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NANOPESTICIDES: A NEW PARADIGM IN CROP PROTECTION

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Abstract

Nanotechnology create such new or vastly different properties in materials or devices that are impossible to achieve by the conventional systems. It reduces spoilage of food items including fruits and vegetable through smart packaging. We can apply nanotechnology in various field *i.e,* in different field of science, agriculture (nanomaterials, e.g. zeolites and nano-clays, for water or liquid agrochemicals retention in the soil for their slow release to the plants), water purification etc. Nanopesticides or nano-plant protection products represent a hopeful scientific development that offer a variety of benefits including increased effectiveness, durability, and a reduction in the amounts of active ingredients (AIs) that is being used in protecting crops against diseases, insects and weeds.

Key words: Nanotechnology, benifits, nanopesticide and effect.

Introduction

Nanotechnology is the manipulation or self-assembly of individual atoms, molecules, or molecular clusters into structures to create materials and devices with new or vastly different properties that are impossible to achieve by the conventional systems. Nanotechnology is one such cutting edge technology which can provide sustenance to our food production by many ways including early detection and management of pests, diseases and nutrient deficiencies, enhancing input use efficiency and, avoiding/reducing spoilage of food items including fruit & vegetables through smart packaging.

The potential uses and benefits of nanotechnology are enormous. These include agricultural productivity enhancement involving nanoporous zeolites for slow release and efficient dosage of water and fertilizer, nanocapsules for herbicide delivery and vector and pest management and nanosensors for pest detection. The atom by atom arrangement allows the manipulation of nanoparticles thus influencing their size, shape and orientation for reaction with the targeted tissues.

International organization for standardization (ISO), the world's largest developer of standards, has defined nanomaterial as a material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale, where length range from approximately 1-100 nm is considered as nanoscale.

Nanomaterial Dimension	Nanomaterial type
All three Dimension<100nm	Nanoparticles, Quantum dots, nanoshells, nanorings, microcapsules
Two Dimensions<100n m	Nanotubes, fibres, nanowires
One Dimensions<100nm	Thin films, layers and coatings

According to Bhattacharyyal *et al.* (2010), the word “Nano” is developed from the Greek word “nanos” meaning “dwarf. It is a prefix meaning extremely small, when quantifiable, it translate to one-Billionth (10^{-9}).

- **Nano-objects:** Materials with one, two or three external dimensions in the nanoscale are nano-objects.
- **Nanoparticles:** Nanoparticles are those nano-objects in which all three external dimensions lie in the nanoscale range where the lengths of the longest and the shortest axes of the nano-object do not differ significantly.

Nanotechnology Applications

In Different field of Science

Most of the strategies utilized is to a great degree broad furthermore include the utilization of poisonous risky chemicals, which may posture potential environmental and biological dangers organic techniques for nanoparticle amalgamation utilizing microorganisms enzymes fungus and plants and plant extracts have been recommended as could be expected under the circumstances eco-accommodating contrasting option to chemical and physical techniques. Its application in science includes: Drug Delivery, Fabrics, Reactivity of Material, Strength of Material, Micro/Nano electro Mechanical systems and Molecular manufacturing.

Applications of Nanotechnology in the Field of Agriculture

Brilliant sensors and savvy conveyance frameworks will help the agricultural industry battle infections and other crop pathogens Nanotechnology will likewise secure environment in a roundabout way using elective (renewable) vitality supplies and channels or impetuses to diminish contamination and tidy up existing pollutant.

The component of insect pest control utilizing nano silica depends on the way that insect pest utilized an assortment of cuticular lipids for securing their water boundary and in this way keep passing from parching. In any case, nano silica gets ingested into the cuticular lipids by physiosorption and in this manner cause demise of insects absolutely by physical means when applied on the leaves of plant. El-Bendary and El-Helaly (2013) called attention to that Silica nanoparticles is a

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potential new insecticide for pest control. They included that consequences of treatment of hydrophobic nano-silica in *Spodoptera littoralis* larvae demonstrated high lethal activity at all concentrations utilized parallel with focuses, high resistance in tomato plants was found against this insect-pest particularly at 300, 350 ppm, separately. It can be reasoned this is likely the primary report that exhibited that nano silica could be utilized as a part of *Spodoptera littoralis* control.

