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REVIEW

Nanopesticides in agricultural pest management and their environmental risks: a review

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Abstract
Increasing global population demands modernization in agricultural production to achieve sustainable food security. The frequent pest infestation causes a significant economic loss and deleterious impact on agriculture production. While, the traditional application of conventional pesticides leads to loss of soil biodiversity, decline in pollinator population, and negative impacts on non-target organisms. In recent years, nanotechnology has gained much interest in agricultural application. Various studies have demonstrated the beneficial effect of engineered nanomaterials as an active ingredients or the nanoformulations in insect pest control and plant protection. Nanopesticides have shown more advantages over conventional pesticides in terms of high adsorption, reduced volatilization, improved tissue permeation, controlled release, etc. However, studies are also highlighting the potential toxicity of nanopesticides in non-target organism and their environmental risk. The goal of this review is to provide a comprehensive information on recent developments in nanopesticides and its consequences in the environment. This review highlights various aspects of nanopesticides including, preparation methods, types, characterization techniques, importance in pest control, toxicity in plant and animal models, environmental risk, and current approaches in risk assessment and regulatory strategies.

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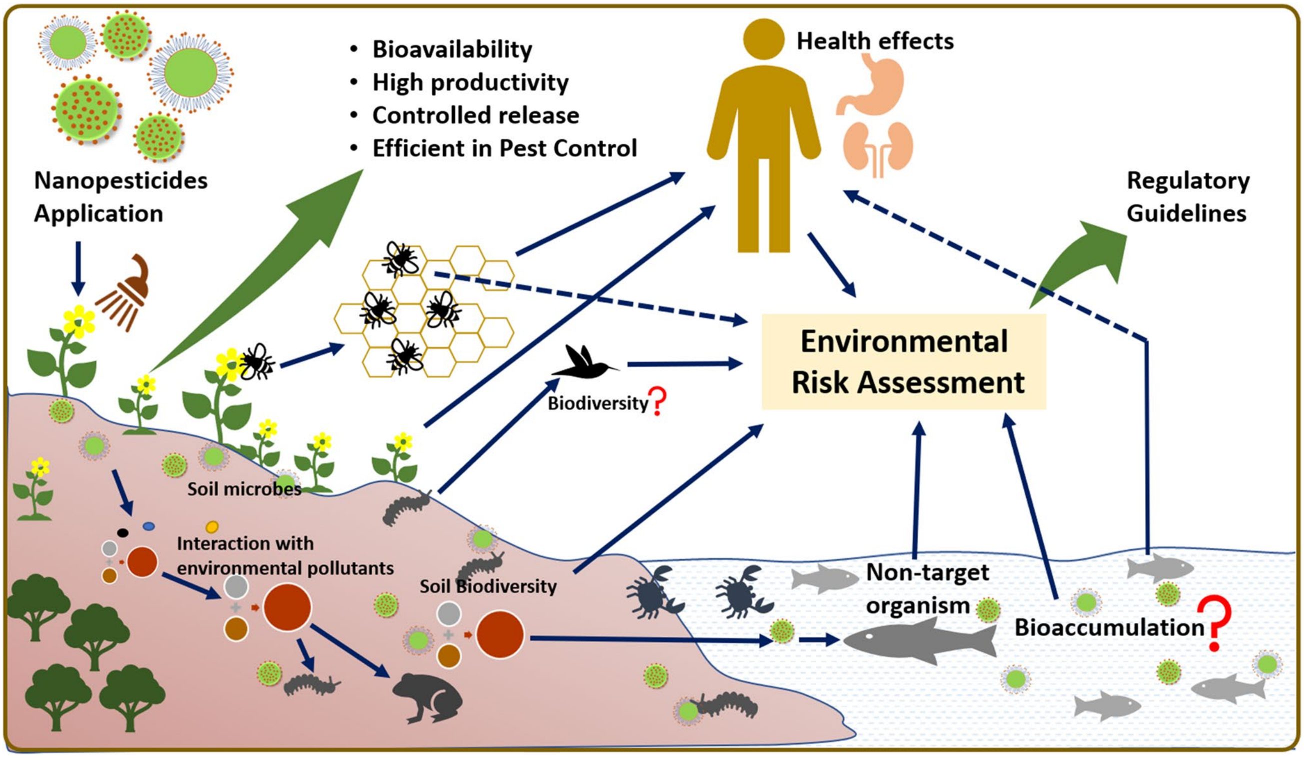
Graphical abstract



Keywords Nanotechnology · Pest control · Toxicity · Non-target organisms · Environmental risk · Regulatory strategies

Introduction

Agriculture provides the majority of food and nutrition for humans and domestic animals, while the food demand is predicted to increase by 70% by 2050 (Adisa et al. 2019). High agricultural yields are important for sustainability, but they have negative consequences for the environment in the form of water use, ecosystem contamination, and agrochemical treatment in the land (Shekhar et al. 2021). Crop rotation, integrated pest management systems, biological or mechanical weed control, and pesticide reduction are some of the strategies of sustainable agriculture practices (Rai and Ingle 2012). However, there is a significant loss of global crop production in conventional farming methods due to plant pathogens, weeds and pests, poor soil quality, natural disasters and lower nutrient availability, which altogether limits achieving food security in addition to climate change (Sundström et al. 2014; Raza et al. 2019; Mittal et al. 2020).

The excessive use of agrochemicals results in reduced biodiversity and nitrogen fixation, increased disease resistance, and pesticide bioaccumulation in aquatic organisms, livestock products, and agricultural commodities, which are detrimental to the ecosystem, wildlife and human (Chaud et al. 2021). The limitations in existing control methods are anticipated to be addressed by advanced technical developments like nanotechnology, which provide new and advanced solutions for sustainable agriculture. The development of novel technologies can reduce the harmful effects of pesticides by using a controlled release strategy with active ingredients that are nanoscale encapsulated (de Albuquerque et al. 2021). Through a unique nanoscale formulation of the active component, the nanopesticides and nanofertilizers can improve delivery and effectiveness, leading to improvement in the dispersion stability, create slow- or controlled release formulations, and provide greater control in the field applications (Grillo et al. 2021). Nanopesticides have a range of benefits, including more durability and potency as well as reduced active components, which provides scope of effective means of reducing the environmental impact that chemical pesticides have on the ecosystem (Awad et al. 2022).

The aim of this review is to understand the recent scientific advancements in agricultural practices from conventional methods to emerging technologies, viz. nanotechnology in agriculture with a special focus on the importance of nanopesticides. In this context, a brief review of the literature was conducted with the demerits of conventional pesticides and the importance of nanopesticides in crop protection and pest management along with its preparation methods, effectiveness on target pests, adverse effects in non-target organisms and other environmental components, and current strategies of risk assessment and regulatory guidelines. Overall, this review highlights the pros and cons of nanopesticides in agricultural pest management.

Conventional pesticides

Pesticides that are generated synthetically to repel or destroy a pest organism are known as conventional pesticides (EPA 2021). They are indispensable to control pests and pathogens in modern agricultural practices (Huang et al. 2018). The common types of pesticides are organochlorine pesticides, organophosphates, carbamate pesticides and synthetic pyrethroids (Dhananjayan et al. 2020; Abdollahdokht et al. 2022). They are categorized into insecticide (Plhalova et al. 2018; Faria et al. 2021; Forouhar Vajargah et al. 2021; Saha et al. 2021), herbicide (Stara et al. 2019b; Blahova et al. 2020; Yalsuyi et al. 2021), rodenticide, fungicide and bactericides (Sharma et al. 2021a; 2021b) based on the target such as insects, weeds, rodents, fungi and pathogens, respectively (Gharaei et al. 2020; Petrovici et al. 2020; Stara et al. 2019a; 2020, 2021; Radovanović et al. 2021). Recently, Dhananjayan et al. (2020) have described twenty different types of pesticides depending on the target organism. Insecticides mainly acts on damaging nervous system of the organism by inhibiting acetylcholinesterase (organophosphates and carbamates), voltage-gated sodium channels through the nerve membrane (pyrethroids and dichlorodiphenyltrichloroethane, DDT), and the acetylcholine receptor (neonicotinoids) (Abdollahdokht et al. 2022). Between 2016 and 2021, the global pesticide market was expected to increase at a compound annual growth rate of 5.15 percent, reaching $70.57 billion (Kumar et al. 2019). However, only around 0.1 percent of pesticides used are effective against the organisms targeted, and a large portion is lost after application due to photolysis, volatilization, and degradation (Camara et al. 2019). Besides, conventional pesticides have low dispersibility and biological activity (Shekhar et al. 2021). The continuous and excessive usage of pesticides altered the genetic makeup of pests due to a strong selection pressure, which made the pests resistant to pesticides (Rai and Ingle 2012). Further, 90% of the pesticides run-off into the environment before reaching the target organism (Tang et al. 2019). Traditional integrated pest management practices applied in agriculture are insufficient and pose risks to the environment (Duhan et al. 2017). The ineffective practice of pesticides causes various problems like pest resistance, water and soil pollution and affects non-target organisms (Gahukar and Das 2020).

The persistence and bioaccumulation nature of pesticides through food chain and environment as well as by occupational exposure affect the human health (Dhananjayan et al. 2020). Organochlorine pesticides have the ability to bioaccumulate in the organism through food chain and its residues levels have been detected in fish (Plhalova et al. 2018). The lipophilicity and high persistence of organochlorine pesticides tend to accumulate in lipophilic human body parts particularly in fatty tissues and lipid-rich tissues (Qi et al. 2022). Several studies have reported the health effect of pesticides in human. For instance, chronic or prolonged exposures to diazinon poses risks of cancer, lung lesions, and cytogenetic effects in humans (Saha et al. 2021). DDT, hexachlorocyclohexane, hexachlorobenzene, methoxychlor, chlordane, heptachlor and endosulfan have been detected in breast milk and affect infant health (Qi et al. 2022). Therefore, conventional pesticides are discouraged due to potential health dangers to the environment and human health. As a result, there is a growing demand for sustainable alternative techniques involving modern technologies such as nanotechnology to boost crop yield and manage plant pests and diseases.

