A Review on Nanotechnological approaches for the management of stored insect-pests: present scenario and future prospects

ABSTRACT

Approximately 10% to 30% of the stored agricultural produce is damaged out of which 26% is due to insect-pest infestation thus seriously impacting the food security. The infestation also leads to loss of quality and thereby affecting the overall profitability. In absence of enough storage space, usually farmers dispose-off their produce immediately after harvest and thus do not get remunerative prices. For thoseopting for storage, physical and chemical methods are in vogue to manage the storage insect-pests. Fumigation with chemical pesticides such as methyl bromide and aluminium phosphide is a common method, though it has its own health and environmental risks.Inhalation of phosphine gas released when aluminium phosphide is used could seriously affect human animal health, sometimes leading to deaths. Thus for using these fumigants, strict supervision of government recognized experts is required. Due to their wide usage, some insect-pests have developed resistance against these molecules.Nanotechnology has created numerous new opportunities in agriculture and allied sectors.Insecticide formulations based on nanotechnology could be a viable alternative to toxic chemicals like aluminium phosphide to manage storage insect-pests. In recent years, a variety of formulations including solid nanopesticides, controlled-release formulations, nano-emulsions, and nano-suspensions have been developed possessing different modes of actions and applications. Their small size is a significant advantage because it provides higher insect-body surface area coverage and thus enhanced efficacy as compared to traditional pesticides. Aside from their small size, they are reported to be safe for non-target beneficial organisms. Nano-pesticides can thus prove as effective and eco-friendlyalternatives for insect pest control in storage. However, there is a need to establish their safety on the human and animal ecosystems to rule out their ecological hazards over time. In absence of such information, nanopesticides will not be widely accepted despite their other beneficial effects. In this article, an effort is made to review the current status of nano-formulations for the management of storage-insect-pests, the research and extension gaps and ways to bridge the gaps to ensure safe use of the technology for efficient management of postharvest storage losses.

Keywords: Nanotechnology, storage, insect control, Nano-pesticides, formulation

1 INTRODUCTION

Friedrich (2015) predicted a 70% increase in global food production by 2050, despite a projected population rise to 9.2 billion. Though, India has attained self-sustainability in food production and meeting the current demands, regional inequality, food insecurity and malnutrition problems continue to exist. Rising average household income levels have led to diversification of diets leading to increased consumption of dairy and horticultural produce as compared to cereals. Gradual increase in total factor productivity of Indian agriculture is due to adoption of new technologies (Beintema et al., 2012). Alexandros and Bruinsma (2012) projected about 3.7% of arable land by 2050. However, considering the projected population of 1.6 billion by 2050, climate change impacts and water scarcity, Indian agricultural production has to double from current levels (Srinivasarao, 2021). The challenge is further compounded as the large segment of farming community constitute small and marginal land holders.The key to achieving high-quality crop production lies in implementing sustainable, abundant, safe, and innovative production and logistics technologies. Various cultivation methods prove extremely beneficial in growing the crops in areas where they would otherwise fail. Plant-specific protection measures, such as pesticide and herbicide-tolerant varieties and nutritionally enhanced traits, play a crucial role in adapting bio-intensive crop health management strategies (Friedrich, 2015).

The term "Nano" derived from the Greek word for "dwarf" denotes small, specifically one billionth of a unit (10^{-9}). According to Bhattacharyya et al. (2010) nanotechnology involves particles with sizes ranging from 1 to 100 nanometers (nm). Over the last decade, nanotechnology has yielded innovative materials in agriculture, engineering, medicine, environmental science, food processing, biotechnology, and analytical chemistry. These materials have been employed in creating sensors, medical devices, catalytic agents, pesticide coatings, conductors, and semiconductors (Jordan, 2010). Nanomaterials hold promise in mitigating the destructive effects of insect-pests on crops (Khot et al., 2012). Despite its potential, the application of nanotechnology in protecting crops against insect-pests is still in its infancy (Resham et al., 2015). Not only the conventional agricultural systems but thesteady shift from synthetic chemical-based agriculture to organic agriculture gain could hugely benefit from nanoparticle-impregnated bio-pesticides. These bio-pesticides effectively suppress pest populations, contributing to a more sustainable agricultural approach (Bhattacharyya et al., 2010; De et al., 2014). Various plants, including *Azadirachta indica, Chrysanthemum cinerariifolium, Tanacetum cinerariifolium, Asimina triloba, Annona* *muricata, Annona squamosa*, and *Pyrethrum cinerariifolium*, have the potential to produce a range of nanoparticles (Shahid et al. 2021).

Conventional pest management techniques are now inadequate, necessitating the development of new innovative approaches. Nanotechnology emerges as a promising tool, offering solutions to challenges like environmental contamination, pest resistance, bioaccumulation, and health hazards. Nanopesticides, which reduce pesticide use, leverage nanotechnology's potential to enhance efficacy, stabilize active ingredients, and conserve agricultural inputs (Jasrotia et al., 2018; Rikta and Rajiv, 2021). These novel formulations are expected to be target-specific, cost-effective, stable, and adaptable to different environments, with a unique mode of action (Smith et al., 2008; Singh et al., 2021). Although laboratory studies on nanomaterial efficacy abound, large-scale application for postharvest insect pest management is yet to be fully explored (Hamel et al., 2020). This chapter aims to explore the potential of nanoparticles in storage insect-pest management and also overcome environmental and toxicological risks due to the use of conventional pesticides.