1. Precision Farming

Remote detecting gadgets to gauge very restricted ecological conditions, in this way figuring out if yields are developing at most extreme proficiency or unequivocally distinguishing the nature and area of issues. Exactness cultivating can likewise help in diminishing farming waste and along these lines keep environment contamination to a minimum.

2. Other Applications include

a. **Plant protection Products:** Nanocapsules, nanoparticles, nanoparticles, nanoemulsions and viral capsids as smart delivery systems of active ingredients for disease and pest control in plants. For example: Neem oil (*Azadirachta indica*) nano emulsion as larvicidal agent (VIT University, INDIA).

b. **Fertilizers:** Nanocapsules, nanoparticles and viral capsids for the enhancement of nutrients absorption by plants and the delivery of nutrients to specific Sites: For example: Macronutrient Fertilizers Coated with Zinc Oxide Nanoparticles (University of Adelaide, AU CSIRO Land and Water AU Kansas State University, US).

c. **Soil Improvement:** Nanomaterials, e.g. zeolites and nano-clays, for water or liquid agrochemicals retention in the soil for their slow release to the plants. For example: Soil-enhancer product, basedona nano-clay component, for water retention and release (Geohumus Frankfurt, DE).

d. **Water Purification:** Nanomaterials, e.g. nano-clays, filtering and binding to a variety of toxic substances, including pesticides, to be removed from the environment. For example: Filters coated withTiO2 nanoparticles for the photo catalytic degradation of agrochemicals in contaminated waters (University of Ulster, UK).

e. **Diagnostics:** Nanomaterials and nanostructures (e.g. electro chemically active carbon nanotubes, nanofibers and fullerenes) that are highly sensitive biochemical sensors to closely monitor environmental conditions, plant health and growth. For example: Pesticide detection with a liposome-based nano biosensor (University of Crete, GR).

f. **Plant Breeding:** Nanoparticles carrying DNA or RNA to be delivered to plant cells for their genetic transformation or to trigger defence responses, activated by pathogens. For example: Mesoporus silica nanoparticles transporting DNA to transform plant cells (Iowa State University, US).

Morphological representation of different nanoparticles

- Nanospheres: aggregate in which the active compound is homogeneously distributed into the polymeric matrix.
- Nanocapsules: aggregate in which the active compound is concentrated near the center core, lined by the matrix polymer.
- Nanogels: hydrophilic (generally cross-linked) polymers which can absorb high volumes of water.
- Micelles: aggregate formed in aqueous solutions by molecules containing hydrophilic and hydrophobic moieties.

Nano Based Products in Agriculture

Nano Pesticides

Nanoemulsions: Particle size of less than 200 nm. The term "Nanoemulsion" refers to a thermodynamically stable isotropic clear dispersion of two immiscible liquid such as oil and water, stabilized by an interfacial film of surfactant molecule. Contain 5-10 % of surfactant, as compared to 20 % in micro emulsions (Kah and Hofmann, 2014). Nanoemulsions are promising candidates for the delivery of water-insoluble. These are developed for the efficient delivery of poorly-water soluble/insoluble naturally occurring compounds having insecticidal properties. **Example:** β-cypermethrin (β-CP) loaded nanoemulsions were compared with β-CP micro emulsion. Precipitation of commercial β-CP micro emulsion occured in the sprayed solution within 24 h of dilution, whereas excellent stability with no precipitation of sprayed solution diluted from the nanoemulsion was observed (Wang *et al.,* 2007). β- CP loaded nanoemulsion was demonstrated to have excellent spreading performance and was found homogeneous after dilution (Du *et al.*, 2016). Micro emulsions are thermodynamically stable, whereas nanoemulsions are thermodynamically unstable (Mc Clements *et al*., 2012).

