, altering the membrane properties which resulted in a change in permeability and respiration of cell, they damage DNA and release toxic Ag^+ ions. Ag nanoparticles interfere with melanin synthesis.

Inhalation of nanoparticles leads to internalization in cells via phagocytosis which causes midgut deterioration and alters the activity of metabolic genes and reduces lipid, protein, and glucose levels. Reduced food intake ultimately leads to the death of the insect (Gustafson *et al*., 2015) [16]. Inhalation also altered the activity of nervous system enzymes and membrane potential.eg. Zn NPS and Tio_2 NPS are bind to acetylcholine esterase and β carboxyl esterase and affect their activity. The mode of action of these nanoparticles is similar to the organo phosphorous and carbamate group of insecticide. Ag nanoparticles affect the Glutathione S transferase enzyme. In *Spodoptera litura* Ag nanoparticles act as an amylase inhibitor (Vinutha *et al*., 2013) [38].

Generation of reactive oxygen species is considered as one of the most cellular effects induced by nanoparticles and the excessive free radical generation induce DNA damage through inflammatory processes (Saini *et al*., 2020) [33]

Mode of Entry

NP Type	Insect	Impact	Reference
Ag NPS	*Bombyx mori*	Induce cell necrosis and signal transduction was affected	(Meng *et al*., 2017) [27]
Ag NPS	*Drosophila*	Depigmentation, impaired movement, compromised fertility, accumulation of ROS and DNA damage	(Armstrong *et al*., 2013) [3]
Ag NPS	*Spodoptera litura*	Accumulation of carboxylesterase in the midgut	Yasur and Usha-Rani (2015) [40]
Ag NPS	*Helicoverpa armigera*	Inhibition of gut protease enzyme activity	(Kantrao *et al*., 2017) [22]
Au NPS	*Drosophila*	Distributed in the reproductive and digestive enzyme	(Vecchio *et al*., 2012) [37]
Silica NPS	*Callosobruchus maculates*	Retarded growth and reduced oviposition	(Cáceres *et al*., 2016) [7]
ZnO NPS coated with *Bacillus thuringiensis*	*Callosobruchus maculates*	Decrease fecundity, midgut amylase, and GST activity	(Malaikozhundan *et al*., 2017) [27]

Nanopesticides

Target released nano pesticides

A controlled pesticide release or smart delivery system of pesticide is used on land by selecting a suitable route to regulate the target pest. This approach minimizes pesticide usage and gradually achieve more effective usage of pesticide. This system allows only simple, slow-release rather than a responsive release based on an environmental condition such as light, temperature, soil, PH, humidity, and enzyme (Huang *et al*., 2018) [18].

Light sensitive nano pesticides

Luminophore and light-sensitive materials are coated with pesticides and exposed to light. The physical and chemical properties of these carrier materials are changed which resulted in the breakdown and release of pesticides. Some light-sensitive molecules can convert light into heat energy which can make light-sensitive pesticides. One of light-sensitive carrier material is coumarin. Coumarin nanocarrier was coated with fipronil which resulted in light-dependent insecticide release. Nanopesticide fipronil effectively control

Aedes larva, when exposed to blue light (LC_{50}= 0.56 µmolL^{-1}) and sunlight (LC_{50}= 0.37 µmolL^{-1}) (Djiwanti and Kaushik, 2019) [12].

pH-sensitive nanopesticides

The pH-sensitive carrier material is coated with pesticides. pH-sensitive nano pesticides are two types. The ionization or deionization of monoacid generally occurs within a pH range of 4-8, for which protons are accepted at low pH and pesticide is released at neutral and base pH. The base pH-responsive polymer contains an amino group on their side chain accept proton under acidic condition and then release. Patel *et al*. (2018) [31] developed a pH-responsive alginate nanocarrier for cypermethrin. In acidic pH, a high degree of ionization occurs and an alginate polymer interacts with calcium ions and increases their cross-linkage, hence making the interior of nanoparticles more hydrophobic and reduces the release rate of insecticide.

Gutbuster

It breaks open to release its content when it comes into contact with the alkaline environment, such as the stomach of a certain insect. Syngenta manufactured this type of product.

Enzyme responsive pesticide

When a pest interacts with plants, a series of changes occur including changes in plant enzymes. Enzyme responsive polymer can react physically and chemically to such stimulation**.** These polymers can be used to coat the pesticides. When Lepidopteran insects attack the crop, change in plant enzymes causes the polymer capsule materials to break under the action of cutinase and release the pesticide (Guo *et al*., 2015) [15].

Temperature responsive nano pesticides

Liang *et al*. (2018) [25] developed silica-coated nanoparticles with temperature-responsive chitosan in avermectin insecticide. His result showed that a higher release of avermectin was obtained by raising the temperature, with a release of 18.85% at 25^0c and 34.21% at 50^0c.