Nanotechnology in agriculture

Nanotechnology extends to precision farming to improve the crop yield and to control target action based on environmental conditions (Chhipa 2017). Nanotechnology have been extensively applied in agricultural fields to increase the crop yield by promoting its growth, pest control, seed

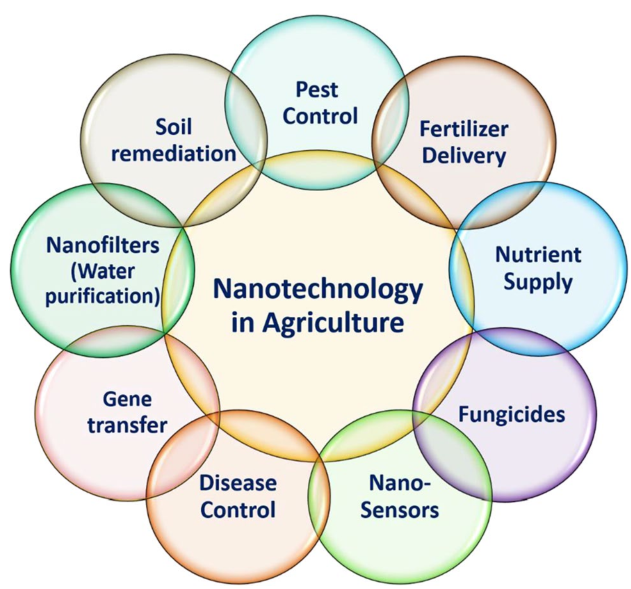


Fig. 1 Application of nanotechnology in agriculture and crop protection

treatment and germination, nutrient balance, fertilizer delivery, gene transfer, nanosensor (pathogen detection), nanofilters (water purification), detection and reduction of toxic agrochemicals (Duhan et al. 2017; Adisa et al. 2019; Kumar et al. 2019; Bahrulolum et al. 2021). Various applications of nanotechnology in agriculture and crop protection are shown in Fig. 1. The unique qualities of nanomaterials, such as tiny size (1–100 nm), large surface area, increased permeability, thermal stability, dispersion, and biodegradability, have led to widespread use of nanotechnology in agriculture (Kumar et al. 2015; Athanassiou et al. 2018).

Nanomaterials are considered as effective carriers for stabilizing pesticides and fertilizers due to their distinct features, which also make them effective for aiding controlled nutrient transfer and enhancing crop protection (Abdel-Aziz et al. 2019; Bahrulolum et al. 2021). Nanofertilizers have advantages over traditional fertilizers due to their rapid absorption and controlled distribution of nutrients in plants (Abdelmigid et al. 2022). It enhances the photosynthesis process and crop production by increasing the absorption capacity of plant roots (Zulfiqar et al. 2019). The importance of nanoparticles as nutrient carriers in crop development have been demonstrated in several studies. For instance, Cota-Ruiz et al. (2020) investigated copper nanowires as fertilizers in alfalfa (*Medicago sativa*) crops and observed that nano-copper increased the plant's physiology and micronutrient value. As a nanofertilizer, zinc oxide nanoparticles were found to boost the crop production and food quality of soybean (*Glycine max*) grown in Zinc-deficient soil (Yusefi-Tanha et al. 2020). Nanomaterials have also been proven to affect seed germination and growth in experiments (Khot et al. 2012). For instance, Zheng et al. (2005) have investigated influence of nano-titanium dioxide (nano-TiO_2) on spinach seed germination and growth. Multi-walled carbon nanotubes (MWCNTs) have increased the germination rate of tomato seeds by increasing the water uptake potential (Khodakovskaya et al. 2009).

Criterion for the selection of nanomaterials in agricultural application

Generally, the materials selection for agricultural application are depending on the important characteristics such as biocompatibility, biodegradability, nontoxicity and cost-effectiveness (Pandey 2018). In this context, various nanocarriers are required based on their specific targets such as crops, weeds, pest organism, viruses and fungi, indicating that nanocarriers must meet the physicochemical and physiological conditions of the targets (Li et al. 2021). The main criteria for selecting nanostructured materials to deliver nutrients can be based on nutrient loading capacity, nutrient release rate, nutrient use efficiency, crop quality and productivity, economic performance, and environmental compatibility (Guo et al. 2018). The complex nature of the plant cell wall imposes demanding parameters for the selection of penetrating nanocarriers in terms of their size, morphology, and surface characteristics (Li et al. 2021). For instance, the controlled release matrices and antimicrobial potential of chitosan micro/nanoparticles are considered as a new strategy for microbial control (Cota-Arriola et al. (2013). Besides, the polymer and matrix selection for controlled release of a pesticide depends on number of factors, including the matrix preparation technique, the pesticide type and the experimental conditions as well as an important aspect is that the polymer be biodegradable.

The selection of suitable nanomaterial for the design and development of a food packaging are depending on important factors including technical characteristics, environmental consequences, safety and economic feasibility (Reig et al. 2014). Recently, Dima et al. (2020) reviewed the selection criteria of nanocarrier materials in functional foods. They reported that the basis of selection depends on (a) physicochemical and biological characteristics such as colour, taste, odour, resistance to pH, temperature, oxygen, light, moisture content, chemical reactivity and low toxicity; (b) functional properties including solubility, surface tension, electric charge and gelling ability; (c) sources; (d) economic feasibility; and (e) cultural and nutritional restrictions. In nanosensor application of pathogen detection and contaminating agents in agro-products packaging, the nanoparticles are selected with good adhesive characteristics for binding and elimination of pathogens. The nanosensors provide various advantages such as high sensitivity, compatibility, cost-effective, and proximate real-time detection (Ndukwu et al. 2020 and references within).

Nanoparticles synthesis methods

Several methods have been described for synthesizing nanomaterials such as physical (as-phase deposition, pulsed laser ablation and power ball milling), chemical (chemical co-precipitation, wet chemical deposition, micro-emulsions, hydrothermal synthesis), and biological methods (plant extracts and microorganisms) (Nayak 2010; Ahmed et al. 2021; Basit et al. 2022). The conventional production of nanoparticles by physical and chemical methods requires various hazardous chemicals and advanced equipment to achieve a controlled synthesis, which usually have high toxicity and adverse impacts on the environment (Bahrulolum et al. 2021; Abdelmigid et al. 2022). In this context, nanotechnology has been focused towards ecofriendly and economically viable 'green' synthesis approach to facilitate the growing demand of nanoparticles in various sectors (Bahrulolum et al. 2021). Green synthesis, as part of bioinspired protocols, provides reliable and sustainable methods for the biosynthesis of nanoparticles by a wide range of biological systems such as bacteria, fungi, and plant extracts (Saratale et al. 2018; Bahrulolum et al. 2021 and reference therein). The green synthesis of nanoparticles is considered as advantageous over chemical synthesis due to low hazardous nature, environmentally friendly, less resource utilization, reduced by-product generation, more stability and high reaction rate (Ahmed et al. 2021). Since this sector is growing rapidly, new techniques are continually developed to enhance the properties of nanoparticles and its application.

Mechanism of nanoparticle-meditated crop improvement

The application of nanomaterials is a versatile tool in agriculture that promote plant growth and development, improve nutritional content, and ultimately produce more yield as well as protect them from biotic and abiotic stresses (Ndukwu et al. 2020; Basit et al. 2022). Several studies have emphasized the potential role of nanomaterials in crop improvement as a pesticide, herbicides, fertilizers, fungicides and antimicrobial agents including metal-based (silver, copper, iron, zinc, gold, titanium) and carbon-based (fullerenes, carbon dots, graphenes, and carbon nanotubes) nanoformulations or nanocarriers (Basit et al. 2022). However, the current nano-based development is depending on phenomenological studies and the mechanism of action are not completely understood. Nanomaterial–plant interfacial interactions with the leaf cuticle, chloroplast cell walls, and phloem sieve plates are controlled by biophysical features such as size, shape, solubility, surface chemistry, and surface charge (Lowry et al. 2019). Besides, another challenging factors may be determining the required nanomaterial concentration and its delivery at the right time and place in plants.

Various climatic conditions such as temperature, cold, and wind speed and direction as well as environmental factors like, pH, soil type, and salinity may affect the efficiency of the nanomaterials in improving plant function (Lowry et al. 2019). A recent study by Wang et al. (2020) analysed Type 1 metal-based nanopesticides impact on the biomass, yield and nutritional quality of crop plants and found the improvement in the nutritional value of crops, including their edible tissues like, vitamin (2.8%), organic acid (9.6%), protein (9.9%), amino acid (10.8%), and antioxidant content (18.0%). Potential explanations for Type 1 nanopesticides induced enhancements in sugar, fatty acids, chlorophyll, carotenoid content, and essential elements include improved light absorption and electron transfer efficiency mediated by improved chlorophyll content; increased photosynthesis capacity by CO2 assimilation and water uptake; effective scavenging of excess reactive oxygen species; and inhibition of pathogenic activity and improved plant immune response through modification of plant metabolism (Wang et al. 2022).

Based on the literatures, nanoformulated pesticides have ten times the toxic effects in target pests and nanofertilizers may increase the crop production up to 30% compared to conventional analogues, while the consumption of agrochemicals in crop protection and nutrition may be reduced by 20–30% that may help to reduce environmental pollution (Kah et al. 2018). In terms of overall effectiveness against target organisms, nanopesticides outperform non-nano size pesticides by 32%, including a 19% improvement in outdoor studies (Vasseghian et al. 2022). Besides, nanopesticides are 43.2% less harmful to non-target organisms, indicating less collateral environmental impact. In food packaging industries, metallic nanoparticles like silver, titanium, gold, magnesium oxide, copper oxide, and zinc oxide provide potential remedies for the issues caused by limited shelf-life products, enhancing its quality and preventing microbial adherence (Mustapha et al. 2022). For instance, in fruits and vegetables packaging, nanoparticles have been developed to enhance the flexibility, moisture and temperature stability, low volatility and gas barriers (Ndukwu et al. 2020).