Polymer Based Nanopesticides:

Polymer	Active Ingradient	Nanomaterial
Chitosan	Etofenprox	Capsule
Methyl methacrylate	Cypermethrin	Gel
Lignin	Aldicarb	Gel
Polyethyleneglycol-dimethyl esters	Carbofuran	Micelle
Glyceryl ester of fatty acids	Carbaryl	Spheres
Cashew gum	Moringa Oleifera Extract	Particle
Polyvinylpyrrolidone	Carbofuran	Suspension
Starch-based polyethylene	Endosulfan	Film
Vinylacetate	Pheromones	Resin
Polyethylene glycol	Garlic Essential Oil	Capsule

Nanophermones: Pheromones are generally volatile and extremely unstable due to their chemical structure; and it is highly desirable to protect them from decomposition and the formulation must ensure a controlled release (Heuskin *et al.,* 2011).

- Nanofiber webs obtained by incorporating pheromones in Polyamide 6 as well as cellulose acetate polymer carriers via electrospinning.
- Releases pheromones in a nearly linear fashion over several weeks (Hellmann *et al*., 2011).
- Reduce the frequency of pheromone recharging in field conditions.
- For example: pheromone hydrogels can be replaced with Pheromone nanogels having the fiber diameters ranging from 500 nm to 1 um was developed by immobilizing methyl eugenol (ME) into nanosized low-molecular mass gelators (LMMGs).
- Bhagat *et al.* (2013) stated that environment-friendly management of fruit flies involving pheromones is useful in reducing the undesirable pest populations responsible for

decreasing the yield and the crop quality. A nanogel has been prepared from a pheromone, methyl eugenol (ME) using a low-molecular mass gelator. This was very stable at open ambient conditions and slowed down the evaporation of pheromone significantly. This enabled its easy handling and transportation without refrigeration, and reduction in the frequency of pheromone recharging in the orchard. Notably the involvement of the nanogelled pheromone brought about an effective management of oriental fruit fly, *Bactrocera dorsalis*, a prevalent harmful pest for a number of fruits including guava

Nano Fungicides

1. Silver Nano Particles (AgNPs)
2. Titanium Dioxide Nanoparticles (TiO_2NPs)
3. Zinc Oxide Nanoparticles (ZnONPs)
4. Chitosan Nanoparticles (CNPs)
5. Nano Sulphur (NS)
6. Copper Nanoparticles (CuNPs)

Nano Herbicides

It develops target specific herbicides, which may enter the roots and get transported in all plant parts, restricts the glycolysis, thus ultimately causing the death of the target due to starvation (Ali *et al.,* 2014). Moreover, due to their tiny size, nano herbicides are being able to mix easily in soil and eradicate the target species without leaving any contradictory effects (Prasad *et al*., 2014).

Nano Fertilizers (nanonat and ferbanat)

The major advantages of using slow-release nanoformulation are:

(i) Improved NUE efficiency, higher crop yield.

(ii) Less environmental burdens from leaching of N, as compared to the conventional water-soluble fertilizers (Kottegoda *et al.,* 2011).

Iron (Fe), P and K nanofertilizers were demonstrated to significantly increase yield, flower number, fresh stigma weight, dry stigma weight,stigma length, fresh flower weight and dry flower weight of saffron (Amirnia *et al.,* 2014).

Conventional pesticides v/s Nanopesticides

Worldwide, about 3 million metric tons of pesticides, costing around $40 billion are applied annually. This situation calls an alarming condition of more than 26 million cases of non-fatal pesticide poisonings. In addition, deleterious effect on non-target beneficial microorganisms, risk to humans and other life forms, ground and surface water contamination and development of pesticide resistance are some major risks associated with heavy pesticide use. This inevitable risk to food security and agriculture will invite more troubles in developing countries.

Nanopesticides or nano-plant protection products represent a hopeful scientific development that offer a variety of benefits including increased effectiveness, durability, and a reduction in the amounts of active ingredients (AIs) that is being used in protecting crops against diseases, insects and weeds.

