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Nanopesticides: An emerging tool for pest management

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Abstract

Pesticides have become one of the inevitable parts of Indian agriculture. Higher doses of these chemicals per hectare have led to many environmental and health risks. The development of a new scientific era, nanotechnology, led to the development of nanopesticides. Nanotechnology is an interdisciplinary science that has the potential to revolutionize current technology. Nanotechnology is commonly defined as any engineered material, structure, and system that operates at a scale of hundred nanometers or less. Due to their nanoscale, nanoparticles exhibit properties and behaviors that differ from those of coarser bulk materials with similar chemical composition. Nanopesticides have distinct physical, biological and chemical properties associated with their atomic strength. These chemicals contain a nano-sized carrier molecule or active ingredient. The research community has developed several formulations, e.g., nanoemulsions, nanosuspensions, nanoencapsulation, nanoparticles. The smaller size of the chemicals helps to spread properly on the surface of the pest and the host and therefore provides a better effect than conventional pesticides. Nano pesticides significantly reduce the dosage of chemical insecticides. Nanoparticles have been reported to pass through biological membranes and cause cell death. The role of nanotechnology in the development of nanopesticides is therefore one of the best alternatives to overcome the lacunas of the conventional group of insecticides.

Keywords: Pest management, nanotechnology, nano-pesticides, nanoparticles

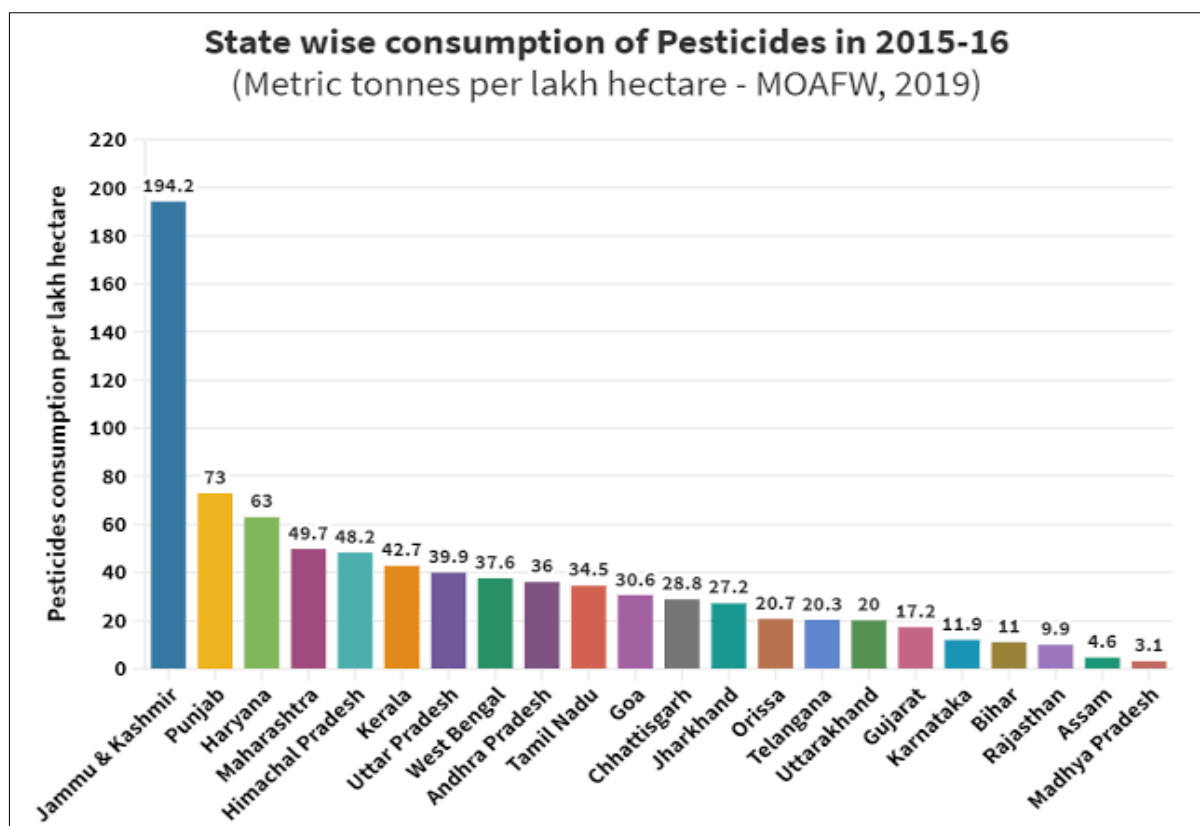
Introduction

Pesticides are indispensable in agriculture to increase crop yield. More than 90 percent of used insecticides are lost due to drift, leaching in the soil, degradation process (photolysis, hydrolysis). Only a small amount of pesticides reach the target site (1%), which requires repeated application of pesticides and has led to increased costs and pollution of the ecosystem. Farmers in the United States have spent \$200 billion on pollination every year because the indiscriminate use of neonicotinoids has caused bee colony collapse disorder. In India, 28 percent of available pesticides are emulsifiable concentrates and oil-in-water emulsions, which are poorly soluble in water due to their non-polar nature. To increase their solubility, higher amounts of organic solvents such as xylene and surfactant are added. But organic solvents are expensive, flammable and dermally toxic, and heavy metals present in surfactants accumulate in soil, creating abiotic stress in plants (Rice *et al.