Nanopesticides

The nanopesticide targets the precise or controlled release of the optimum amount of their active ingredient formulations in response to the environment (Zhao et al. 2017a). Through precise farming, it is possible to improve pesticide usage and reduce pollution (Huang et al. 2018). In pest control strategies, several nanopesticide formulations are being developed for the controlled release of various organic and inorganic ingredients (Shoaib et al. 2018; Gahukar and Das 2020). Various multifunctional nanocarriers have been reported as pesticide delivery systems such as polymer, mesoporous silica nanoparticles, clay and porous inorganic materials (Shoaib et al. 2018; Song et al. 2019). The important drivers of nanotechnology in pesticide sector are to reduce the volume of pesticide requirement in crop protection through improved solubility, controlled release, targeted delivery, enhanced adhesion, and increased bioavailability and stability of active ingredients in the environment (Kah et al. 2018).

Categories of nanopesticides

Nanopesticides have the potential to increase the effectiveness and durability of pesticides while lowering the quantity of active ingredients needed (Vasseghian et al. 2022). Generally, there are two categories of nanopesticides, viz. (1) Type 1 metal-based (silver, copper and titanium) nanopesticides (inorganic nanoscale nanoparticles are active ingredients without carriers) and (2) Type 2 nanopesticides in which the active ingredients are encapsulated by nanocarriers like polymers, clays and zein nanoparticles or in the form of emulsion or liposome (Li et al. 2019; Grillo et al. 2021; Wang et al. 2022). The third type of nanopesticides is the combination of type 1 and type 2 (Grillo et al. 2021). Type 1 nanopesticides are the most common analytes that exhibit potent antimicrobial activity through adhesion, dissolution, oxidative stress, cytotoxicity and genotoxicity-induced cell death. Type 2 nanopesticides, which have additional novel properties that affect the release of active ingredients for pest control, such as encapsulation, loading, and release efficiency of active ingredients, place a greater emphasis on the responsive nanoscale delivery platform that have the potential to meet sustainable agriculture goals (Vasseghian et al. 2022). Most nanocarriers are biocompatible, cost-effective and stimuli-responsive, and are further categorized into polymer- and clay-based nanocarriers. The natural polymer including chitosan, cellulose and polylactide are commonly used for the preparation of nanocapsules, nanospheres, nano-hydrogels and nanomicelles with active ingredients, whereas in clay-based mesoporous silica and montmorillonite have demonstrated high active ingredient encapsulation capacity (Wang et al. 2022). Regardless of the type a nanopesticides formulation falls under, it is anticipated that it will be able to increase pesticide effectiveness, boost active ingredient stability, extend its period of effectiveness, and lower pesticide environmental burdens.

Advantages of nanopesticides advantages over conventional pesticides

Nanopesticides are expected to overcome the limitations with the existing strategies and provide novel formulations with cost effectiveness, diminish the pest resistance, and remain active in targets pest and benign in the non-target organisms (Deka et al. 2021 and references therein). The advantages of nano-based pesticide formulations have been well documented (Zhao et al. 2017a; Athanassiou et al. 2018; Cui et al. 2019) including increased stability of nano-formulation, low volatility, elimination of toxic organic solvents, slow release of active ingredients, increased bio-availability, UV protection, improved mobility and higher insecticidal activity, low dose requirement and less run-off and environmental residuals. Table 1 describes the advantages and disadvantages of conventional pesticides and nanopesticides. The nanoformulations of pesticides provide great efficacy and low consumption as well as efficient in producing hydrophobic insecticides with improved solubility (Vasseghian et al. 2022). Figure 2 shows the pictorial representation of factors related to nanopesticides and their advantages in crop protection.

Nanopesticide development and formulation methods

Nanopesticides can be produced in two ways, (i) directly developed into nanosized pesticides and (ii) by loading

Table 1 Comparison of advantage and disadvantages of conventional pesticides and nanopesticides

Characteristics	Conventional pesticides	Nanopesticides
Active ingredients	Pesticides as active ingredients	Nanoparticles as active ingredients or nanoformulation with pesticides as active ingredients active ingredients
Organic solvent content	High	Low or not required
Solubility	Low	High
Dispersibility	Low	High
Dosage requirement and frequency	High	Low
Efficiency	Low	Increased uptake/efficacy
Bioavailability	Low	High
Degradation in soil or plant	Slower	Faster degradation
Controlled release and targeted delivery	Low	High
Protection against premature degradation	Low	High
Toxicity to target organism	Present	Enhanced toxicity to target organism
Toxicity to Non-target organism	Present	Present (comparatively low)
Bioaccumulation	High	Moderate or low
Environmental risk assessment methods	Available	Partially available
Regulatory guidelines	Available	Partially available (under development)

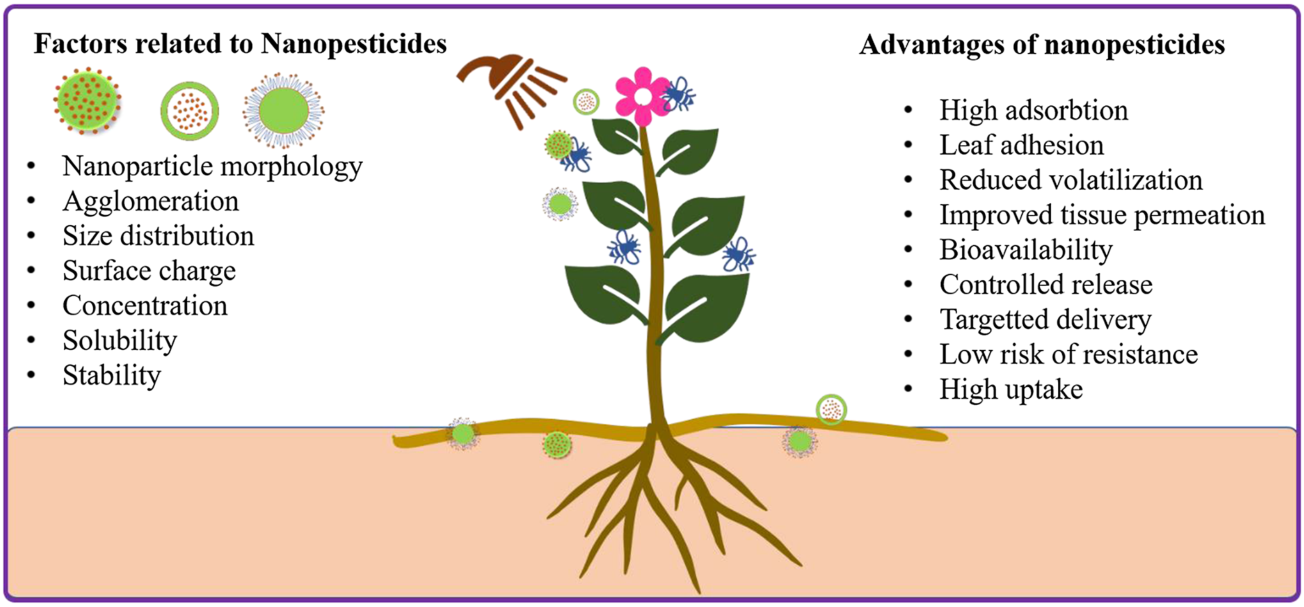


Fig. 2 Pictorial representation of factors related to nanopesticides and their advantages in crop protection

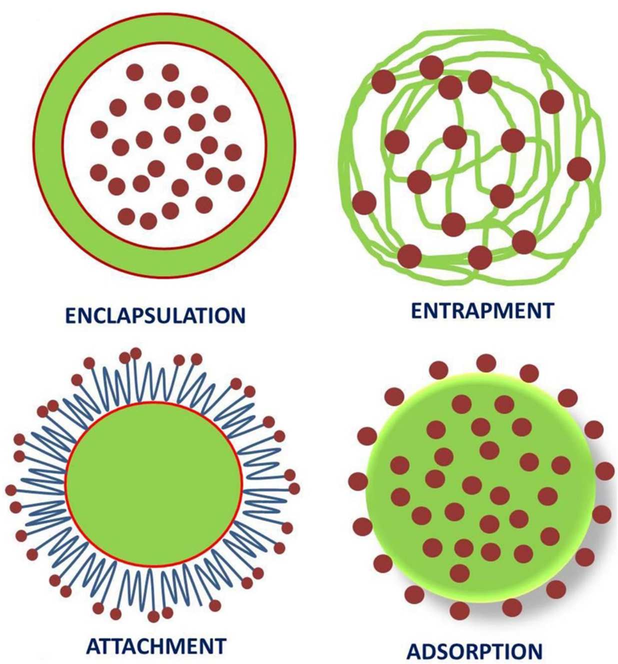


Fig. 3 Nanocarriers used in nanopesticide formulations

active ingredients of pesticides into nanocarriers. In the latter method, the pesticides are loaded into the nanocarriers by encapsulation, absorption, attachment or entrapment (Zhao et al. 2017a). The different types of nanocarriers used in pesticide formulations are shown such as metal (Ahmed et al. 2019), metal oxides (Vignardi et al. 2020), non-metal oxides (Stadler et al. 2017), polymers (Kumar et al. 2014), carbon (Song et al. 2019), lipid (Jacques et al. 2017), etc. Nanocarriers are used in nanopesticide formulations (Fig. 3).

Nanoencapsulation

Nanocapsules are nanometer-sized solid hollow particles with the ability to encapsulate a large number of molecules into their core domain (Kumar et al. 2014). In nanoencapsulation of active ingredients, nanopolymers or nanocomposites are widely used due to their biodegradable and ecofriendly nature. Nanoencapsulation decreases the leaching and vaporization of harmful substances, which helps to safeguard the environment (Duhan et al. 2017). Sodium alginate have been used as an encapsulating agent in the development of nanoformulation of pyridalyl (Saini et al. 2015), imidacloprid (Kumar et al. 2014) and acetamiprid (Kumar et al. 2015). Recently, Preisler et al. (2020) have reported that nanocapsules formed with atrazine-containing poly(ε-caprolactone) showed effective weed control with no phytotoxic effects.