Conventional Pesticides	Nanopesticides
• Thermal unstability	• Thermal stability
• Affect Non target or beneficial insect	• Target specific
• Pollute air, water and soil	• No pollution
• Development of Resistance among target pests	• No resistance occur
• Efficiency of usage is less,waste is more	• Good efficiency, no wastage
• Problem of recharging	• No need of reapplication
• Residue problem	• Applied in less quantity, so no residue problem

Preparation Methods

According to Wilkins (2004) the methods for CRF (Controlled Release Formulations) preparation can be separated in chemical or physical ones 2 and 3.

Chemical methods: The chemical methods are based on a chemical bond (usually a covalent one) formed between the active compound and the coating matrix, such as a polymer. This bound can be placed in two different sites: in the main polymeric chain or in a side chain. In the first one, the new "macromolecule" is also called a pro-biocide, because the compound will get its properties in fact when it is released.

Physical methods: In this method, the insecticide molecule can bind initially to the side-chain of one monomer and then the polymerization reaction takes place or the polymerization occurs first and only after that, the biocide binds to the side chain.

There is still a third way, based on the intermolecular interactions. In this case, the biocide is "immobilized" in the net produced by the cross-linkages in the polymer. The physical methods can also be split in two distinct categories. In the first, a mixture of biocide and polymer is made.

Biological methods: Although naturally occurring nano-structures are being neglected, they are a potentially rich source of products that meet certain specifications. The emerging industries based on nanotechnology have so far made little use of 'free' technology available in nature (Ehrlich *et al.,* 2008). A good example is the ordered hexagonal packed array of structures in the wings of cicada for instance, *Psaltoda claripennis* Ashton and termite for example, family Rhinotermitidae.Studies have shown that the size of the nanoparticles may vary from 200 to 1000 nm. The structures tend to have a rounded shape at the apex and protrude some 150-350 nm out from the surface plane. These wing nanoparticles help in the aerodynamic efficiency of the insect. Isolated nanoparticles of insects have diameters of about 12 and 11 nm in abdomen with petiole and head with antennae, respectively. Nanostructure components are also present in compound eyes of insects. Wings of butterflies possess bright color components and these color components are nothing but nanoparticles. Recently, a novel photodegradable insecticide involving nanoparticles has been prepared (Guan *et al.,* 2008).

Mechanisms of Nano Fomulation release

- Nanoencapsulation: Nanoencapsulation is a process through which a chemical is slowly but efficiently released to the particular host for insect pests control.
- Release mechanisms include dissolution, biodegradation, diffusion and osmotic pressure with specific pH.
- Encapsulated citronella oil nano-emulsion is prepared by high-pressure homogenization of 2.5% surfactant and 100% glycerol, to create stable droplets that increase the retention of the oil and slow release.
- Nanopesticides, nanofungicides and nanoherbicides are being used efficiently in agriculture (Owolade *et al.,* 2008).

Important methods include

Diffusion: In the paper published by Kratz *et al.,* 2012 the text begins with the statement: "Nanoparticles only start working after they are placed in a desired location". In other words, an efficient CR formulation must remain inactive until the active compound is released. The way how an inert material, such the nanopolymers, controls the amount and rate a chemical is released is object of study since the late 1960's

(Furmidge *et al.,* 1968) and early 1970's (Allan and Neogi, 1972). How the release of the bioactive compound occurs depends basically on the chemical nature of the formulation. In various polymeric nanomaterials, the controlled release proceeds via diffusion.

Hydrolysis: According to Allan *et al.,* (1971) to the release takes place, a chemical interaction must be broken. It usually occurs via a hydrolysis reaction, what affects many polymer-insecticide bounds in a chain reaction. The release control depends on the strength of those chemical bounds, the chemical properties of both molecules and on the size and structure of the macromolecule formed.