*, 2001) [24]. Repeated use of certain pesticides, such as Malathion, has produced genotoxicity in humans. Almost 20,000 human deaths are recorded each year due to the consumption of pesticides through food. Pesticides interact with the microbiome present in the human gastrointestinal tract and cause digestive problems, lung cancer and hormonal imbalance. Premature degradation of the active ingredient in pesticide formulations by soil bacteria also reduces pesticide efficacy (Anderson *et al.*, 2016) [3].

Nanotechnology is poised to revolutionize the state of various industries today, including agriculture, food, pharmaceutical, aerospace, medical and construction. The potential uses and benefits of nanotechnology are enormous as these nanomaterials have many applications in various other fields such as electronics, cosmetics, coatings, packaging, biotechnology (Khatoon *et al.*, 2017) [14], materials science, medicine and agriculture. Nanomaterials used as nano-encapsulated conventional fertilizers, pesticides and herbicides help in slow and sustained release of nutrients and agrochemicals, resulting in precise dosing to plants. Nanofertilizers (nanoparticle-sized nutrients, nano layered fertilizers or artificial metal oxide or carbon-based nanomaterials) and nanopesticides (nanofertilizers of traditional active ingredients or inorganic nanomaterials) can provide targeted release of agrochemicals aimed at achieving their maximum biological efficacy without overdosing. Nanomaterials can also help in the detection and removal of environmental contaminants using nanosensors and nanoremediation methods (Lavicoli *et al.*, 2017) [17].

Modern tools and techniques based on nanotechnology have the potential to solve various problems of conventional insect pest management, which may revolutionize the sector (Duhan *et al.*, 2017) ⁽⁷⁾. The promising results have opened up a large space in the field of insect pest control. Nanoparticles hold great promise for the management and control of insect pests. These include protection against insect pests through nanomaterial-based formulations of pesticides and insecticides, nanoparticle-mediated gene or DNA transfer into plants to develop varieties resistant to insect pests, increasing

agricultural productivity using nanoparticles (encapsulation) for slow release of nutrients. Inadequate traditional strategies used in agriculture, such as integrated pest management and application of synthetic pesticides such as dichlorodiphenyltrichloroethane (DDT), fenthion, malathion, etc., have adverse effects on animals and humans in addition to the decline in soil fertility. To overcome this problem, research has been extremely active in developing new pesticides based on nanotechnology i.e. "Nanopesticide".



