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A review on nano-pesticides in pest management

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Abstract

Nano-pesticides could offer a range of benefits including less environmental contamination through reduction in pesticide application rates; enhanced efficiency of chemical and natural insecticides by controlled release; easy/safe handling with reduced toxicity risks to animals and less toxicity towards non-target organisms compared with bulk. Among other benefits, nano-formulation of many natural insecticides (e.g. neem oil) has protected them from premature degradation in the environment and thus helped in delivering maximum impacts on the target organisms. For insecticide encapsulation, several polymer-based or non-polymer-based nano-formulations, such as nanospheres, nano-capsules, nanogels, micelles, nanofibers, nanometals, and nano-emulsions, have been proposed. Nano-capsules are by far the most extensively utilized of these for controlled release of pesticides. Very recently, a novel concept of hybrid nano-formulation (encapsulation of nano-emulsion or liposome coating) has been suggested for the controlled release of some insecticides. However, the efficacy of the proposed novel approach needs to be tested for a broad-spectrum line of insecticides.

Keywords: nanotechnology, nano-pesticides, hybrid nano-formulation, nano-emulsions, nanogels

Introduction

The word "nano" is developed from the Greek word meaning "dwarf". In more technical terms, the word "nano" means 10, or one billionth of a material. Enhanced properties exhibited by nano sized particles and materials enable widespread potential applications. Nano-pesticides are nearly effective as traditional pesticides at controlling pests (Rani and Sushil, 2018). Biopesticides, plant-derived products and semio-chemicals are replacing chemical plant protection formulations (Sahayaraj, 2014). Non-target organisms are projected to be less harmed by nano-pesticides than by conventional pesticides (Deka et al., 2021).

Scope of nanotechnology

Nanotechnology is a promising field of interdisciplinary research. This includes insect pest management through the formulations of nano-material based pesticides which provide green and efficient alternatives.

Nano-pesticides

One sector where the use of encapsulated nanoparticles is receiving increasing interest is the pesticide sector with the development of a range of plant protection products that are termed "nano-pesticides". Any formulation that purposely incorporates components in the nano-metre size range and/or claims unique characteristics related with these tiny size ranges appears to have been on the market for some years. It is plant protection products where nanotechnology is employed to enhance the efficacy or reduce the environmental footprint of a pesticide active ingredient. It can consist of organic ingredients (e.g. polymers) and/or inorganic ingredients (e.g. metal oxides) in various forms (e.g. particles and micelles). It encompasses a great variety of products and cannot be considered as a single category.

It could offer a range of benefits including increased efficacy, durability, and a reduction in the amounts of active ingredients that need to be in use. It has high efficacy and safety and minimal chemical use. The aims of nano formulations are generally common to other pesticide formulations and consist in increasing the apparent solubility of poorly soluble active ingredient and releasing the active ingredient in a slow/targeted manner and/or protecting the active ingredient against premature degradation.

Nano formulations are expected to have significant impact on the fate of active ingredient. Introducing new ingredients whose environmental fate is still poorly understood (eg. nano silver) is yet a challenge.

Reason for using nano-pesticides

- Great effect with lower chemical use
- Smart treatment system
- Reduce damage by frost
- Decreases toxicity
- Pesticide degradation

Formulation of a nano pesticide

Nano emulsion

Nano emulsions can be defined as oil-in-water (o/w) emulsions with mean droplet diameters ranging from 50 to 1000 nm. Phytochemicals like essential oils face problems of chemical instability in presence of air, light, moisture & high temperature. Incorporation of essential oils into controlled release nano formulation prevents rapid evaporation & degradation, enhances stability & maintains minimum effective dosage. Downsizing of natural oils to form nano emulsions could be effective as larvicidal agents (Anjali et al., 2012).