Nanoemulsions

Nanoemulsions are prepared by dispersing pesticides in water in nano-form, which is often known as the oil-in-water emulsion method, with surfactant molecules present at the interface. Kumar et al. (2014) used an emulsion cross-linking approach to make imidacloprid loaded sodium alginate nanoparticles and exhibited their insecticidal potential against sucking pests (leafhopper). Emamectin benzoate–sodium lignosulfonate nanoformulation was developed by oil-in-water emulsion method in the form of nanospheres, which revealed their pesticide activity against *Prodenia litura* (Cui et al. 2019). Recently, Assalin et al. (2019) investigated a thiamethoxam insecticide–polycaprolactone (PCL)–chitosan nanoformulation prepared using double-emulsion–solvent evaporation method.

Nanospheres

Nanospheres are prepared with the pesticide trapping inside or adsorbed on the surface of the spherical structures with a dense polymeric network that can be amorphous or crystalline which protects the active ingredient from chemical and enzymatic degradation (Prado-Audelo et al. 2022). For example, nanospheres of 146.28 nm was reported with propiconazole encapsulated using poly lactic acid and polymer poly (lactic-co-glycolic) acid as carrier and observed an encapsulation efficiency over 42% (Barrera-Méndez et al. 2019).

Nanomicelles

Nanomicelles can be formed from amphiphilic copolymers in aqueous solution in which hydrophobic pesticides can be solubilized in the interior region of the micelles (Nuruzzaman et al. 2016). Nanomicelles was developed with the copolymers of polyethylene glycol and various dimethyl esters for the encapsulation of carbofuran (2,3–dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate), and reported their controlled release formulation (Shakil et al. 2010).

Colloidal delivery system

The photostability and efficacy of pesticides have been improved by colloidal delivery systems. Shoaib et al. (2018) have developed nanoformulations of emamectin benzoate by colloidal delivery systems with polymeric nanocapsules, mesoporous nanosilica and silicon dioxide nanoparticles and studied their insecticidal effect in *Plutella xylostella*.

Other methods

Acetamiprid-Alginate-chitosan nanocapsules were prepared by ionic pre-gelation and polyelectrolyte complexation method (Kumar et al. 2015). Assalin et al. (2019) used an ionic gelification technique to load the pesticide thiamethoxam into a chitosan–tripolyphosphate nanocarrier. In-situ deposition method was reported cypermethrin loaded in the micro-/nano-pores of diatomite/Fe_3O_4, a magnetic nanocarrier (Xiang et al. 2017). In addition, Pho et al. (2020) have reviewed plasma-assisted synthesis of nitrogen-doped nanoparticles in pest management.

Physicochemical properties and characterization of nanopesticides

Characterization data are the crucial to understand the physicochemical properties, mode of action, evaluation of the benefits and the novel qualities of the products (Kah et al. 2018). The efficacy, fate, transport, and effects on the environment and human health are all influenced by the physicochemical characteristics of nanomaterials. Various studies have reported many types of characterization techniques in nanopesticides development including UV–Visible spectroscopy (UV), dynamic light scattering (DLS), Fourier infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive atomic spectroscopy analysis (EDAS), transmission electron microscopy (TEM), atomic force microscopy (AFM), Brunauer–Emmett–Teller (BET), thermogravimetric analysis (TGA), etc., (Supplementary material Table S1). Each of these characterization techniques reveals unique information of the composition in the nanopesticides.

The morphology of the nanoformulation can be characterized by UV, FTIR, DLS, SEM, TEM and fluorescence spectra (FS). Size, homogeneity, surface area, and surface charge are all important qualities that possessed by both types of nanopesticides (Wang et al. 2022). The measure of surface plasmon resonance by UV absorbance have been used to study reduction state of nanomaterial. For instance, absorbance peak at 252 nm indicates the conversion of nickel salt solution to nickel nanoparticles through the reaction of secondary metabolites with metal salts (Elango et al. 2016). Furthermore, the reduction of silver nitrate to silver nanoparticles using *Solanum lycopersicum* was confirmed by the excitation of surface plasmon resonance at 445 nm (Bhattacharyya et al. 2016). Studies have showed various different shape and surface morphology nanopesticides such as spherical (Cui et al. 2019; Khoshraftar et al. 2020b; Ye et al. 2022), hexagonal (Bharani and Namasivayam 2017), rectangular parallelepiped structure (Peng et al. 2022), platelet (Buteler et al. 2015) and cubical (Elango et al. 2016) based on the DLS, SEM, TEM and AFM.

DLS and zeta potential analysis have been used to determine the size and surface charge of the nanoparticles (Abdelmigid et al. 2022). The polydispersity index (PDI) is a measure of homogeneous particle size distribution in a dispersion that can be studied by DLS, while PDI of less than 0.5 indicates the good physical stability of nanopesticides (Khoshraftar et al. 2020b). Generally, PDI values of Type 2 nanopesticides are often lower than type I nanopesticides (Vasseghian et al. 2022). For instance, nanoliposomes loaded with Plantago major seed extract showed

PDI of 0.41 ± 0.014 (Cui et al. 2019) and tannic acid-based azoxystrobin nanopesticides with 0.05 ± 0.03 (Yu et al. 2019). The stability of the nanopesticides can be studied by Zeta potential (ζ-potential). In emamectin benzoate–sodium lignosulfonate nanoformulation, ζ-potential was reported as 0.0555 ± 0.0332 mV, indicating that positive ions and negative ions had combined to form electroneutral nanoparticles in this formulation (Cui et al. 2019). The ζ-potential of nanoliposomes loaded with *Plantago* major seed extract loaded was equal to − 27.23 ± 5.31 mV (Khoshraftar et al. 2020b). The high stability of green synthesized nickel nanoparticles was reported as ζ-potential of − 53.9 meV (Elango et al. 2016). Based on DLS and TEM measurement, the mean size of type 1 nanopesticides (Ag- and Cu-based) ranges 22.8–153.2 nm and type 2 nanopesticides varies in size like 166.7 to 358.6 nm (Chhipa 2019; Vasseghian et al. 2022; Wang et al. 2022). In a study, TEM results showed 12 nm of emamectin benzoate-loaded carboxymethyl chitosan-modified carbon nanoparticle, while the hydrate particle size (hydrodynamic size) measured by DLS was 28.21 nm (Song et al. 2019), suggesting the hydration effect of nanoparticles in aqueous solution.

The crystalline nature and possible functional groups in the formation of nanoformulation can be studied by XRD and FTIR, based on the diffraction peaks and absorption bands, respectively. In FTIR, the absorption bands were attributed to the stretching vibration N–H, C–O–C, –CH2–, C=0, N–H, C–N, C–C, C=C, O–H, –CONH–, etc., For instance, the spectra of emamectin benzoate were found as 2967, 2933 and 1120 cm^{-1}, while the similar absorption bands in emamectin benzoate by functionalized polysuccinimide nanoparticles reveals the presence of active ingredient emamectin benzoate in the developed nanopesticide formulation (Ye et al. 2022). XRD have been used to understand the crystalline or amorphous nature of the nanoparticles based on the peaks at 2θ values. For example, 2θ values of 38.068, 44.28, 64.34 and 77.41 corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) confirmed that the silver nanoparticles formed by the reduction of Ag+ ions using pomegranate peel extract are crystalline in nature (Bharani and Namasivayam 2017). Size, homogeneity, surface area, and surface charge are all important qualities that possessed by both types of nanopesticides, while the efficiency in encapsulation, loading and release of active ingredients are additional properties of type 2 nanopesticides that impact pests (Wang et al. 2022). Although there are some exceptions, nanopesticides are known to have a size between a few and 500 nm (Li et al. 2019). BET analysis can measure the surface area of both the agglomerated or dispersed surface (Buteler et al. 2015). For instance, the specific surface area of the graphene oxide–pyraclostrobin nanocomposite analysed by BET was reported as 137 m^2/g, which is beneficial to promote the adsorption of pesticides (Peng et al. 2022).

After spraying the nanopesticides, wettability and retention on leaf surface affects the adhesion and utilization rate, which can be studied by contact angle measurement (Peng et al. 2022). The smaller value of contact angle refers to higher affinity of the nanopesticides to crop leaves, indicating the reduction in pesticide loss and increases the efficacy (Cui et al. 2019). The contact angle of water was 107° in paraffin film, while the graphene oxide–pyraclostrobin nanocomposite showed 74° in paraffin film (Peng et al. 2022), indicates good adsorption and deposition capacity of nanopesticides. Similarly, Yu et al. (2019) reported the contact angles for water in corn leaves as 57.50 ± 2.04°, whereas they found the mean contact angle values for tannic acid-based abamectin and azoxystrobin nanopesticides on cucumber foliage as 91.0° and 91.5°, respectively.

One of the key measures for determining the quality of pesticide formulations is the stability. In as study, Song et al. (2019) have described various types of stability analysis such as colloidal stability, long-term storage stability, temperature mediated stability, and water quality resistance stability for emamectin benzoate loaded carboxymethyl chitosan modified carbon nanoparticle. They revealed that the nanoformulation was stable for 48 at room temperature (colloidal), no precipitation or stratification was found in long-term stability (12-month storage period), stable in low (0 °C, 7 days) and high (54 °C, 14 days) temperature treatment, and no apparent precipitation or flocculation showed water quality resistance (water, standard hard water, and tap water). Additionally, silver nanoparticles synthesized from pomegranate peel extract showed stability of more than six months with no sign of aggregation (Bharani and Namasivayam 2017). Nano-based agrochemicals enable controlled release of functional ingredients and site-directed delivery to control the pest and enhancing crop productivity (Chaud et al. 2021; Sarkar et al. 2022). In this context, Cui et al. (2019) have investigated the controlled release properties of emamectin benzoate–sodium lignosulfonate nanoformulation. They found that the nanoformulation have a pH-responsive controlled release function with the 59.95%, 39.82% and complete release of emamectin benzoate in neutral, basic and acidic medium, respectively. Besides, Song et al. (2019) also reported pH-responsive controlled release of emamectin benzoate-loaded carboxymethyl chitosan-modified carbon nanoparticles. Furthermore, a recent study by Dong et al. (2021) using cyclodextrin polymer-valued, benzimidazole-functionalized, MoS2-embedded mesoporous silica nanopesticides evidenced the multidimensional stimuli induced controlled release of pesticides including low pH, amylase enzymes, competitors, and sunlight.