Nano-pesticides

Nanopesticides are one of the alternatives to overcome the shortcomings of the conventional group of insecticides. Nanopesticides are plant protection chemicals in which the active ingredient or carrier molecule is engineered using nanotechnology. Indeed, as this suggests, the word of Greek origin "nano" means dwarf. The main goal in the development of nanopesticides is to reduce the environmental risks of the pesticide active ingredient by improving the effectiveness of the chemical. The size of a nanoparticle generally ranges from 1-100 nanometers, and a nanometer is one billionth of a meter. As the size decreases, the particles reach a very large surface area and thus a greater volume of pesticide comes into contact with the pests. The ability of nanoparticles to penetrate is due to their extremely small size and shape. Like other pesticide formulations, nanopesticide formulations will also consist of an active ingredient, a carrier molecule, and surfactants. The main advantages of these nanoparticles include improved solubility of active ingredients, better formulation stability, slow release of the active ingredient, and improved mobility due to smaller particle size and larger surface area. The mode of action against target pests is expected to be improved using nanoparticles, as opposed to bulk materials. In addition, nanoformulations provide

systemic properties, uniform foliar coverage and improved soil properties to support their constructive use in agriculture. Nanopesticides are the best alternative for increasing solubility, dispersion, bioavailability, for protection against premature degradation and for targeted release of active substances. Controlled release based on light, pH, humidity and temperature is possible with nano pesticides. In nature, essential oils with insecticidal properties are extremely volatile, sensitive to UV radiation, and decompose when exposed to sunlight. Encapsulation of these essential oils into nanoparticles alleviates these problems and turns these essential oils into good pesticide candidates. The term nano is derived from the Greek word and means dwarf 10⁻⁹ almost 1 to 100 nm. Nanotechnology is an emerging technology in which the structure of matter is controlled at the nanoscale to create a material with 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) an internal structure that is on the nanoscale (ISO and Organization for Economic Co-operation and Development). The term nanopesticides are used to describe any pesticide formulation that intentionally includes entities in the nanometer size range (European Commission for Standardization).