Nano emulsion produced was thermodynamically stable, optically transparent and of small droplet size. Neem oil with polyethylene glycol sorbitane monostearate at 1:4 ratio produced a nano emulsion with droplet size of less than 200nm. The larvicidal activity of eucalyptus oil nano emulsion (1:2) and bulk emulsion (1:2) was recorded against *Culex quinquefasciatus*. It was observed that at a concentration of 250ppm nano emulsion, 98% mortality in 4h of treatment was observed whereas for the bulk emulsion 100% mortality was observed at 24h. Thus, this proves that the nano emulsion formulation of eucalyptus oil is far more effective than bulk emulsion. Nano emulsion of essential oil (hairy basil oil: vetiver oil, citronella oil at 5:5;10%w/w) prepared using high speed homogenizer had improved physical stability and smaller droplet size of 150-220nm. The nano emulsion had protection against mosquito *Aedes aegyptii* (Sugumar *et al*., 2014). The nano emulsion of DDVP developed for the management of German cockroach revealed that inhibition of acetylcholine esterase was higher in nano emulsion when compared to EC. There was also an increase in the reduction of alkaline phosphatase activity in the nano emulsion when compared to EC (Nuchuchua *et al.* 2009).

Nano suspension

Submicron colloidal dispersions of pure active compounds typically range from 50-500 nm. It is produced by homogenization or milling mechanical forces. It improves the efficacy due to higher surface area. It has higher solubility, higher mobility, induction of systemic activity due to smaller particle size. It has lower toxicity due to elimination of organic solvents. Two kinds of carbofuran formulations, micro suspension and a nanosuspension, were administered to a diamondback moth (DBM) to test their efficacy and stability as a pesticide. The results show that carbofuran has the same effectiveness at a lower dosage in nanosuspension as in micro suspension. The nanosuspension system remained physically and chemically stable over a two-year period, as evidenced by unaltered particle size and specification tests (Chin *et al*., 2011).

Nano encapsulation

Packing of nanoscale active ingredient within tiny envelope is slowly but efficiently released to the particular host for insect pest control. Its size range is around 1-100 nm. In this formulation the active ingredient is encapsulated by a synthetic or biological polymer to allow for prolonged release of a pesticide over a period of time.

Pesticides via encapsulation

Ethiprole

A phenylpyrazole compound affects GABA gated chloride channels and faces problems of photoinactivation. It is a stable polymeric polycaprolactone & polylactic acid nanosphere, encapsulating 3.5% of ethiprole. Initial biological testing was done on cotton aphids which revealed that speed of action &

controlled release was not at par with chemical application. However, it showed enhanced systemicity of active ingredient and improved penetration due to small size.

Avermectin

Insect chloride channel inhibitor faced problems of photoinactivation. Porous hollow silica NPs protect from UV degradation. Porous hollow silica nanoparticles shell thickness of 15 nm & pore diameter of 4-5 nm. Slow release of avermectin reported for 30 days.

Imidacloprid

IMI is photodegradable hence it is nano encapsulated by LbL technique. Photocatalysts like TiO2, SDS/ TO. Ag/TiO2. SDS/Ag/ TIO, constructed for photocatalytic degradation, SDS/Ag/ Tio, has highest photocatalytic activity. Toxicity of 50% nano SDS/Ag/ TiO IMI was higher than 95% IMI in the adult stage of *Martianus dermestoides*.

Efficiency of pyrethroid treated fabrics

Mosquito Repellency Test

Fabric sample (4x4 cm^2) is placed over a person's hand back covered around by a rubber glove. Inserted into a cage (40x30x30 cm^3) (300 *Aedes albopictus*). No. of persons stung during this time (2 min) & textile exposed to mosquitoes were recorded. This method provided better mosquito repellency with higher insecticide retention during washing than the polymeric binder -larger surface area, fine encapsulation and hydrophobicity of vinyl polymer.

Cyhalothrin (Micro encapsulated)

Karate Zeon 5 CS

A quick release microencapsulated product of 2.5 µm size breaks open on contact with leaves provided better rain fastness, improved residual activity. It breaks open to release its contents when it encounters alkaline environments (stomach of insect).