Table 2 Impact of engineered nanopesticides or nanoformulations in pest control

S. no.	Nanoproduct	Active ingredient	Concentration	Target pest	Efficiency/observation	References
1	Nanoalumina dust	Aluminium oxide	125 ppm and 250 ppm	Rice weevil (*Sitophilus oryzae*), Lesser grain borer (*Rhyzopertha dominica*)	The mortality rate was 100% after three days	Buteler et al. (2015)
2	Novaluron nanoparticles	Novaluron	0.05 or 0.2 mg a.i./L	Egyptian cotton leafworm *Spodoptera littoralis*	The mortality rate was 92% after 6 days in 1st instars	Elek et al. (2010)
3	Silver nanoparticles	Silver	25, 50 and 75 g/kg soil	Cyst nematodes *Heterodera sacchari*	Showed good nematicidal effects	Fabiyi et al. (2018)
4	Nano-calcium	Calcium carbonate	0.625, 1.25, 5, 10 and 25 mL	California red scale (*Aonidiella aurantii*) and Oriental fruit flies (*Bactrocera dorsalis*)	Showed protection efficacy against oviposition punctures LC_{50}—6530 mg/L	Hua et al. (2015)
5	Pesticide-loaded sodium alginate nanoparticles	Imidacloprid	5 and 10 g/mL with 2.46% Imidacloprid	Sucking pests (leafhopper)	Nanoencapsulated insecticidal treatment showed more superior effect	Kumar et al. (2014)
6	Nanoformulated natural pyrethrin	Pyrethrin	1.86 and 3.1 g a.i./hl	Cotton aphid, *Aphis gossypii*	The mortality rate was 94–95%	Papanikolaou et al. (2018)
7	PEGylated acephate nanoparticles	Acephate	180, 240 and 300 ppm	Tobacco cutworm or Cotton leafworm, *Spodoptera litura*	The mortality rate was 100% at 300 ppm within 7 days	Pradhan et al. (2013)
8	Carboxymethyl chitosan modified carbon nanoparticles	Emamectin benzoate	0, 0.25, 0.5, 1, 2, 4, 8, 16 mg/L	Oriental armyworm *Mythimna separata*	Above 80% mortality at 4 mg/L	Song et al. (2019)
9	Diacyl hydrazine-based nanoformulation	Diacyl hydrazine derivative	0.001, 0.005, 0.01, 0.05, and 0.1%	Cotton leafworm, *Spodoptera litura*	Maximum potency with GI_{90} (growth inhibition) values of 0.015 mg/L and 0.010 mg/L by topical and diet incorporation method	Pandey et al. (2020)
10	Lambda-Cyhalothrin/Silver nanoparticles	Lambda-Cyhalothrin	0.005, 0.01, 0.02, 0.04, and 0.08 ppm	African cotton leafworm, *Spodoptera littoralis*	The nanocomposite was 37 times more effective than pesticide	Ahmed et al. (2019)
11	Emamectin Benzoate – Sodium Lignosulfonate Nanoformulation	Emamectin benzoate	0.32, 1.6, 8, 40, 100 and 200 ppm	Egyptian cotton leafworm, *Prodenia litura*	The fatality rate of 100 ppm was 83.1% after 5 days of spraying	Cui et al. (2019)
12	Emamectin benzoate nanoformulations	Emamectin benzoate	0.1, 0.2, 0.4, 0.6 and 16 mg/L	Diamondback moth, *Plutella xylostella*	Effective with 100% mortality at 0.4 mg/L after 72 h	Shoaib et al. (2018)
13	Emamectin Benzoate functionalized polysuccinimide with glycine methylester nanoparticles (EB@PGA NPs)	Emamectin benzoate	20 µg FITC-cad-PGA NPs	*Plutella xylostella*	Bioactivity was 1.6-fold higher and enhances the penetration of the drug and insecticidal activity	Ye et al. (2022)
14	Poly(ethylene glycols)/β-cyfluthrin nanoformulations	β-cyfluthrin	31.25, 62.5, 125, 250, 500, and 1000 mg/L	Cowpea bruchid, *Callosobruchus maculatus*	Nanoformulation showed the lowest mean EC_{50} as 32.23 mg/L	Loha et al. (2012)

Table 2 (continued)

S. no.	Nanoproduct	Active ingredient	Concentration	Target pest	Efficiency/observation	References
15	Nanostructured alumina	Aluminium nitrate nonahydrate	36, 75, 125, 250, 350, and 500 ppm	Rice weevil, *Sitophilus oryzae*	Act by binding to the cuticle, sorbing its wax layer and results in dehydration of insect (LC_{50}—79.91 ppm)	Stadler et al. (2017)
16	Nano-(chlorine) chlorantraniliprole and nano-(sulphur) thiocyclam	Chlorantraniliprole and thiocyclam	LC_{15} and LC_{50}	Black cutworm, *Agrotis ipsilon*	Showed higher toxicities than their original compounds with LC50 values of 0.015 and 4.46 mg/L as well as increases oxidative stress enzyme activities and mutagenic effects	Awad et al. (2022)

a.i., active ingredient; hl, hectolitre; ppm, parts per million; LC_{15}, lethal concentration 15%, LC_{50}, lethal concentration 50%; EC_{50}, effective concentration 50%

Nanopesticides in crop protection

Engineered nanomaterials/nanoformulations in pest control

Engineered nanomaterials are widely studied as an alternative strategy for conventional pesticides in pest control strategies. The efficacies of various engineered nanomaterials/nanoformulations are outlined below (Table 2). Imidacloprid-loaded sodium alginate nanoparticles showed insecticidal activity against sucking pests (leafhopper) (Kumar et al. 2014). Pradhan et al. (2013) have demonstrated the PEGylated acephate nanoparticles as an alternative neurotoxic pesticide against *Spodoptera litura*. Lambda-Cyhalothrin/Silver nanoparticles nanoformulation have shown insecticidal activity in *Spodoptera littoralis* with 37 times more efficiency than pesticide alone treatment (Ahmed et al. 2019). Similarly, Elek et al. (2010) found a 92 percent mortality rate in first instars after 6 days of employing Novaluron nanoparticles in a previous work on *S. littoralis.* Silver nanoparticles showed a good nematicidal effect against *Heterodera sacchari* (Fabiyi et al. 2018) and nanocalcium showed protection against oviposition punctures by *Aonidella aurantii* and *Bactrocera dorsalis* (Hua et al. 2015). Recently, Pandey et al. (2020) have observed that diacyl hydrazine-based nanoformulation showed anti-pest activity of maximum potency in *Spodoptera litura* with GI_{90} (growth inhibition) level of 0.015 and 0.010 mg/L, respectively, using topical and diet incorporation methods. *Sitophilus oryzae* becomes dehydrated after nanostructured aluminium oxide adheres to its surface (Stadler et al. 2017). Nanoparticulate dust improves the coverage, stability and traditional efficiency of pesticide formulations. For instance, Buteler et al. (2015) found that nanoalumina dust prepared with aluminium oxide showed a higher mortality rate in stored grain pests, *Sitophilus oryzae* and *Rhyzopertha dominica*. Poly(ethylene glycols)/β-cyfluthrin nanoformulations have exhibited insecticidal activity in stored pest *Callosobruchus maculatus* with the mean effective concentration (EC_{50}) of 32.23 mg/L (Loha et al. 2012).

Natural/Bio-nanoformulations in pest control

Bio-nanotechnology integrates biotechnology and nanotechnology to develop nanomaterials with specialized functions by merging biological principles with physical and chemical techniques (Sahayaraj and Rajesh 2011). Since the growing need of ecofriendly approach, the green synthesis or biological method of nanoparticle production have drawn great attention recently. Due to the biocompatibility, biosafety, and environmental safety of the biosynthesized NPs, they have been widely used in agriculture (Vasseghian et al. 2022). Green synthesis approaches can synthesize materials with these beneficial properties by using eco-friendly stabilizing agents, non-hazardous reducing agents, and green substitute solvents. In green chemistry perspectives, the nanoparticle synthesis process can be divided into intracellular and extracellular with the assessment of three major steps such as selection of solvents, ecofriendly reducing agent and non-toxic material for the stability (Sahayaraj and Rajesh 2011).

The research and industrial sectors are interested in green synthesis of silver nanoparticles for various applications in biomedicine, the environment, and industries, due to its simple development process and cost-effectiveness (Mustapha et al. 2022). Various green synthesis of nanoparticles have been reviewed in Sahayaraj and Rajesh (2011) including, polysaccharide, irradiation, Tollens, polyoxometalates and biological methods. Green methods also involve a bottom-up, fundamental sol–gel method that enables the production of nanoparticles that naturally scale up (Vasseghian et al. 2022).

The creation of innovative nanoparticle-based products has become a scientific and technological priority worldwide in the last two decades (León-Silva et al. 2016). Many countries are transitioning from chemical-based agriculture to green agriculture, with biopesticides and biological nanomaterials playing an increasingly important role in pest management (Bhattacharyya et al. 2010; Gogos et al. 2012; Sahayaraj 2014). The biosynthesis of nanoparticles is eco-friendly and simple to carry out without the requirement of high-end instrument facilities. Biomolecules of plant extract can reduce ionic metals to nanoparticles in a one-step synthesis process and it can be easily scaled up based on the needs. Table 3 shows the various studies showing the application bio-nanopesticides in pest control. For instance, the application of *Euphorbia prostrata*-based green synthesis of silver nanoparticles (AgNPs) inhibits the development of *Sitophilus oryzae* (Zahir et al. 2012). Jafer and Annon (2018) reported that green synthesis of silver nanoparticles from *Nerium oleander* has shown high larvicidal effect in *Tribolium castaneum* and *Callosobruchus maculatus,* and Ali et al. (2019) have reported that green silver nanoparticles cause more than 80% mortality rate in Diamondback moth, *Plutella xylostella*. Elango et al. (2016) reported anti-pest activity of nickel nanoparticles synthesized via green method using *Cocos nucifera* methanolic against the *Callasobruchus maculates*. The pesticidal activity of silver and lead nanoparticles produced from a mangrove plant extract of *Avivennia marina* against *Sitophilus oryzae* showed 100 percent mortality within 4 days of treatment (Sankar and Abideen 2015). Kantrao et al. (2017) have investigated that silver nanoparticles affect the gut protease activity of insecticide-resistant gram caterpillar, *Helicoverpa armigera*. Nano/microparticles containing *Azadirachta indica* extracts can affect complete larval mortality in *P. xylostella* (Forim et al. 2013). Bio-nanopesticide prepared from the neem gum extract exhibited antifeedant, larvicidal and pupicidal activities against *H. armigera* and *S. litura* (Kamaraj et al. 2018). Neem based polymeric nanoformulation, nanospheres of poly (β-hydroxybityrate) suspension showed 76.67% mortality in one day after spraying against *S. frugiperda* (Giongo et al. 2016).