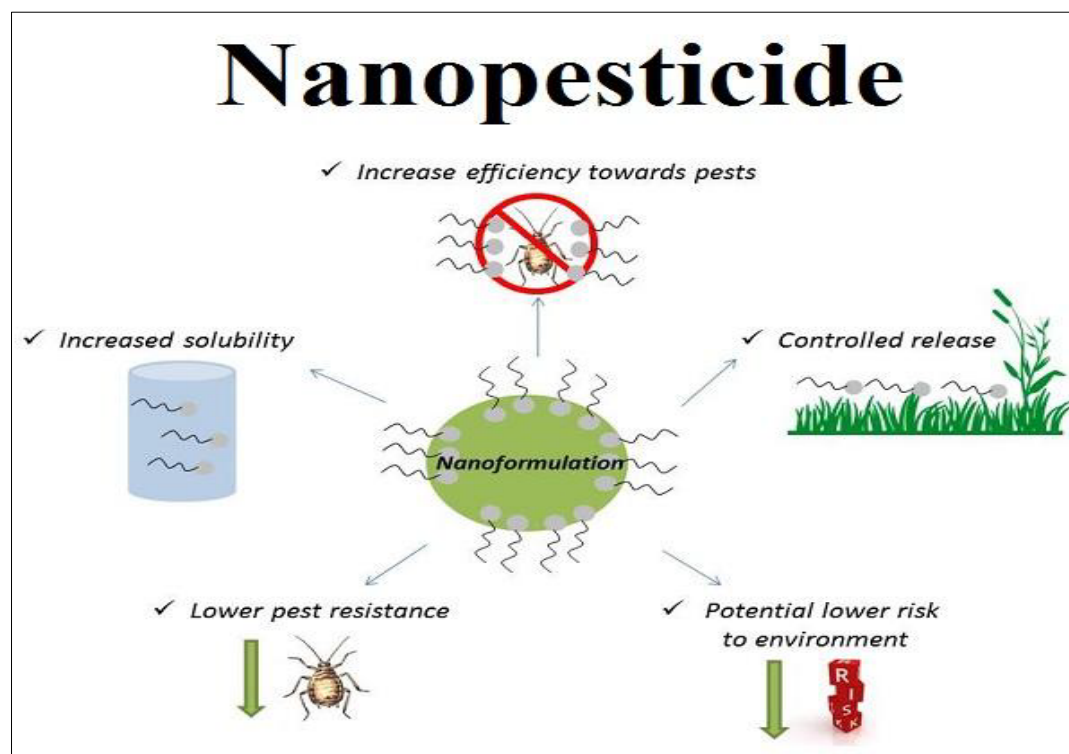


Fig 1: Nano pesticide Properties

Applications of nanotechnology in the field of agriculture

Nanotechnology as a powerful new technology has the ability to create massive changes in agricultural systems. Agricultural applications of nanotechnology are also a strong awareness. Nanomaterials are being developed that offer the possibility to use more effective, safer and more reliable direct pesticides, herbicides and fertilizers by precisely controlling when and where they are released (Kuzma and VerHage, 2006)^[15]. Nanotechnology is able to introduce new instruments for use in molecular biology and new materials to identify plant disease microorganisms (Mousavi and Rezaei, 2011)^[20]. The use of nanotechnology in agriculture can revolutionize this sector with new tools for disease detection, targeted treatment, increasing the ability of plants to absorb nutrients, fight pests and withstand environmental pressures. Nanotechnology has provided new solutions to problems in plants (postharvest products) and offers new approaches to the rational selection of raw materials or the processing of such materials to develop the quality of plant products (Sharon *et al.*, 2010)^[31]. The potential uses and benefits of nanotechnology are enormous. These include agricultural productivity enhancements involving non-porous zeolites for slow release and efficient dosing of water and fertilizers, nanocapsules for herbicide delivery and vector and pest management, and nanosensors for pest detection (Scrinis and Lyons, 2007; Scott, 2007; Joseph and Morrison, 2006)^[29, 28, 11]. Nanotechnology can possibly disrupt various segments of the agricultural and food industries with current tools for treating diseases, quickly detecting diseases, increasing the ability of plants to retain supplements and grow, and so on. Brilliant sensors and savvy transport frameworks will help the agricultural industry fight infections and other crop pathogens (Rickmann *et al.*, 2003)^[25]. Nanotechnology will also provide a roundabout environment with optional (renewable) vitality sources and channels or impulses to reduce contamination and cleanup. Increase the existing pollutant (Tungitiplakorn *et al.*, 2004)^[33]. Nanomaterials in agriculture are specifically shown

to reduce spray chemicals through smart transport of dynamic fixatives, minimize supplement misfortune in treatments (Gogos *et al.*, 2012)^[9], and increase yields through improved water and supplement delivery. Nanotechnology enhancements are also being explored in plant breeding and genetic modification (Tomey *et al.*, 2007)^[32]. Also, agriculture could be a well of bio-nanocomposites with improved physico-mechanical properties based on rationally harvested materials, similar to wheat straw and soybeans, for bio-industry purposes (Alamdard and Sain, 2008)^[2].

Nanotechnology Sensor

Smart delivery systems, as well as smart sensors, will help agricultural production fight viruses and other crop pathogens. In the coming years, nanostructured materials will become available that will increase the effectiveness of insecticides and allow the use of lower doses. Smart sensors are the dominant tools for the detection and control of animal and plant pests. The detection of very small amounts of contaminating viruses or bacteria in agriculture is envisaged from the integration of chemical, physical and biological devices that work together as an embedded nanoscale sensor (Scott and Chen, 2003)^[27]. At the University of Manitoba, the Departments of Microelectronics and Nanotechnology have developed a small sensor that can help farm owners detect grain spoilage during storage.

Correspondingly, if the fungus attacks the grain, it produces various chemicals. The sensor has seven fragments in it and identifies which fungus is causing the spoilage. "The sensor also measures changes in carbon dioxide to detect incipient and ongoing deterioration of stored grains (Mousavi and Rezaei, 2011)^[20]. Nano sensors could be deployed throughout a field where they can monitor soil conditions and crop growth. One of the most important features of nanotechnology-enabled devices will be the increased use of self-directing sensors connected to a GPS system for real-time observations. Finally, precision agriculture that uses smart

sensors will allow for improved agricultural productivity, provided that accurate information helps farmers make the best decisions (Joseph and Morrison, 2006) [11]. Nanosmart dust and gas sensors are used in determining the amount of pollutants and dust in the air. The presence of pollutants in the atmosphere can be estimated using sensors within minutes (Scott and Chen, 2003) [27].

Nanotechnology-based sensor systems for agricultural applications are still at the basic research level. The development of sensors and diagnostic devices for on-site monitoring will allow farmers to closely monitor environmental conditions, plant growth and protection. With timely intervention, these detection systems can contribute to increasing productivity and reducing the use of agrochemicals (e.g. pesticides, nutrients) (Ghormade *et al.*, 2011) [8].