Advantages

1. Smart delivery System: Smart delivery system for agriculture can possess timely controlled, spatially targeted, self regulated, remotely regulated, pre programmed or multifunctional characteristics to avoid biological barriers to successfully targeting.
2. Reduces problem of leaching and drifting
3. No need of Reapplication
4. Improves bioavailability for longer time
5. Prevent Volatilization of pesticides
6. Improves solubility of active ingredient
7. Reduction of effective pesticide concentration
8. Biosynthesized nanopesticide: Nanoformulation of neem oil, Garlic essential oil. Biosynthesised nanoparticles have also been introduced in nano-pesticide industry to provide eco-friendly nanoparticles and found more effective and stable tools to control phytopathogens and pest.
9. Stable at high temperature: Brown *et al.,* 2002, studied urea-formaldehyde resins with different encapsulation approaches and also examined their physical properties along with thermal resistivity.
10. Nanoemulsions: They poses greater spreadability, wettability, and superior mechanical stability.

Risks of Nanopesticides

The most reliable data on environmental contamination indicates that 260,000–309,000 metric tonnes of global engineered nanomaterials (ENMs) produced during 2010, ended up in landfills (63–91 %), soils (8–28 %), water bodies (0.4–7 %), and the atmosphere (0.1–1.5 %) (Keller *et al*., 2013).

Effects on Beneficial Soil Microorganisms

Methanotrophs, that metabolize methane as their only source of carbon and energy, declined by both the nanoparticles (Ge *et al*., 2012). Therefore, application of these nanoparticles as agrochemicals may have serious consequences by hampering symbiotic nitrogen-fixation in major legume crops and preventing methane emissions from soil. Effects of CuONPs and AgNPs were accompanied by cell death whereas ZnONPs were bacteriostatic. Further, bulk materials of these nanoparticles lacked inhibitory activity suggesting the aggregation of nanoparticles into larger particles may reduce their non-target effects (Gajjar *et al*., 2009)

Effects on Terrestrial Ecosystem

Sophisticated exposure models and ecotoxicological literature explain that AgNPs concentration below the current and future predicted environmental concentrations (PECs) in diverse ecological compartments can affect prokaryotes, invertebrates and fish, is an indicative of noteworthy environmental hazards (Fabrega *et al*., 2011).

Moreover, trophic transfer of AuNPs from soil along a simulated terrestrial food chain using earthworms (*E. fetida*) and juvenile bullfrogs (*Rana catesbeiana*) indicates the efficient transfer and more bioavailability of nanoparticles to higher order consumers through trophic exposure, as compared to direct exposure (Unrine *et al*., 2012).

Phytotoxicity

A significant decrease in the root elongation was observed with AgNPs even at the lowest (50 mg/L) concentrations, while TiO_2NPs showed no phytotoxicity on tomatoes (*Lycopersicon esculentum*) (Song *et al*., 2013). Both nanoforms were taken up by the plants and deposited in the stems, leaves and fruits. Moreover, lower chlorophyll contents, higher superoxide dismutase activity and less fruit productivity was observed with AgNPs, whereas TiO_2NPs only resulted in higher superoxide dismutase activity at the highest concentration (5000 mg/kg) in green house trials.

Human Toxicity

Interestingly, nanosized TiO_2 and ZnO are used in cosmetics or sunscreens and regarded safe for human (Schilling *et al.,* 2010) Unfortunately, based on sufficient evidence in experimental animals and inadequate evidence from epidemiological studies, a report by the International Agency for Research on Cancer (IARC) of the World Health Organization declared TiO_2 as a possible Group 2B carcinogenic to humans.

Environmental Impact

The environmental effect of nanotechnology is the conceivable impacts that the utilization of nanotechnological materials and gadgets will have on the earth. As nanotechnology is a rising field, there is awesome level headed discussion in regards to what degree mechanical and commercial utilization of nanomaterials will influence creatures and environment. Nanotechnology's ecological effect can be isolated into two viewpoints. Nanotechnological developments to help enhancing the earth, and the likelihood the novel kind of contamination and pollution that nanotechnological may bring about if discharged into environment.