Natural compounds like secondary metabolites of plants have been widely reported to have pest control properties (Knaak & Fiuza 2010). Essential oils obtained from aromatic plants come under this category, and they showed insecticidal action against a range of insects (Rocha et al. 2018). The effectiveness of essential oil-based nanoformulations in pest management has been studied in several research. For example, polyethylene glycol-coated nanoparticles containing garlic essential oil were insecticidal against adult *Tribolium castaneum* (Yang et al. 2009). Christofoli et al. (2015) reported that poly-(caprolactone) nanospheres with essential oils from *Zanthoxylum rhoifolium* leaves act against *Bemisia tabaci*. Furthermore, the formulations have offered better protection to these essential oils against the degradation and oxidation processes. Furthermore, Rocha et al. (2018) found that insecticidal effect of essential oil from Pogostemon cablin-based nanoformulations in leaf-cutting ants, *Atta opaciceps, A. sexdens,* and *A. sexdens rubropilosa*, with a decrease in displacement and velocity speed.

Chitosan, a hydrophilic natural biopolymer with hydroxyl and amine groups is widely used in various carrier systems (Campos et al. 2018). It's a chitin-derived linear polymer with significant insecticidal effect against plant pests (Rabea et al. 2005). Biocompatibility, biodegradability, non-allergenicity, and antimicrobial activity have all been demonstrated in chitosan nanoparticles, with low toxicity to animals and humans (Kumar et al. 2015). In this context, Campos et al. (2018) have investigated β-cyclodextrin-grafted chitosan nanoparticles co-loaded with carvacrol and linalool against Corn earworm, *Helicoverpa armigera* and Spider mite *Tetranychus urticae*.

The liposome is a phospholipid bilayered microscopic vesicle with an aqueous space inside that have shown potential application in pest control (Khoshraftar et al. 2020a). The insecticidal activity of *Plantago major* seed extract nanoliposome was investigated against *Tribolium castaneum* and the mortality percentage was noted as 16.25% and 62.50%, respectively (Khoshraftar et al. 2020b). In another work, Khoshraftar et al. (2020a) have demonstrated that a high mortality rate was noted against *Trialeurodes vaporariorum* and *Myzus persicae* pests at the highest concentration of the *Melia azedarach* (Leaf) extract-loaded nanoliposomes. Khoshraftar et al. (2020c) similarly studied the effect of *Eucalyptus globulus* extract on Peach potato aphid (*M. persicae*) and showed significant mortality on tests pests with LC_{50} of 14.93 mg/mL.

Table 3 Impact of bio-nanopesticides in pest control

S. no.	Nanoproduct	Ingredient	Concentration	Target pest	Efficiency/observation	References
1	Neem-based polymeric nanoformulations	Neem seed kernel extract	3.87 mg/L	Fall armyworm, *Spodoptera frugiperda*	Nanospheres—poly(β-hydroxybutyrate) suspension showed 76.67% mortality in 1 day after spraying	Giongo et al. (2016)
2	Essential oil nanoformulation	*Pogostemon cablin* extract	6–13 different concentrations	Leaf-Cutting Ants, *Atta opaciceps, Atta sexdens* and *Atta sexdens rubropilosa*	The LC_{90} for workers varied from 2.43 to 3.11 µL/L. Reduced the displacement and velocity speed	Rocha et al. (2018)
3	Biogenic silver nanoparticles	*Punica granatum* peel extract	0.001, 0.01, 0.1 and 1.0 g/mL	Cotton leafworm, *Spodoptera litura*	LC_{50}—19.21 µg in III instar. Reduced amylase, protease, lipase, and invertase activities	Bharani and Namasivayam (2017)
4	Carvacrol and linalool co-loaded in *β*-cyclodextrin-grafted chitosan nanoparticles	Carvacrol and linalool	1.25 mg/mL	Corn earworm, *Helicoverpa armigera* and Spider mite, *Tetranychus urticae*	Mortality was considered to be at least 80%	Campos et al. (2018)
5	Neem gum mediated nanoformulation	Neem gum	6.25, 12.5, 25, 50 and 100 ppm	Corn earworm, *Helicoverpa armigera* and Cotton leafworm, *Spodoptera litura*	LC_{90} values of 32.68, and 36.68 ppm for *H. armigera* and *S. litura*, respectively. Exhibited potential antifeedant, larvicidal and pupicidal activities	Kamaraj et al. (2018)
6	Nanoliposomes	*Plantago major* seeds extract	10, 25, 40, 65, 80, and 100 mg/mL	Red flour beetle, *Tribolium castaneum*	The mortality percentage was 62.50%	Khoshraftar et al. (2020b)
7	Natural nanopesticides	*Eucalyptus globulus* extract	10, 15, 25, 35, 50 mg/mL	Peach potato aphid, *Myzus persicae*	Showed significant mortality on test pests with LC_{50} of 14.93 mg/mL	Khoshraftar et al. (2020c)
8	Tannic acid-based nanopesticides	Abamectin and azoxystrobin	0.78125, 1.625, 3.125, 6.25, 12.5, 25 and 50 ppm	Peach potato aphid, *Myzus persicae*	Showed mortality with LC_{50} of 10.68 ppm	Yu et al. (2019)
9	Biosynthesized Silver nanoparticles	*Ficus religiosa* and *Ficus religiosa* leaf extract	6.6, 13.3, 26.6, 40, 53.3, and 66.6 µL/gm diet	Corn earworm, *Helicoverpa armigera*	Reduced both larval weight and survival rate, inhibited the Gut protease activity	Kantrao et al. (2017)
10	Green silver nanoparticles	Eight plants extract (neem, bakain, bitter gourd, clove, eucalyptus, datura, garlic and ginger)	23, 24, 20 and 30 mg/mL	Diamondback moth, *Plutella xylostella*	More than 80% mortality rate was observed after 72 h interval	Ali et al. (2019)
11	Biosynthesized nickel nanoparticles	Extract of *Cocos nucifera*	1.25, 2.5, 5, 10 and 20 mg/L	Cowpea bruchid, *Callasobruchus maculates*	The mortality rate was observed as 97.31%	Elango et al. (2016)
12	Nanoencapsulated essential oils	*Zanthoxylum rhoifolium* leaves	2 and 5%	Whitefly, *Bemisia tabaci*	Resulted in reductions in the number of eggs and nymphs as high as 95%	Christofoli et al. (2015)

ppm, parts per million; LC_{50}, lethal concentration 50%; LC_{90}, lethal concentration 90%

Table 4 Adverse effects of nanopesticides in plant models

S. no.	Nanoproduct	Active Ingredient	Concentration	Organism	Efficiency/observation	References
1	Kocide® 3000, nanopesticide	Copper (II) hydroxide, $Cu(OH)_2$	6.68 mg/L for 1 year (Terrestrial mesocosm) 35 mg/week for 9 months (Wetland mesocosm)	Forage crops	Limited effects on the terrestrial soil biodiversity Aquatic communities are more sensitive particularly protists	Carley et al. (2020)
2	Thiamethoxam insecticide nanoformulation	Thiamethoxam	0.06, 0.6, 6, 60, 600 and 1200 mg/L	Algae, *Raphidocelis subcapta*	EC_{50} values for *Raphidocelis subcapitata* was 56.15 mg/L	Assalin et al. (2019)
3	Citric acid-coated cerium oxide nanoparticles	Cerium oxide nanoparticles	0, 62.5, 125, 250 and 500 mg/kg	Tomato, *Solanum lycopersicum*	Not affect the homeostasis of nutrient elements in plant tissues Increased catalase activity in leaves	Barrios et al. (2016)
4	Poly(epsilon-caprolactone) nanocapsules	Atrazine	1 mg/mL (Equivalent to 200 g atrazine per hectare)	Maize, *Zea mays*	Increased lipid peroxidation in the leaf No impacts on shoot growth	Oliveira et al. (2015)
5	Kocide® 3000, $Cu(OH)_2$ nanopesticide	$Cu(OH)_2$	Three times of 6.68 mg/L at a 2.5-month interval	*Trifolium pretense, Chamaecrista fasciculate, Brassica napus, Cichorium intybus, Sorghastrum nutans, Urochloa ramose, Medicago sativa*	No negative effects on forage biomass, root mycorrhizal colonization or soil nitrogen fixation rates	Simonin et al. (2018)
6	Engineered nanomaterials	TiO_2, CeO_2, or $Cu(OH)_2$	1, 10, or 100 mg/L	Elegant clarkia, *Clarkia unguiculata*	Decreased photosynthetic rate and CO_2 assimilation efficiency	Conway et al. (2015)
7	Kocide® 3000, $Cu(OH)_2$ nanopesticide	$Cu(OH)_2$	0.18 and 18 mg/plant	Spinach, *Spinacia oleracea*	Reduced the low molecular mass antioxidant in leaves	Zhao et al. (2017c)
8	Kocide® 3000, $Cu(OH)_2$ nanopesticide	$Cu(OH)_2$	100 and 1000 mg/L	Maize, *Zea mays*	Decreased the leaf chlorophyll content and biomass POD1 and GST1 gene expression was increased	Zhao et al. (2017b)
9	Kocide® 3000, $Cu(OH)_2$ nanopesticide	$Cu(OH)_2$	0, 2.5 and 25 mg/plant	Cucumber, *Cucumis sativus*	Induced significant changes in mRNA levels of antioxidant and detoxification-related genes	Zhao et al. (2017d)
10	Kocide® 3000, $Cu(OH)_2$ nanopesticide	$Cu(OH)_2$	0, 1050 and 1555 mg/L	Lettuce, *Lactuca sativa*	Reduced the antioxidants and total antioxidant capacity	Zhao et al. (2016)
11	$Cu(OH)_2$ nanowires	$Cu(OH)_2$	4.8 mg/pot	Basil, *Ocimum basilicum*	Increased n-decanoic, dodecanoic, octanoic, and nonanoic acids Reduced Mn accumulation	Tan et al. (2018)
12	Diuron nanoformulation	Diuron	2.5 mg/pot	Chinese cabbage, *Brassica rapa*	Showed early signs of leaf chlorosis and mortality	Yearla and Padmasree (2016)