Formulations of nano-pesticides

Research in nanotechnology has led to the development of various nanoformulations that can be used in crop protection, such as nanoinsecticides, nanoherbicides, nanofungicides and nanonematicides. Nanopesticides are formulated according to their intended purpose as preparations improving solubility, slow release of active ingredients, preventing degradation, etc. To achieve these purposes, modifications in the chemical carrier molecule have been modified and classified as preparations based on organic polymers, lipids, formulations based on nanoparticles, metals and oxides metals, clay-based nanomaterials, etc. Some of the leading nanoformulations are mentioned below:

- **Nano-emulsions:** In general, an oil-in-water (O/W) emulsion is more commonly known as a Nanoemulsion, where the active chemical component is dispersed as nanoparticles in water, with the surfactant molecules confined to the pesticide-water interface. Nanoemulsions are further classified according to the amount and type of surfactants as thermodynamically stable and kinetically stable. If the pesticide is partially soluble in the aqueous phase and a stable emulsion spontaneously forms when the surfactant, pesticide and water components are combined, it is a thermodynamically stable nanoemulsion. The insolubility of the active ingredient leads to the fact that the pesticide and the surfactant initially form a two-phase system and thus are mixed together by continuous shear and the pesticide droplets in the nanoemulsions remain dispersed for a longer time and are thus considered kinetically stable. E.g; oil-in-water neem oil nanoemulsions has been developed for insect control using Tween 20 as a surfactant.
- **Nano-suspension:** Nano-suspensions, also called nano-dispersions, are formulated by dispersing the pesticide as solid nanoparticles in an aqueous medium. In nanodispersions, the surfactant molecules are confined to the surface of the particles, where the polar parts extend into the aqueous solution and the non-polar parts are associated with the solid pesticide. Eg: Scientists have developed aqueous dispersions of nano-permethin, Novaluran and β -cypermethrin.
- **Polymer based nano-particles:** Polymer-based pesticide nanocarriers are mainly used for the slow and controlled release of active substances to the target site. In addition, they can serve to improve dispersion in aqueous media and also as a protective reservoir. Nanoencapsulation, nanospheres, nanogels, nanofibers, etc. are some of them that fall into this category. Nano-encapsulation: Nano-

capsules or nano-encapsulation are heterogeneous reservoir-type structures containing an internal central cavity that confines a hydrophobic or hydrophilic active ingredient, surrounded by a polymeric coating or membrane. The active ingredient in the neem-azadirachtin formulation can be protected by this formulation. e.g; Controlled-release nanoformulations of neonicotinoid insecticide, i.e., acetamiprid and imidacloprid, have been developed.

- **Nanospheres:** These are homogeneous vesicular structures in which the bioactive component is uniformly dispersed in the polymer matrix. Eg: Polymer-stabilized bifenthrin nanoparticles are developed as nanospheres.
- **Nanogel:** Hydrogel nanoparticles are also known. These are formulated by cross-linking polymer particles with hydrophilic groups so they absorb more water, e.g; Chitosan nanogel.
- **Nano-fibres:** Nanofibers are developed using electrospinning, a thermally induced phase separation. Researchers have developed electrospun nanofibers loaded with the chemical, (Z)-9-dodecenyl acetate, a pheromone component that embeds itself into a polymer matrix to control many insect pests of the order Lepidoptera.
- **Nano Encapsulation:** Encapsulation is the packaging of an active ingredient on a nanoscale into a sort of small "envelope or shell". Nanotechnology allows us to manipulate the properties of the capsule's outer shell.

