REVIEW ARTICLE

Nano-pesticides: Composition, Bioavailability and Release Mechanism in the Environment

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Abstract

Nanoscience and nanotechnology offer a new life for conventional pesticides with superior qualities by virtue of the physico-chemical properties of the Nano-sized materials. The rapid development of Nano-pesticides research over the past two years is capable of fulfilling the food demand of the growing population. Recent advancements in newly produced nanoparticles to combat pests have resulted in a new type of environmental waste. This manuscript discusses the sources of nano-pesticides, bioavailability, release mechanism, the hazardous environment, and the health effects of pesticide exposure. The potential effect of nanoparticles on agricultural productivity and ecosystem challenges are discussed in detail. Various sources of nanoparticles, special attention to the environmental behavior of nano pesticides in crops, and the latest advancements in modified nano-pesticides are studied from various experimental results. This review also addresses some concerns about pesticide product development, formulation, and toxicity. The need to develop nano-pesticides that are less harmful to the environment than traditional formulations is now growing. Future research should also assess whether any promising products have been developed with competitive properties with existing formulations in terms of cost and performance. Studies on the environmental behavior of nano-pesticides are still rare and the current state of knowledge is not enough to reliably assess the benefits and risks. Therefore, a lot of research will be required in the next few years.

Keywords: Agricultural Productivity, Controlled Release, Cost, Environmental Risk, Nano-pesticides.

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Introduction

Research into nanotechnology applications for agricultural use has become popular in recent years to fulfill the need for adequate, high-quality food for the increasing population (Yadav *et al.*, 2020). Agrochemical technology normally aims to protect agricultural fields against pests (pathogens, harmful insects, parasitic weeds, and control of livestock and fisheries products) that undermine output and productivity. However, the indiscriminate use of pesticides sprayed against harmful pests and insects has also had a negative impact on output, leading to the development of disease and insect resistance, increased demand for new agrochemicals, and worsening the imbalance in the environment (Bombo *et al.*, 2019; Awasthi *et al.*, 2017; Jaiman *et al.,* 2022). The greater the total surface area occupied by pesticide nanoparticles, the greater the overall contact with crop pests, making them as efficient as they are unpredictable. The irrational and unsystematic use of pesticides increases pathogen resistance, reduces nitrogen fixation and biodiversity, increases pesticide bioaccumulation in agricultural products, livestock, and aquatic organisms, and affects both ecosystems and humans. It poses a serious and persistent threat to biodiversity and is an obstacle to biodiversity (Osorio-Echavarría *et al.,* 2021; Vigneshwaran *et al.,* 2006; Kumar *et al.,* 2021).

Innovative Nano pesticides are nanomaterials designed to protect crops, minimize spray losses, increase leaf coverage, improve stability and reduce formulation ingredient levels. Nano-pesticide formulations can be divided into self-assembled systems such as liposomes, dendrimers, metallic and bimetallic nanoparticles, and encapsulated active ingredients such as Nanoemulsions, polymeric nanoparticles, lipid nanoparticles and nanotubes.

This review discusses the major morphologies and compositions of innovative nano-insecticides, along with the advantages and disadvantages of nanomaterials in controlling agricultural pests, environmental risks, and impacts on human and animal health. Particular attention has been paid to the key nanomaterials used in the agrochemical industry, usually focused on crop spawning, regardless of their safety profile.

Amazing opportunities to innovate agricultural practices have been introduced through the use of nanotechnology-based delivery systems. This is attributed to the intelligently controlled release profiles of fertilizers and pesticides required to increase crop productivity (Prasad, *et al.,* 2017; Awasthi *et al.,*

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2020a; Agrawal *et al.,* 2021). Such systems play an important role in agriculture, improving the performance of fertilizers and pesticides (Fraceto *et al., 2016*; Awasthi *et al.,* 2020b). Although the future of Nano pesticides in agricultural development looks promising, human exposure to harmful pesticides that cross biological barriers (e.g., blood-brain barrier, blood-placental barrier, blood-retinal barrier) is increasing and may cause serious problems and irreversible damage to vital organs. The risks posed by exposure to harmful nano-pesticides, which can cause toxic and genotoxic events, are currently receiving much attention, considering their effects not only on the chemical composition of the bulk materials but also on their physio-chemical properties (Fig. 1) (Zielińska *et al.,* 2020; Grillo *et al.,* 2012).