Nanoparticles

Nanoparticles are atomic or molecular aggregates having dimension between 1-100mm. Nanoparticles are loaded with pesticides and released slowly based on environmental trigger. Nanoparticles possess distinct physical, biological and chemical properties associated with their atomic strength.

The application of nano-silica on the resistance of tomato plants, aiming at providing relevant inputs to the management of cotton leaf worm. Nano silica was tested in six doses 100, 180, 200, 350, 300, 350 ppm respectively. Nano silica at various concentrations 250, 300 and 350 caused more than 50% death percentage, it gave 64.18, 68.93 and 78.24%, respectively in comparison to control which gave zero death. Total number of eggs laid per female was affected in all treatments compared with control, the percentage of hatchability was reduced in nano silica treatments compared with control. Thus, it reduces the reproductive potential of females on tomato plants. Therefore, it reduces the insect population density, damages and yield losses to the crop (Bendary *et al.* 2013).

Silver nanoparticles (AgNPs) were synthesized by using aqueous leaves extracts of *Euphorbia prostrata* as a simple, non-toxic and eco-friendly green material. *E. prostrata* and silver nitrate ($AgNO_3$) solution (1mM) and synthesized AgNPs are tested against the control adult of *Sitophilus oryzae*. This is the first report on the pesticidal activity of the plant extracts and synthesized nanoparticles. Silver nanoparticles (AgNPs) using leaf extract of *Euphorbia hirta* (Euphorbiaceae) against the first to fourth instar larvae and pupae of the crop pest of cotton boll worm, *Helicoverpa armigera*. The leaf extract exhibited larval toxicity against the first instar to fourth instar larvae and pupae of *Helicoverpa armigera*. Silver nanoparticles synthesized using an aqueous leaf extract of *Tinospora cordifolia* showed maximum mortality against the head louse *Pediculus humanus* and fourth instar larvae of *Anopheles subpictus* and *Culex quinquefasciatus* (Zahir et al. 2012).

Silica nanoparticles (SNP) and silver nanoparticles (AgNP) act on larval stage and adults of *Callosobruchus maculatus* on cowpea seed. Nanoparticles of silica and silver were synthesized through a solvo thermal method and different concentrations (1. 1.5. 2 and 2.5 g kg ^{1}) of them were tested on *C. maculatus*. LCs value for SiO_2 and Ag nanoparticles were calculated as 0.68 and 2:06 g kg cowpeas on adults and 1.03 and 1.00 g kg on larvae, respectively. Result - both nanoparticles (silica and silver) were highly effective on adults and larvae with 100% and 83% mortality, respectively. The result also showed that SiO2 nanoparticles can be used as a valuable tool in pest management programs of *C. maculatus* (Rouhani et al. 2013).

Second instar larvae of *S. litura* of surface treatment with DNA-tagged gold nanoparticles, at all four concentrations viz., 200, 300, 400 and 500 ppm. As the concentration and days after treatment increased, the larval mortality of second instar *S. litura* larvae also increased. The maximum mortality of 30.0, 57.5 and 75.0 was obtained at 500 ppm on 3rd, 4th and 5th day, respectively. At the highest concentration (500 ppm) of the DNA tagged gold nano particle, feeding was reduced, larvae turned sluggish and were unable to orientate towards the source. It demonstrates that DNA-tagged gold nanoparticle has a devastating effect on the larval tissue of *S. litura*. (Chakravarthy *et al.*, 2012).

Nanogel pheromone

Nanogel pheromones are prepared by using methyl eugenol (ME) low-molecular mass gelator. It is very stable at ambient conditions and works well in rainy season. It lasts for a month.

Microbial products – nano based delivery

Lagenidium giganteum, (aquatic fungus) a mosquito larvicide registered with USEPA (Registration No. 56984-2). It has poor stability during storage & expensive storage requirements. Addition of hydrophobic silica NPs (7-14 nm) to water in oil emulsion reduced desiccation. Thickened formulations are recorded up to 95% efficacy after 12 weeks of storage.