Nanoparticles as nano-pesticides

In addition to the above formulations, solid nanoparticles can also be used as nanopesticides. Inert dusts such as silica, alumina, and clays cause damage to the wax coating on insect cuticles by both sorption and abrasion. This physical damage can cause water loss and thus lead to dehydration of the insect. Silica nanoparticles can be proposed as a suitable candidate among solid nanoparticles due to their additional benefit of helping the plant to increase tolerance to abiotic and biotic stress. However, for a better result, high doses must be applied, which can adversely affect the characteristics of the grain. Alumina nanostructures have also been reported to have pesticidal properties. Additionally, nanoclays developed from montmorillonite have been shown to have pesticidal function but low toxicity. Among the metals, silver, titanium dioxide and copper are most preferred as nanoparticles. The bactericidal and viricidal activity of silver nanoparticles makes them favorable for nanotechnology researchers. Low toxicity, intrinsic charge, larger surface area and crystallographic structure increase its preference. Application of titanium dioxide to crops has been shown to have effective antimicrobial and antifungal activity. Nano-copper formulations can cause damage to the cell wall of bacterial cells and have been found to be effective against bacterial downy mildew of pomegranate at very low concentrations. Cell wall damage was observed in bacterial cell treated with nano-copper. Considerable research has been done in the field of nanotechnology over the past ten years. Yet we are only recently beginning to realize how nanoparticles can affect our lives and lead to both positive and negative outcomes. Research into the development of nanopesticides is picking up at a faster pace, but this topic has not yet reached the public or regulatory authorities. In general, innovation constantly leads to both benefits and problems for human and environmental health. The current level of knowledge about the fate of the

environment does not allow us to fairly assess the advantages and disadvantages that arise from the use of nanopesticides. Nanoparticles have distinct physical, biological and chemical properties associated with their atomic strength (Leiderer and Dekorsy, 2008) [16]. Targeted nanoparticles often exhibit novel properties such as extraordinary strength, greater chemical reactivity, and high electrical conductivity. Nanotechnology has thus become one of the most promising new technologies in the last decade. Nanoparticles (1-100 nm in diameter) are

agglomerated atom by atom and their size (and sometimes shape) can be maintained by a specific experimental procedure (Roy, 2009) [26]. Such self-assembly is caused by forces such as hydrogen bonding, dipolar forces, hydrophilic or hydrophobic interactions, surface tension, gravity, and other forces. Many naturally occurring biological structures such as membranes, vesicles, and deoxyribonucleic acid (DNA) formed by self-assembly.