Nano pesticides in environment

Nanopesticides are pesticides formulated from nanomaterials to boost crop production in the agricultural field. It is specifically immobilized in hybrid substrates, encapsulated in matrices, or triggered by external stimuli or enzyme-mediated triggers. It is a functionalized nanocarrier for nano-sized particles, associated with their shape and special properties to study pesticide activity in innovative formulations of nanocarriers based on various materials such as silica, lipids, polymers, copolymers, ceramics, metals and carbon (Agostini *et al.,* 2012).

Nano-pesticide formulations improve water solubility and bioavailability, protect pesticides from environmental degradation, and revolutionize the control of crop pathogens, weeds, and insects (Yadav *et al.,* 2020; Singhal *et al.,* 2021; Sankhla *et al.,* 2018). However, the properties of nanomaterials also lie on the borderline between cytotoxicity and genotoxicity.

Indiscriminate and irrational use of pesticides affects the balance of ecosystems and endangers the health of all people. Short-term (acute) and long-term (chronic) side effects from occupational or accidental intake of pesticide residues from food and drinking water are fatal or disability-adjusted life years (DALYs). Children are more vulnerable to pesticide exposure and permanent tissue and organ damage. Among them, central

Table 1: Chemical and physical systems as carriers in the formulation of Nano pesticides.

(a) Chemical System				
Covalent Bond	*Carrier System*	*Formulation*	*Pesticides*	*References*
Comonomers	Hybrid materials	(CNT-g-PCA)	Zineb Mancozeb	(Sarlak *et al*. 2014)
Multifunctional system	Peptide-polymer	Trypsin-PEG	Modulating Oostatic factor	(Shen *et al*. 2009)
Electrostatic complex	Polyelectrolyte complex	Clay-gelatin pGPMA-dsRNA	MCPA dsRNA	(Patel *et al*. 2018)
Ionic bond	Hallow sphere	Calcium-alginate	Cypermethrin	(Alromeed *et al*. 2015; Parsons *et al*. 2018)
Cluster	Metallic nanoparticles	Cu—TM Cu0 , Ag0	Thiophanate methyl	(Malandrakis *et al*. 2021; Keller *et al*. 2017; Starnes *et al*. 2015)
(b) Physical System				
Encapsulation	Coprecipitation Polycondensation Vesicle	Polyelectrolytic interaction. Cation vesicular surfactants	Trichlorfon Acetochlor Benzoylurea-paraquat DNA, RNA Copper	(Huang *et al*. 2018; Kandpal *et al*. 2017; Kizilay *et al*. 2011; Skepö and Linse 2002; Guo *et al*. 2014; Nuruzzaman *et al*. 2016; Wang *et al*. 2018; *Yu et al*. 2016; Worthington *et al*. 2013)
Emulsion	Mixed micelles Pickering emulsion Nanoemulsion Liquid crystal Liposome	mPEG13–b–PLGA5–3 Alginate-Ca++ Water-in-oil Monoolein 18-99 PC-chitosan	Pyrethrin γ-cyclodextrin Citronella Phytantriol α-cypermethrin	(Zhang *et al*. 2019; Chen *et al*. 2017; Mustafa and Hussein 2020; Ali *et al*. 2017; Bisset *et al*. 2019; Bang *et al*. 2011)
Matrix system	Hybrid materials	mPEG-PLGA	Metolachlor	(Agostini *et al*. 2012; Parsons *et al*. 2018)
Porous system	Grafted-NP. Sol-gel composite	4-ethylortho-Silicate ATP-biochar colloidal silica	Benzoylurea-Fe2O3 Glyphosate	(Chen *et al*. 2017; Raileanu *et al*. 2010; Ciriminna *et al*. 2011; Xu *et al*. 2018; Chen *et al*. 2018)
Foams	Polymeric emulsion	Poly(alkylene-oxide] alkanol	Glyphosate acid Acetochlor	(Guo *et al*. 2014; Chaud *et al*. 2021)
Osmotic pumps	Polymeric coating	Cellulose ester/ PEG/ Inorganic salt	Diazinon	(Yalamalle *et al*. 2019)