Table 4 (continued)

S. no.	Nanoproduct	Active Ingredient	Concentration	Organism	Efficiency/observation	References
13	Carvacrol and linalool co-loaded in β-cyclodextrin-grafted chitosan nanoparticles	Carvacrol and linalool	0.05, 0.25, and 2.5 mg/mL	Maize, *Zea mays*	Induced no phytotoxic effects in the plants	Campos et al. (2018)
14	Neem oil-loaded zein nanoparticles	*Azadirachta indica*	5 mg/mL	Onion, *Allium cepa*	Mitigated the increase in the DNA relative damage index	Pascoli et al. (2019)
15	Atrazine/poly(ε-caprolactone) nanocapsules	Atrazine	0.1 and 1 mg/mL	Soybean, *Glycine max*	Not enhanced the long-term residual effect of the herbicide on soybean	Preisler et al. (2020)

Impact of nanopesticides and their environmental risks

Adverse effect of nanopesticides in plant models

Depending on the absorption efficiency, nanoparticles have different effects on plant growth and metabolic activities (Duhan et al. 2017). Plant uptake the nanoparticles by various mechanisms such as phagocytosis, pinocytosis and endocytosis. They can adapt in response to unfavourable conditions like nanomaterial-mediated toxicity, while the responses are varied between them (Dev et al. 2018). Pascoli et al. (2019) have reported that neem oil-loaded zein nanoparticles mitigated the DNA damage index in *Allium cepa.* In basil varieties (*Ocimum basilicum*) with low anthocyanin content, copper (II) hydroxide (Cu(OH)2) nanowires boosted n-decanoic, dodecanoic, octanoic, and nonanoic acids while reducing Mn accumulation (Tan et al. 2018). While, Barrios et al. (2016) have observed that citric acid-coated cerium oxide nanoparticles have no effect on nutrient element balance in tissues of tomato (*Solanum lycopersicum*). Furthermore, no phytotoxic effects were found in maize plants treated to β-cyclodextrin-grafted chitosan nanoparticles co-loaded with carvacrol and linalool (Campos et al. 2018).

Although nanoparticles have positive effects in agricultural application, there are detrimental effects on crops due to their unique characteristics (Table 4). Various studies have shown the phytotoxicity of nanopesticide formulations in commercial food crops. For instance, Oliveira et al. (2015) have observed that treating nanocapsules containing atrazine-loaded poly(epsilon-caprolactone) have increased the lipid peroxidation in the leaf of maize (*Zea mays*). While $Cu(OH)_2$ nanopesticide has lowered leaf chlorophyll content and biomass in maize (Zhao et al. 2017b), it has reduced the antioxidants and total antioxidant capacity of lettuce (*Lactuca sativa*) Zhao et al. (2016) and spinach *(Spinacia oleracea)* (Zhao et al. 2017c). Furthermore, Yearla and Padmasree (2016) reported early indications of leaf chlorosis and death in *Brassica rapa* plants exposed to diuron nanoformulation. Carley et al. (2020) demonstrated that Copper (II) hydroxide $Cu(OH)_2$ used on Forage crops (used for a year on terrestrial microcosm and 9 months in wetland microcosm) limited effects on the terrestrial soil biodiversity with the higher effects on the aquatic communities that are more sensitive especially protists.

Adverse effect of nanopesticides non-target animal models

Agricultural development has a strong impact on various non-target organisms, populations, communities, and ecosystems (Carley et al. 2020). Nanoparticles once released

Table 5 Adverse effects of nanopesticides in animal models

S. no.	Nanoproduct	Active ingredient	Concentration	Organisms	Adverse effects	References
1	Kocide 3000	$Cu(OH)_2$	0.5, 1, and 1.5 ppm	Crustacean, *Daphnia magna*	Alters the gene expression of detoxification mechanism and reproductive system	Aksakal and Arslan (2020)
2	Kocide 3000	$Cu(OH)_2$	1.0, 2.0, 4.0, 8.0, and 16.0 mg/L	Zebrafish (*Danio rerio*) embryos	Causes developmental abnormities like tail deformities, scoliosis, and decreased heart rate by altered gene expression	Aksakal and Sisman (2020)
3	Nanoencapsulated formulations of bifenthrin	Bifenthrin	10 µg/g soil	Earthworm, *Eisenia fetida* and *Lumbricus terrestris*	The nano-form of bifenthrin gets accumulated in the gut	Mohd Firdaus et al. (2018)
4	Solid lipid and polymeric nanoparticles	Atrazine, Simazine	0.0025–0.05%	Nematode, *Caenorhabditis elegans*	Polymeric nanoparticles are more toxic to the developmental rate	Jacques et al. (2017)
5	Thiamethoxam insecticide nanoformulation	Thiamethoxam	Crustacean 10.00, 16.00, 25.60, 40.96, 65.53 and 104.85 mg/L and Nematode 0.02, 0.2, 2, 20 and 200 mg/L	Crustacean, *Artemia salina* and Nematode, *Caernohabditis elegans*	EC_{50} values for *C. elegans* were 66.07 mg/L. No toxicity was found in *Artemia salina*	Assalin et al. (2019)
6	Neem gum mediated nano formulation	Neem gum	6.25, 12.5, 25, 50 and 100 ppm	Earthworm, *Eudrilus eugeniae*	Showed no significant toxicity	Kamaraj et al. (2018)
7	Neem oil-loaded zein nanoparticles	*Azadirachta indica*	0.05, 0.25, 0.5, and 0.75 mg/mL	Nematode, *Caenorhabditis elegans*	Showed no toxic effect	Pascoli et al. (2019)
8	CuPRO and Kocide nanopesticides	nano-copper pesticides	0.1, 0.25, 1.0, and 2.5 mg/L	Amphipod, *Leptocheirus plumulosus*	Released relatively low levels of Cu into the environment. No-effect body burden for survival and respiration	Vignardi et al. (2020)
9	Nanopesticide based on botanical insecticide	Pyrethrum	1 and 10 ng/µL	Honey bee, *Apis mellifera*	Caused no morphological changes in digestive cells	Oliveira et al. (2019a)
10	Pyrethrum extract encapsulated in nanoparticles	Pyrethrum	80 µg/L	Bullfrog, *Lithobates catesbeianus*	Altered haematological parameters, increased the genotoxic and mutagenic effect	Oliveira et al. (2019b)
11	Nanoencapsulated atrazine	Atrazine	2 and 20 µg/L	Neotropical teleost, *Prochilodus lineatus*	Decreases haemoglobin content, increases erythrocyte DNA damage, as well as changes in Ca^{2+}-ATPase activity after 96 h exposure	de Andrade et al. (2019)

into the agro-environment, instantly begin to undergo several transformations, which facilitate their accumulation into the soil (Rajput et al. 2020). The functional features of the carrier and the stability of the active ingredients-carrier combination is anticipated to influence the environmental distribution and behaviour of nano-enabled insecticides. These properties are important to be considered in the development of nano-enabled pesticides preparation, since they may have a considerable impact on the spatial and temporal nature of non-target organism exposure (Walker et al. 2018). Overall, the knowledge base for a reliable assessment of the threats connected with the use of nano-agrochemicals appears to be limited (Kah 2015; Bai and Tang 2020). As a result, determining the possible hazards, effects, and toxicity of nanopesticides on non-target animals is essential for the safe use of nanocarrier systems in agriculture (Oliveira et al. 2019a).

Ecotoxicological studies for nanopesticide have been conducted on invertebrate and vertebrate animal models (Table 5). Clemente et al. (2014) examined the impact of nanoencapsulated atrazine in *Daphnia similis* and found that the atrazine nanocapsules were more harmful than the pure herbicide. After 96-h exposure, atrazine nanocapsules showed a significant decrease in haemoglobin content, an elevation in erythrocyte DNA damage and alteration in Ca^{2+}-ATPase level in fish *Prochilodus lineatus* (de Andrade et al. 2019). Oliveira et al. (2019b) investigated the adverse effect of nanoparticles encapsulated pyrethrum extract on bullfrog tadpoles (*Lithobates catesbeianus*) and revealed that it induced severe DNA damage and nuclear abnormalities after short-time exposure (48 h). Several studies on silver nanoparticles (Ag-NPs) in different freshwater fish like common molly (*Poecilia sphenops*), gibel carp (*Carassius auratus gibelio*) and guppy (*Poecilia reticulate*) have shown multiple effects such as: an increased mortality rate in the highest concentration of silver nanoparticles. Alteration in gonads development and reproductive parameters; the decrease of red blood cells (RBC), white blood cells (WBC), haematocrit and serum concentration of glucose in addition to a higher percentage of protein and albumin (Forouhar Vajargah et al. 2019; Mohsenpour et al. 2020; Vali et al. 2022).