Methods of nanoparticles production

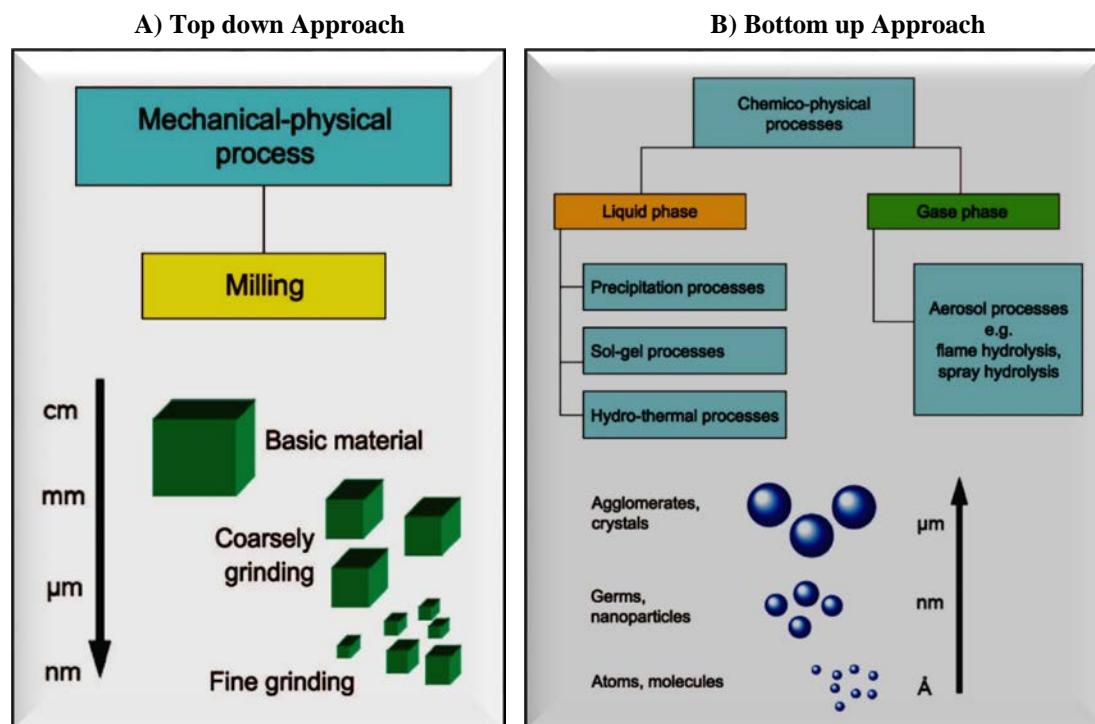


Fig 2: Schematic Diagram of Bottom up and Top-down approach

Mode of entry of nanoparticles in insect

Nanoparticles penetrate insects through physical contact, ingestion and inhalation. Upon physical contact, the nanoparticles penetrate the exoskeleton; bind the nanomaterials to sulfur from protein or phosphorus from DNA in the intracellular space, leading to organelle and enzyme denaturation, leading to cellular fraction and cell death (Abd-Elsalam *et al.*, 2018) [1]. Dust nanoparticles are commonly used to control stored grain pests and the mechanism relies on physical disruption. The nanoparticles dehydrate the insect's body by attaching to their waxy cuticle layer. Nanoclay, nanoalumina, and nanosilica are attached to the insect's cuticle and absorb water from the insect's body. The hydrophobic behavior of nanosilver particles causes cracks and scratches on the insect body, changes membrane properties, resulting in changes in cell permeability and respiration, damages DNA and releases toxic Ag⁺ ions. Ag

nanoparticles interfere with melanin synthesis. Inhalation of nanoparticles leads to internalization in cells via phagocytosis, which causes deterioration of the midgut and alters the activity of metabolic genes and decreases lipid, protein and glucose levels. Inhalation also changed the activity of nervous system enzymes and membrane potential e.g. Zn NPS and Tio₂ NPS bind to acetylcholine esterase and β carboxyl esterase and affect their activity. The mode of action of these nanoparticles is similar to that of organophosphorus and carbamate insecticides. Ag nanoparticles affect the enzyme Glutathione S transferase. In *Spodoptera litura*, Ag nanoparticles act as an amylase inhibitor. The generation of reactive oxygen species is considered to be one of the most cellular effects induced by nanoparticles, and the excessive generation of free radicals induces DNA damage through inflammatory processes.