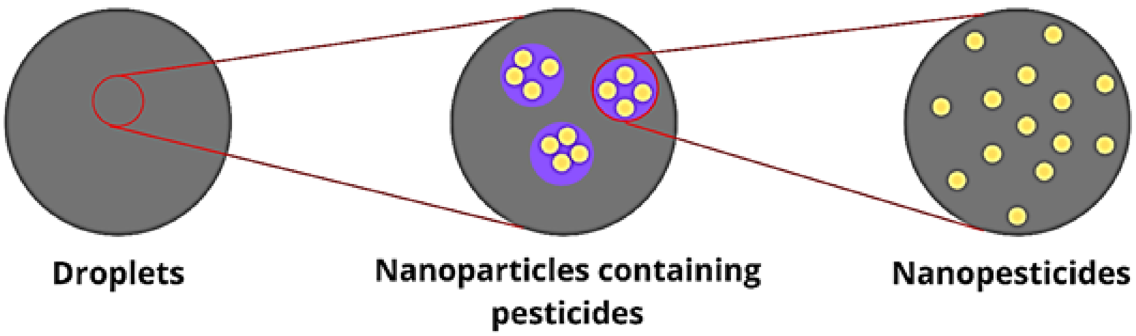

Fig. 1: Nanopesticides in the droplets.

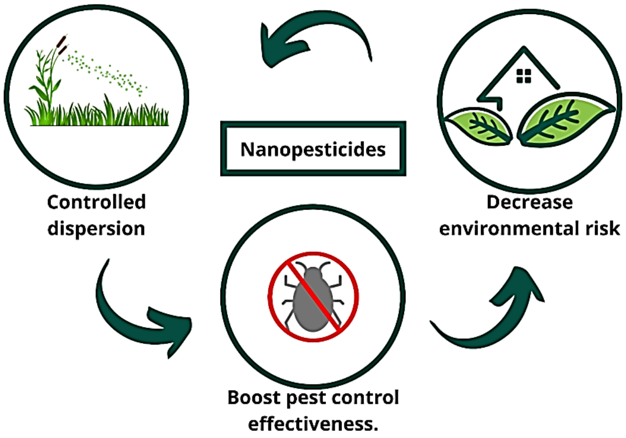

Fig. 2: Nanopesticides in environment

and peripheral neurotoxicity and effects on loss of blood coagulability are reasonable causes for concern (Kuhlbusch,). Indeed, a detailed evaluation of the strengths and weaknesses that affect the activity and toxicity of nonapeptides is critical for the safe and sustainable development of already approved uses of nanoparticles in agriculture (Fig. 2).

The effects of formulations on the behavior of nano pesticides in the environment, ecosystems, farm workers, consumers and all production sectors involved in the agricultural chain are not fully understood (Huang *et al.,* 2018). However, the critical role of Nano formulations in reducing drug degradation, improving water solubility balance, and enhancing drug bioavailability is well known. In particular, avoiding endemic pest infestations, crop damage, and economic losses by reducing the quality and quantity of agricultural products and food (Syafrudin *et al.,* 2021).

Modified-release nano pesticides can be divided into two groups: chemically bound pesticides and physically incorporated formulations of pesticides that are activated shortly after delivery to agriculture (Table 1).

Hybrid Nano formulations

Researchers were inspired to investigate the ability of more complex Nano formulations for pesticide administration by utilizing nanoformulations developed within the pharmaceutical industry. In recent years, various techniques have been proposed for removing contaminants of emerging concern (CECs) from aqueous matrices. A crucial challenge within this framework is the development of new composite materials which can combine diverse processes such as adsorption, enzyme catalysis and photocatalysis. As a result, one-of-a-kind reusable compounds were synthesized and evaluated against herbal and spiked water formulations, including natural and inorganic contaminants in order to increase overall performance and efficiency while lowering costs and reducing the environmental effect of those activities (Table 2). Organic active ingredient conjunction with inorganic nanoparticles.

Bioavailability of Nano pesticides

The carrier properties and the cells or organisms taken into account significantly impact the NC-AI's bioavailability (nano-carriers-active ingredients). Direct uptake is generally unlikely to occur due to the majority of NC-AIs having rather large sizes. It has also been reported that the NC-AI has a low bioavailability by studies that identified growing effectiveness or toxicity after the release of the AI. However, there is currently no information on any research on the bioavailability of nanopesticides. It could be oversimplified to assume that the AI that was loaded onto the NC was fully unavailable because other more complex processes might be involved. For instance, it has been demonstrated that the polysaccharide chitosan, which is frequently used as a polymer carrier for nanopesticides, can alter the enantioselective bioavailability of the chiral herbicide dichlorprop. It has also been suggested that the distribution and location of the AI within the polymeric matrix play a key role in determining how well it is protected against photodegradation. The position of the AIs inside the polymer matrix can also affect bioavailability. For instance, it is possible that soil microbes could reach the AI molecules present on the NC's surface but not its core.