Other clinical signs were found while studying the effects of copper oxide nanoparticles on guppy and common carp (*Cyprinus carpio*) like fast swimming, darkening of the skin, increasing mucus secretion, tissue lesions (encephalomyelitis, haemorrhage of gills, erythrocyte infiltration, epithelial lifting, hyperplasia, and hypertrophy) and death with open mouth (Forouhar Vajargah et al. 2018; 2020). Always on common carp, the green synthesized zinc oxide nanoparticles (ZnO-NPs) were tested and was seen that the alkaline phosphatase in comparison to the control group had statistically lower activity. In the same way, the protease activity and the total protein contents showed a decrease in fish exposed at ZnO-Nps compared to the control group (Rashidian et al. 2021). After 48-h exposure to $Cu(OH)_2$ nanopesticides, detoxification and reproductive system-related genes were upregulated in *Daphnia magna* (Aksakal and Arslan 2020). Furthermore, Mohd Firdaus et al. (2018) documented a 50% accumulation of bifenthrin in the gut region of earthworms after nanoencapsulated treatment. The health risks of nanopesticides on global pollinators, notably bees, have been recorded, including homing ability, reproduction, and foraging behaviour (Kumar et al. 2019). Moreover, Oliveira et al. (2019a) reported a rise in apocrine secretions on the apical regions and morphological changes in midgut digestive cells of honey bees after 48-h exposure to pyrethrum-loaded nanoparticles.

Additionally, exposure to hazardous agrochemicals can cause irreversible damage to vital organs, due to its ability to pass blood–brain barrier, blood-placental barrier, and blood-retinal barrier which is serious concern to human (Chaud et al. 2021). These nanomaterials have the potential to induce toxic and genotoxic effects, and hence, studies on both the chemical composition of the bulk material and the physicochemical properties of nanopesticides such as size, electrical charge, and surface properties receiving great attention. For a better understanding of the influence of nanopesticides on the environment, more in-depth research at the community and molecular levels are required.

Environmental risks and regulatory status of nanopesticides

Interaction of nanopesticides with other environmental substance/pollutant

Engineered nanoparticles are released into the environment more often as a result of their increased production and application (Deng et al. 2017). There will inevitably be more nanopesticides used in agriculture. As a result of the development and production, these substances may be hazardous to organisms that are not intended targets, they may accumulate through transport and bioaccumulation, and may interact with other environmental contaminants as well as dissolved organic matters and subsequently cause more damage to the environment (Deng et al. 2017; Li et al. 2019).

Various nanoparticles like ZnO and TiO_2 have been detected in different environmental matrices including surface water, groundwater, soil and sediment (Besha et al. 2020 and references within). After entering into the environment, the possibility of alteration in surface properties and having high surface area-to-volume ratio of nanoparticles may make them extremely dynamic nature in the environmental systems (Besha et al. 2020). Nanoparticles can directly accumulate in the food web and affect the growth of plants that can subsequently potential exposure of humans and animals.

Although studies have reported the environmental risk of nanomaterials, it have also been attracted a lot of interest in environmental remediation (Roy et al. 2021 and references therein). Studies on the nanopesticides interaction with other environmental contaminants or pollutant are scarcely reported. Hence, it demands more studies on this aspect for the proper understanding of the nanopesticides and its relation to environment. It is equally important to understand the various aspects of nanoformulations such as the mechanism of changes in behaviour of the active ingredients in nanoformulation, and comparison of pure active ingredients with the nanoformulations as well as with conventional formulations (Kah et al. 2018).

Current approaches and strategies for assessing the environmental risks of nanopesticides

Environmental compartments like air, soil and water have their own complexities, which necessitate specific concerns for the assessment and regulation of risks posed by nanopesticides, since they may also enter the environment by accidentally or intentionally as like conventional pesticides (Grillo et al. 2021). The growing interest in using nanopesticides raises concerns regarding their fate, toxicity, and biodegradation, as well as environmental risk assessment evaluation strategies (Awad et al. 2022). Generally, the engineered nanomaterials like carbon nanotubes (CNTs), Ag, and ZnO showed low risks since it have been exposed at lower concentration (Gilbertson et al. 2020). However, the higher application of nanomaterials in agricultural practices or the potential incorporation into food might enhance the exposure level and affect the balance between the benefits and risks. Because of the complex nature of nanostructures, like reactivity, size, shape, and electric charge, it is challenging to characterize the biological safety of nanopesticides as well as to evaluate, and estimate the important aspects of cytotoxicity and genotoxicity (Chaud et al. 2021). Four-tiered approach have been reported for environmental risk assessment of a pesticide (Kookana et al. 2014), such as simple exposure models (tier 1), complex exposure model (tier 2), biomagnification, recovery, and indirect effects (tier 3) and field monitoring of pesticide concentrations and their effects (tier 4). However, the information on ecotoxicological effects of nanopesticides particularly in regard to the fate and behaviour of nano formulations in the environment is scarce (Grillo et al. 2021). For instance, studies in determining the fate, behaviour and toxicity of nanopesticide formulations was reported in different environments and organisms (Walker et al. 2017; Kobetičová and Černý 2017; Grillo et al. 2021).

The standardized ecotoxicological procedures for conventional pesticides may not necessarily be appropriate for assessing nanopesticides since they differ from conventional pesticides in respect to release kinetics or active components dissolution and interactions with plants and the soil (Fojtová et al. 2019; Grillo et al. 2021). Since the nanopesticides may interact with the existing organic or environmental pollutants, conventional pesticides (non-nano) are also likely to play an important role in determining the fate of nanopesticides in the environment (Vryzas 2018). Various physicochemical and environmental parameters can affect the fate and behaviour of nanomaterials such as pH, temperature, salinity, soil type, porosity, water flow, ionic strength in water, mineral composition, microbial community, amount and type of organic matter, while its dynamic interaction leads to changes in particle characteristics (Walker et al. 2017; Grillo et al. 2021). The current approaches for environmental risk assessment (ERA) of conventional pesticides are based on the following characteristics, such as (1) distribution between soil, water, and air; (2) stability in soil, water, and sediment; (3) environmental concentrations; (4) bioaccumulation and (5) environmental toxicity (Kookana et al. 2014). Whereas, they reported that stability, environmental concentrations and ecotoxicity are the relevance characteristics with nanopesticides. Besides, nanopesticides uptake pathway into the organisms may differ greatly from a conventional pesticide in terms of octanol/water partition coefficient (Kow), sorption coefficients (Kd or Koc), half-life (t1/2) or half-dissipation time (DT50), bioconcentration factor (BCF) and hydrophobicity (Kow).

Currently, there is no internationally accepted definition for nanopesticides which results in regulatory agencies follows various criteria of the nanosized particle with different size ranges (Kah et al. 2021). Various organizations like European food safety authority (EFSA) and Organisation for economic co-operation and development (OECD) have been involved to address the limitation and fill these gaps. For instance, European Food Safety Authority have published a guidance on risk assessment of nanomaterials to be applied in the food and feed chain which includes pesticides, food contact materials, food/feed additives and novel foods (EFSA 2021). Guidelines for evaluation of nano-based agri-input and food products in India have been developed to support the existing national regulatory provisions (DBT 2020). Recently, OECD published a document on important issues on risk assessment of manufactured nanomaterials that provides the current practices, challenges and strategies for assessing risk, as well as existing regulatory frameworks on the assessment of nanomaterials (OECD 2022). In the past, severe environmental problems like DDT or neonicotinoids were tolerated since there was lack of a systematic evaluation of the risks to the ecosystem (Li et al. 2019).

Before wide-scale application, a reliable and extensive risk analysis of nanopesticides along with its interaction with plants and soil microbiota is the first line of defence to assure the environmental safety and human health (Li et al. 2019; Vasseghian et al. 2022).

Regulatory strategies for nanopesticides

Although nanotechnology development have shown benefits in agriculture, the potential human health risk and long-term environmental impacts of the intentional release of nanomaterials are to be considered (Gilbertson et al. 2020). To assure the safety of feed and food sources, agriculture is governed by strict regulations (Hofmann et al. 2020). The use of smart nanomaterials in agriculture, a newly developing technology, is reported to be restricted by the lack of sufficient risk assessment and regulation to address safety issues (Lowry et al. 2019). Legislators usually experience new challenges when a new technology is introduced, particularly when that technology's characteristics, which are commercially marketed as benefits, raise issues about potential risks to human health and the environment (Gottardo et al. 2021).

There is still a lack of knowledge on the mechanisms by which nano-enabled strategies accomplish their outcomes, for instance, the impact of nanomaterial features such as size, shape, charge, and hydrophobicity on interactions with plants physiology like uptake, transport, and toxicity as well as environment (Hofmann et al. 2020; Grillo et al. 2021). In European Union, the regulatory guidelines specific for engineered nanomaterials in agricultural food safety are emerging, however, it is challenging due to the nanomaterials design variables and complexity of agricultural systems such as biotic and abiotic factors (Lowry et al. 2019). Environmental toxicity and human health characterization factors were developed for some nanomaterials like, nano-copper, nano-TiO2, CNTs and graphene oxide as a subset of engineered nanomaterials in agriculture, while they are not currently integrated into the standard framework of life-cycle impact assessment (Gilbertson et al. 2020 and references within).

There are various factors that makes regulatory guideline preparation for nanomaterials more challenging such as difficulties in defining nanomaterials, tracing its sources and transport pathways, quantification in environmental samples, bioavailability evaluation and toxicity interpretation (Lai et al. 2018). The other major limitations might be the method development to measure particle-number based concentrations and size distributions and distinguishing the various kinds of nanoparticles such as engineered, organic and inorganic nanoparticles from natural particles (Hofmann et al. 2020 and references therein). In this context, there is a need of developing advanced analytical techniques for the regulatory purpose.

Conclusion and prospects for the future

Nanotechnology has a promising role in agricultural production, while nano-based pesticide formulations showed potential impact in pest control. Although nanotechnology provides numerous benefits, concerns have been raised regarding its risks to the environment. The integration of nanotechnology in agriculture and the food industry is in beginning stage, and hence a deeper understanding of the interactions involving nanomaterials and plants is necessary. Based on the previous research, it is clear that nano-based pesticide exposures can have detrimental effects in non-target organisms including both plants and animals at higher concentrations or prolonged exposure conditions. Moreover, the efficacy of nanoformulations observed in the laboratory conditions is not certain to be transformed into the field application. To evaluate the efficacy of nanopesticides in practical use with a safe and effective delivery strategy for sustainable agriculture, a large-scale field-based research are required. The development of risk assessment and management approaches is also important to address the potential risk of nanopesticides and to formulate the regulatory measures. The ecofriendly development of nano-enabled agriculture will be a critical to attain and maintain global food security and safety.

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