Nanopheromone and Nanoparapheromone

Pheromones are naturally occurring volatile compounds and are used in eco-friendly biological pest control approaches. They are sensitive to wind, heavy rain, and unstable due to photo-oxidation, auto-oxidation, and isomerization. The cost of the pheromone increases when the frequency of their use increased due to the loss of their volatile compounds (Kah and Hofmann, 2014) [20].

Nanomaterials can be used as carriers or dispensers for volatile signaling molecules. These materials have a highly controlled spatiotemporal release rate and improve stability. Mostly nanofibre and zeolites are used as nanomatrix. Nanofibres loaded with pheromone gives high stiffness and enhance the stability of pheromone. The micropores in the zeolite alter the emission rate. Coconut rhinoceros beetle pheromone (ethyl -4 methyl octanoate) and red palm weevil pheromone (4 methyl- 5 nananol+ 4- methyl 5-nananol) are commercially available in India and can be successfully uptaken by silica nanomatrix. The controlled release of the nanoporous matrix delivery method double the lifespan of pheromone up to 180-200 days and even achieves a higher efficacy rate of 106 beetles/ trap and 101 weevil/ trap.

Nano para pheromone

They are a chemical compound of anthropogenic origin not known to exist in insect systems. Para pheromones can be artificially synthesized and have pheromone like action. The most commonly used para pheromone is methyl eugenol and it is extracted from clove leaf. It mainly attracts tephritid fruit flies like *Bactrocera* species. It is one of the polyphagous pests and causes severe economic damage. Male annihilation techniques are used in the management of *Bactrocera dorsalis* due to the attraction of males to methyl eugenol at various concentrations. Methyl eugenol is easily decomposed in ambient conditions and has a limited shelf life. To resolve this problem highly viscous hydrogels are used to deliver the pheromone. However, hydrogel often swells and shrinks with changes in humidity and temperature. To overcome this problem methyl eugenol is used with nanogel. The nanogel provides high pheromone retention capacity, immobilization of methyl eugenol, and enhance the shelf life and protected from environmental decomposition. Methyl eugenol trap is efficient for one week while the nanogel methyl eugenol trap is efficient for up to one month (Vinutha *et al*., 2013) [38]. Min –u-gel formulation with methyl eugenol was developed for spot application in the male annihilation program in California for the eradication of *Bactrocera dorsalis*. Min - u-gel is a high-grade attapulgite nano clay mixed with malathion and methyl eugenol.

Nanoencapsulation

Nanocapsulation is defined as the packaging of solid, liquid, or gaseous material in miniature, a sealed capsule that could release their content at controlled rates under specific conditions. The coated material is called core and the coating material is called shell, carrier, or encapsulant (Berekaa, 2015) [5]. Nanomaterials used as a pesticide or as a carrier material have exhibited useful properties such as stiffness, permeability, crystallinity, thermal stability, and biodegradability over commonly used pesticides.

Polymer-based nanocapsulation

Active ingredients are coated with polymers that are produced from a natural source, biodegradable, and cost-effective. A polymer is contrasting in nature with one end is hydrophilic and the other end is hydrophobic and releases a limited amount of pesticide. Polyethylene glycol (PEG), chitosan, sodium alginate, and cellulose are the most commonly used encapsulating materials. Kumar *et al*., (2019) [23] reported the use of functional dispenser polycaprolectone for encapsulation of imidacloprid with approximately 200 times lower concentration than commercial formulation against sucking pests. González *et al*., (2014) [13] synthesized round shape nanocapsules of PEG (polyethylene glycol) coated with garlic essential oil against *Sitophillus oryzae* and *Rhyzopertha dominica*. The loading efficiency was influenced by the optimal ratio of essential oil to PEG and the loading efficiency reached 86%. Chudhuri *et al*., (2012) [9] developed acephate nanocapsules with high dispersibility. The nanocapsule was synthesized by encapsulating the a.i with PEG 400 (90-120 nm). Azadiractin loaded Zein (maize protein) against nematode reduced the glutathione Stransferase detoxifying enzyme. Zein nanoparticles act as a screen to protect azadiractin from UV rays. Neem oil has more than 300 active principles but they are denatured when exposed to UV rays (Pascoli *et al*., 2018) [30].

Clay-based nanoencapsulation
Clay-based nanoformulation has been developed to promote the adsorption and slow release of neutral and hydrophobic active ingredients. Li *et al.*, (2006) [24] developed a pectin cross-linked silica microcapsule to enhance the loading efficiency up to 42%w/w for the pesticide avarmectin. These nanoformulations offered more larvicidal mortality of *Plutella xyllostella* even after 14 days.