Release mechanisms of nano pesticides

The discharge mechanisms may be covered by using prolixity and dissolution based on the polymer packages, the manner in which the AI (active ingredients) is transported, and the AI loading and solubility (corrosion). In addition, the gel-subcaste fashioned range will trigger the prolixity pathways and regulate the discharge geste for a polymer matrix prone to inflating and disintegration (*i.e.,* hydrophilic polymers) (Kaunisto *et al.,* 2011).

As a result, polymer degrading techniques should significantly impact launch profiles. Bulk-eroding and Floor-eroding polymer spheres are two types of polymer suppliers that

Table 2: Nano formulation system of Nano pesticide

S. No.	*Polymer*	*Material*	*Characteristics*	*Reference*
1.	Chitosan	Zinc nanoparticles	Pathogenic bacteria are inhibited by this compound.	(Deshpande *et al*. 2017)
2.	Poly E Caprolactone	Chitosan nanoparticles	The solvent evaporation process was used to encapsulate thiamethoxam in polymeric nanoparticles. Protection against premature deterioration. To assess toxicity, microalgae and microcrustaceans were evaluated.	(Liang *et al.* 2020)
4.	Poly (Lacti-Co-glycolic acid)	Nanoparticles	The encapsulated nanoparticles displayed thermodynamically advantageous properties for Phytophthora infestans disease control using cyzofamid.	(Fukamachi *et al.* 2019)
5.	Chitosan	Spinosad and Permethrin	Drosophila melanogaster was used to test agrochemical-loaded chitosan nanoparticles under various conditions.	(Sharma *et al.* 2019)
6.	Polyamide 6 Cellulose acetate	Nanofibers	Electrospinning was used to integrate pheromones in high concentrations..	(Hellmann, *et al.* 2011)
7.	Polyethylene glycol	Essential oil (peppermint and palmarosa)	Essential oils have increased their lethal and sub-fatal effects in BlatellagermanicaL.	(Pascoli *et al.* 2020)
8.	Chitosan/ Cashew gum	*Lippiasidoides*	Nanogel loaded with *Lippiasidoides* oil	(Abreu *et al*. 2012)

have been identified. Surface-eroding polymers are frequently water soluble, preventing water from reaching the polymer's important component and breakdown instantly at the polymer/water interface via hydrolysis. As a result of the degradation of the polymer, the AI is launched more frequently on the floor. If the AI is carefully released at a place in the matrix, the best launch charge will appear at first, and as days' pass, both the spheres' floor vicinity and the launch cost will reduce.

In contrast to floor-eroding polymers, bulk-eroding polymers drain moisture into the matrix and are typically characterized by a burst of AI launching, followed by a sluggish, continual, diffusion-managed launch. A 0.33 degree should arise as a result of the extreme disintegration of the polymer matrix, where the final AI is unleashed. Rapid desorption and diffusion from the floor can also produce an increase in AI release if the AIs aren't evenly distributed throughout the polymer matrix. This negative effect was caused by a type of Nano pesticides, encouraging the development of alternatives (*e.g.,* nanogels or nanofibers).

Conclusion

Although the beneficial effects of nanotechnology on agricultural crops are well known, the potential toxicological, environmental, and food safety impacts of Nano-pesticides have received little attention. Short-term and long-term agrochemical adverse events resulting from occupational or accidental ingestion of pesticide residues from food, water and air are fatal due to permanent tissue and organ damage. The focus should be on the interaction of nanoparticle systems with plants and the environment, emphasizing a maximal reduction in bioavailability, retention time, bioaccumulation levels, biodegradation time, waste toxicity, leaching and drift. Experimental research to solve the inconvenience will develop technology-based pesticides using various materials and techniques, transforming agricultural production, ensuring ecosystem and food safety, and ensuring the surface of nanocarriers. We need to produce Nano-pesticides with release systems controlled by stimuli-responsive compounds. The increase in regulations mentioned above indicates the increasing importance of nanotechnology in agriculture. The development of agro-nanotechnology and biotechnology could be a stepping stone to revolutionize agriculture in order to feed a rapidly growing world population and improve living conditions in developing countries.

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