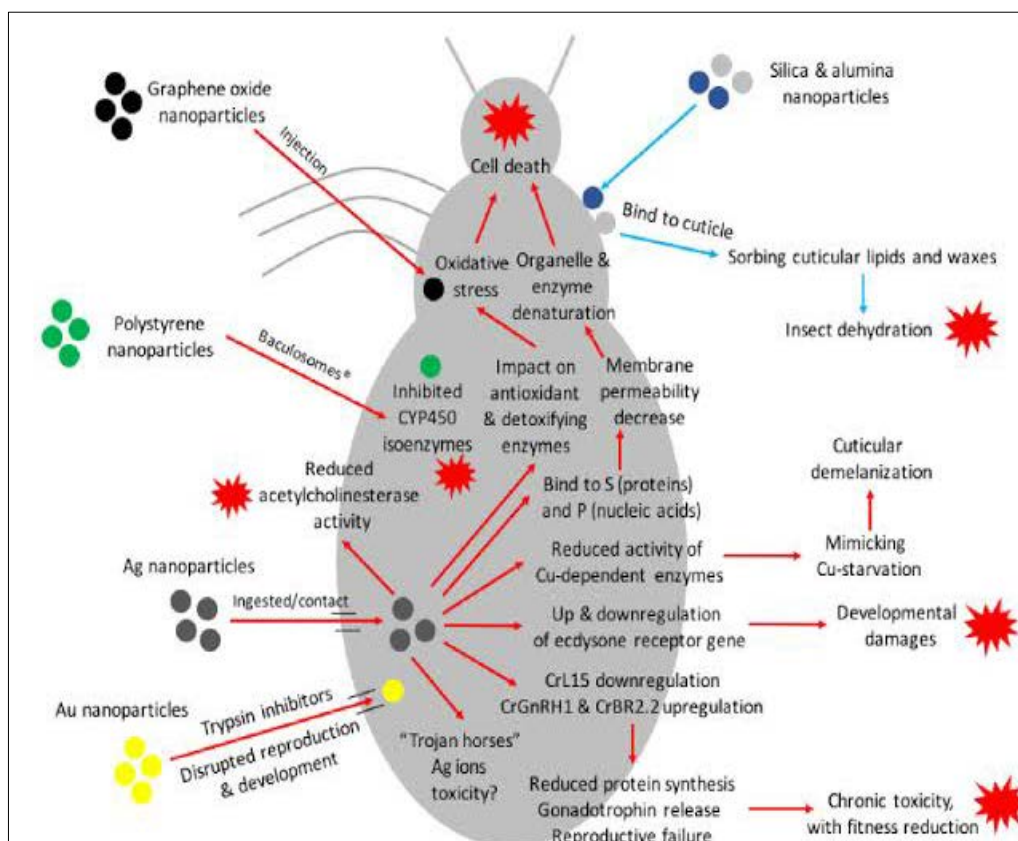


Fig 3: Mode of entry of nanoparticles in insect

Merits of nanopesticides

- Nanopesticides increase the apparent solubility of the poorly soluble active ingredient (a.i.), protect the a.i. against severe environmental degradation and the release of a.i. in a slow/targeted manner (Kah *et al.*, 2013) [12].
- They can reduce environmental contamination through reduced reuse of conventional pesticides and reduced losses. This also reduces costs, reduces human mucosal irritation, phytotoxicity, damage to other non-target organisms and even the crops themselves (Margulis-Goshen and Magdassi, 2012) [18].
- Nanopesticide delivery systems have increased efficacy (Schrof *et al.*, 2003) and are highly toxic, leading to a reduction in the amount of pesticide used, leading to a reduction in pollution load, ultimately to a reduction in input costs (Kuzuma and Verhage, 2006) and are safer from the point of view of the environment (Cao *et al.*, 2005) [5].

Demerits of Nano-pesticides

- Nanopesticides can also create new types of contamination of soils and watercourses due to longer persistence, increased transport and higher toxicity. The applications of some nanoparticles pose potential risks, silver nanoparticles (AgNps) contribute to higher toxic effects than silver nitrate (Griffitt *et al.*, 2009) [10] and are able to penetrate biological barriers such as cell membranes (Verma *et al.*, 2008) [35]. Inhalation and oral ingestion of nanosilver causes liver toxicity (bile duct hyperplasia) (Kim *et al.*, 2009) [13]. Alumina (alumina) nanoparticles slowed root growth in five plant species (cucumber, cabbage, carrot, corn, and soybean) (Yang *et al.*, 2005) [36].
- Nanopesticides can be phytotoxic, affecting plants,

animals and the environment, depending entirely on the type of nanomaterial. Higher concentrations and types of nanomaterials have an adverse effect on root elongation at different growth stages and seed germination percentage. There are about 100 pesticides that contain Ag for its antimicrobial properties. However, the main problem is the toxicity of nanosilver to the ecosystem and humans. However, future research on nanomaterials for plant germination and growth should address some of the following issues as mentioned.

- a) Unpredictability in the response of nanomaterials in different plants.
- b) Phytotoxicity caused by higher concentrations.
- c) Reduced plant uptake and photosynthesis due to larger nanomaterials

Prospectives

Nanotechnology has the potential to revolutionize various sectors of the agricultural and food industries with modern tools for rapid disease detection, disease treatment, increasing the ability of plants to absorb nutrients, etc. Nanoparticle-based formulations will increase the effectiveness of pesticides and herbicides, allowing them to be used at lower doses while protecting the environment (Tungittiplakorn *et al.*, 2004) [33]. Apart from these important applications in insect pest control, nanotechnology can be used in various other sectors such as gene transfer for crop improvement, food packaging, nanofoods, etc. (Bhattacharyya *et al.*, 2011) [4]. It increases the need for more targeted research in energy, environment, crop improvement, disease management and efficient use of resources to increase profit, productivity without compromising the natural environment. Nanotechnology opens up a wide range of opportunities to increase agricultural productivity, including nanoparticles for

slow release, effective dosing of insecticides and fertilizers, nanocapsules for pesticide delivery and vector, insect and pest management. It can therefore be used as an effective and ecological alternative to conventional pesticides in the protection against insect pests without harming nature.

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