Green-based nanoencapsulation
Soil microorganisms have also been reported as nanocarrier due to their abundance, biocompatible nature that can support the pesticide loading. Cyanobacteria commonly present in the rice field and effectively fix the nitrogen in the soil. Yen *et al.*, (2013) [39] used cyanobacteria as a nanocarrier for stimuli delivery of avermectin and found high photostability against UV than free avermectin in soil. The binding affinity of avermectin to cyanobacteria was found in isopropanol. The carbonal resin offers more hydrogen binding site for avermectin, therefore thicker carbonal resin layer create longer distance travel, act as a UV protectant and slow release of pesticide.

Nanoparticle-based encapsulation
Pan *et al.*, (2017) [29] Coated *Bacillus thuringiensis* cry 11Aa toxin with $Mg(OH)_2$. $Mg(OH)_2$ nanoparticle worked as a coating cloth and protect cry protein from UV degradation. The encapsulation of dichlorvas and chlorpyrifos using starch silver nanoparticles showed excellent encapsulation efficiency of about 95-98%. The botanical pesticide PONNEEM encapsulated with tripolyphosphate cross-linked chitosan nanocarriers offered antifeedant activity (88%) and larvicidal activity (90%) against *Helicoverpa armigera* (Kumar *et al*., 2019) [23]. Invitro treatment of neem gum mediated nanoformulation confirmed the survival rate and weight gain of beneficial earthworm however excellent antifeedant, pupicidal, and larvicidal activity against *Spodoptera litura* and *Helicoverpa armigera* (Kamaraj *et al*., 2018) [21].

Nanoparticle
Most commonly used nanoparticle is nano-Ag, Nano-Tio_2, Au, Zn, and silica. The metal nanoparticle can be used for preparing the formulation of insecticide. Insect body walls contain a diversity of lipids in their cuticle to avoid water loss from their bodies thus preventing death from dryness. A nanoparticle is absorbed in lipids of the cuticle by abrasion, thus causing the death of insects (Barik *et al*., 2008) [4]. Guan *et al.*, (2008) [14] reported that toxicity of imidocloprid was increased by 50% when coated with nano-Ag/Tio_2 nanoparticle against *Martianus dermestid* (Tenebrionidae: Coleoptera) adults. Silica nanoparticle having a dermal toxic effect against the stored grain pest *Corcyra cephalonica*. Silica nanoparticle was found to be highly effective and caused 100% insect mortality (Vani and Brindha, 2013) [36]. Debnath *et al.*, (2011) [8] found silica nanoparticle affected 90% mortality in *Sitophillus oryzae.* Stadler *et al.*, (2018) [31] found that nanostructured alumina produced 95% mortality on *S. oryzae* and *R.dominica* three days after treatment. Chakravarthy *et al.*, (2012) [8] reported DNA tagged nanoparticles (Ag) effective against *Spodoptera litura* larvae. Ag nanoparticle affects the phosphorylation due to kinase enzyme activity and denatures the DNA. Jayaseelan *et al.*, (2011) [19] synthesized silver nanoparticle (sol-gel method) using an aqueous leaf extract of *Tinospora cardifolia* showed maximum mortality upon malaria vector *Anopheles subpictus*, dengue vector *Culex quinquefaciatus,* and *pediculus.*

Nanoemulsion
Pesticide nanoemulsion (more generally referred to as an oil in water emulsion) is the pesticide formulation where a pesticide is dispersed as a nanosized droplet in water with surfactant molecules. Hossain *et al.*, (2019) [17] reported insecticidal activity of nanoemulsion peppermint oil *Mentha piperita* against *Sitophylus oryzae.* Choupanian *et al.*, (2017) [10] suggested that neem polysorbate surfactants containing polysurfectant (tween 80) with the smallest droplet size of 208nm and N-APG1(Agnique) were most effective formulation for control of 85% *S. oryzae* and *Tribolium castaneum* compared to the conventional emulsifiable formulation.

Conclusion
Nanomaterials like Sio_2, Tio_2 and ZnO are increasing their presence in fungicides and pesticides to protect the plants from fungal, bacterial, and insect pests. Au, Ag and Cu nanoparticles are being used as bio-nanosensors and electrical-nanosensor to detect the pest. Nanoparticles are one of the effective organic insecticides to solve the current issue of environmental pollution. Encapsulation of green pesticides by using nanoparticle and stabilize active ingredient which will reduce hazards. The level of nanotoxicity in the environment mainly depends on concentration (less than 100 ppm), size (more than 20 nm) and composition of the nanoparticles. But we have to consider the deleterious effects of nanoparticles on human and animal. Inhalation, ingestion, and dermal contact are the main source of exposure of nanoparticles to human and animals. To determine the fate and behavior of nanoparticles in the environment, it is necessary to understand their potential risk.

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