Nano-acaricide

A nano acaricide Allergoff 175 CS composed of permethrin, pyriproxyfen and benzyl benzoate was tested for its efficacy against *Acarus siro*, *Tyrophagus putrescentiae*, *Aleuroglyphus ovatus*. Pesticides were incorporated into the mite diets (10-1000 ug a.i. /g diet). The most effective pesticide Allergoff 175 CS had a range of 463-2453 µg a.i./g (Hubert et al. 2007).

Nano biosensors

A biosensor consists of 2 elements: a biological receptor protein to detect a substance & a sensor, to interpret biological recognition & translate into a measurable signal. "Nano biosensor" properties are modulated because at nanoscale. It has high selectivity, sensitivity, reliability & rapidity. The interaction of target with biosensors are measured by colour, fluorescence or electrical potential.

Nano-biosensor -Pheromone

It is the determination of selectivity/specificity of insect olfactory cells toward odor molecule using whole insect antennae-based micro biosensors. The micro-fabrication of several prototypes of Liquid Ion-Gate Field Effect Transistor (LIGFET) or an array for Organic Field-Effect Transistors (OFET) is as microelectronic readout devices. The synthesis of conductive polymer of nanofibers and semiconducting nanowires produced by using the template method. Functionalization of nanostructures with odorant or pheromone binding proteins results in arrays of nano-biosensors. Testing of nano-biosensor systems with odorants as analytes and comparison with antennae based micro biosensors has been done

Nanosensor-AChE

Immobilization of AChE to MWCNT cross linked cellulose acetate composite, forming stable AChE sensor Carbaryl, a carbamate inhibits action on AChE and causes decrease in oxidation peak current. It is sensitive, rapid, and inexpensive but determines all insecticides which inhibit Ache.

Liposome based nano biosensor

It is unstable AChE encapsulated in internal nano environment of liposomes. OP compounds inhibit hydrolysis of Ach. It produces decreased amounts of acetic acid. Fluorescence of pH sensitive fluorescent indicator pyranine decreases, and there is reduced response related to pesticide concentration. Concentrations down to 100 M can be monitored.

Detection of acetamiprid - aggregation of gold nano particles

Based on the strong interaction of the cyano group of acetamiprid with Au NPs, and the aggregation on AuNPs, its colour changes from red to purple. Concentration is determined by a spectrometer. Rapid and accurate, it eliminates the need for expensive analytical instruments.

Mosquito / Insect repellents

Mosquito repellents are substances that are designed to make surfaces unpleasant or unattractive to mosquitoes. They typically contain an active ingredient that repels mosquitoes as well as secondary ingredients, which aid in delivery and cosmetic appeal. They are available in many forms, from creams to lotions to oils, but are most often sold as aerosol products. The plants used for nano synthesis to control mosquitoes/insects are *Geranium sanguineum, Cymbopogon citratus, Salvia rosmarinus, Allium sativum, Artemisia absinthium, Rubus idaeus, Chromolena ordata.*

Risk involved

ZnO nano particles are toxic to both gram-negative and positive bacterial systems, *Escherichia coli* and *Staphylococcus aureus*. A single high oral dose of nano TiO, caused significant lesions in kidney and liver of female mice. Nano TiO2 is also toxic to algae and water fleas, especially after exposure to UV light. 15 nm Ag nano particles found to be toxic to mouse germ line. Stem cells under in vitro conditions. 50 & 70 nm SiO2 particles taken up into cell nucleus caused aberrant protein formation & inhibited cell growth under in vitro conditions.

Solutions

Early and open examination of the potential risks of a new product or technology. Public and private organization collaboration. Products already in stores, good product management identifying and managing any potential risks.

Conclusion

Nanotechnology in agriculture is in its nascent stage. Nano technological tools are to study the insect physiology & behavior. It has promising results in use of nano materials for delivery of pesticides & fertilizers. Nano particles are used as insecticide, with safety measures. Nano particles can stabilize biocontrol preparations. Nano sensors are effective in detecting pesticides at lower level.

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