Successful examples of nanopesticides against major insect pest of agriculture

1. The developed β-cyfluthrin nanoformulation showed prolonged activity and found more effective against *Callosobruchus maculatus,* as compared to commercial formulation (Loha *et al.,* 2011).
2. Nanoacephate (80-120 nm), prepared by encapsulation of acephate in PEG, was found more promising against *Spodoptera litura* and did not induce any cytotoxicity in human fibroblast cell line (Pradhan *et al.,* 2013).
3. Bhagat *et al.,* 2013 stated that environment-friendly management of fruit flies involving pheromones is useful in reducing the undesirable pest populations responsible for decreasing the yield and the crop quality. A nanogel has been prepared from a pheromone, methyl eugenol (ME) using a low-molecular mass gelator. This was very stable at open ambient conditions and slowed down the evaporation of pheromone significantly. This enabled its

easy handling and transportation without refrigeration, and reduction in the frequency of pheromone recharging in the orchard. Notably the involvement of the nanogelled pheromone brought about an effective management of oriental fruit fly, *Bactrocera dorsalis*, a prevalent harmful pest for a number of fruits including guava.

4. Nanoemulsion (155.2 ± 3.8 nm) containing apolar fraction from fruits of *Manilkara subsericea* (5 %), octyldodecyl myristate as oil (5 %), sorbitan monooleate/polysorbate 80 as surfactants (5 %) and water (85 %) exhibited significantly higher levels of mortality of cotton pest *Dysdercus peruvianus* (Fernandes *et al*., 2014).

5. Nanoemulsion (43.31 nm) developed using *Simmondsia chinensis*(Jojoba) seed-oil and Tween-20 as a nonionic surfactant and water was found more promising against *Sitophilus oryzae*, as compared to the bulk jojoba oil (Abouelkassem *et al*., 2015).

6. Chitosan, a biodegradable polymer obtained from the deacetylation of chitin, has attracted considerable interest to achieve effective and controlled release. Nano types of pyrifluquinazon prepared using chitosan as a carrier, showed best lethal efficiency against green peach aphid, *Myzus persicae* at 14 days after treatment.

7. Recently, neem-based nanocapsules prepared using biodegradable polymers, *viz.,* poly-ε-caprolactone (PCL) and poly-β-hydroxybutyrate (PHB), caused higher mortality of *Bemisia tabaci*, a serious pest of many crops (Carvalho *et al.,* 2015).

8. Werdin *et al*. developed PEG nanoparticles with essential oil (EO) extracted from Geranium sp. and *Citrus reticulata* for insect *Blatella germanica* control. They found that EO containing PEG nanoparticles showed slow release of terpenes that enhanced the toxicity multifold to insect *Blatella germanica.*

9. El-Bendary and El-Helaly (2013) called attention to that Silica nanoparticles is a potential new insecticide for pest control. They included that consequences of treatment of hydrophobic nano-silica in *Spodoptera littoralis* larvae demonstrated high lethal activity at all concentrations utilized parallel with focuses, high resistance in tomato plants was found against this insect-pest particularly at 300, 350 ppm, separately. It can be reasoned this is likely the primary report that exhibited that nanosilica could be utilized as a part of *Spodoptera littoralis* control.

Future Possibilities

1. These nano system have shown great capability of controlled release pattern of active ingredient (AI) make them more efficient for long time period usability that can be solve eutrophication and residual pesticide accumulation problem.
2. Still, there is need to improve the techniques for significant contribution in agricultural practices, some aspects are identified by Fraceto *et al*. (2016) in their review like.
3. Use of green chemistry and environmental sustainability principals in nanopesticide development to maximize their efficiency.
4. Process development for up scaling of nanopesticide for commercial level.
5. Comparison of nano-formulation activity with preexisting commercial product at field level to determine practical utility.
6. Environmental impact assessment of nanopesticide to determine toxicity level.
7. Improvement in regulation for nanomaterial application in agriculture.
8. Development of smart nanopesticide will provide many solution to the agro-chemical industry i.e. solubility of active ingredient, stability, controlled release and targeted delivery of active ingredient but still lots of research is required.
9. More Concern for Biopesticides.

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