2 MAJOR STORED GRAIN INSECT-PESTS AND THEIR DAMAGE

Technological advancements in agriculture have resulted in a consistent annual increase in food production. In numerous countries, a significant portion of harvested food grains is allocated for contingency and regular supply. Prolonged storage of these commodities makes them vulnerable to contamination and harm caused by both biotic and abiotic factors. Biotic agents such as insects, mites, rodents, birds, and microorganisms contribute significantly to storage losses. In particular, insects emerge as the primary culprits, accounting for an average of 10-20 percent of storage losses (Phillips and Throne, 2010). In the broader context, stored agricultural and animal products face threats from over 600 species of coleopterans, 70 species of lepidopterans, and approximately 355 species of mites. The consequences of these infestations manifest as both quantitative and qualitative losses (Rajendran and Sriranjini, 2008).

Based on the severity of damage in a particular region, pests can be categorized as major or minor. Additionally, their feeding preferences can be distinguished as either superficial or boring. The primary classification of storage insects revolves around their feeding habits, specifically as "primary pests" and "secondary pests" (Srivastava and Subramanian, 2016). Primary pests predominantly infest and damage entire, undamaged grains, posing a significant threat to grain lots. If left unnoticed until their population is established, they can cause severe damage that is challenging to control. Therefore, vigilant surveillance is essential to prevent their infestation and subsequent damage. In contrast, secondary feeders or pests are commonly referred to as "bran bugs." They thrive on grains that have already been damaged, either by primary pests or other miscellaneous factors (Bell, 2014). These pests subsist on broken kernels, debris, or weed seeds with higher moisture content. Identifying damage caused by secondary feeders is relatively straightforward, as their life stages are visible in the commodity area. Some of these secondary pests are also known to be mold or fungal feeders, contaminating grains through their presence and metabolic wastes. This contamination can lead to moisture-laden conditions, including excretion and condensed heat, fostering mold development (Magan et al., 2003).

Table 1. List of major insect pests that infest stored products (Guru et al. 2022)

Sl. No.	Scientific name	Host range	Distribution range (in India
1.	Sitophilus oryzae (L.)	Cereal grains and other processed foods	Tropical and temperate regions of India; the least cold-tolerant of all grain weevils.
2.	Rhyzoperthadominica (F.)	Cereal grains and groundnut	India-wide, particularly in warmer regions.
3.	Callosobruchus chinensis (L.)	Pulses	India-wide
4.	Callosobruchus maculates (F.)		
5.	Oryzaephilus surinamenis (L.)	Vegetables, grain or grain product.	This pest is widely found in India and affects grains, grain products, chocolate, drugs, and tobacco.
6.	Triboliumcastaneum (Herbst)	Cereals, flour, starch, fruit nuts, millets, and prepared foods	This pest is widely distributed throughout India and can infest any stored commodities. T. castaneum thrives in warm climates and migrates during the winter season. C. confusum grows in cooler climates.
7.	Triboliumconfusum (Jacquelin du Val)		
8.	Latheticus oryzae Waterhouse	Wheat, rice, maize, barley, rye and cereal products	India-wide occurrence in warm climates.
9.	Trogoderma granarium Everts	Crops include wheat, jowar, rice, maize, sorghum, oilseeds, pulses and a diverse range of stored and packaged products.	Tropical/subtropical insects are typically found in hot and dry regions. It prefers low humidity and high temperatures.

10.	Lasiodermaserrzcorne (F.)	Spices, chocolate, cocoa and tobacco leaves	Cosmopolitan but prefers a warm environment. Insects are active year-round in warm dwellings in temperate and subtropical regions, with slower development during winter.
11.	Stegobiumpaniceum (L.)	Serious pest of tobacco	Damage is more prevalent in temperate regions than tropical areas across India.
12.	Caryedon serratus (Olivier)	Groundnut, Tamarind, Acacia,Cassia, Prosopis seeds.	Tropical areas of across India.
13.	Cylas formicarius (F.)	Sweet potatoes in field andstorage	The occurrence is widespread throughout India, primarily in tropical regions.
14.	Sitotrogacerealella (Olivier)	Maize, paddy, sorghum etc.,	India-wide, more abundant inwarmer regions.
15.	Corcyra cephalonica (Stainton)	Paddy, rice, other cereals, millets, soybeans, oilseeds, flour, and dried fruits are kept in storage	It is widely distributed throughout India's rice-growing areas. Preferably warm climate.
16.	Plodia interpunctella (Hubner)	Stored grains, pulses, dried fruits, nuts, dried vegetables andprocessed foods	India-wide
17.	Cadracautella (Walker)	Fig, rough rice, dry fruits, wheat, barley, sorghum,soybean, and oilseeds etc.	Widely distributed in the tropics and subtropics, warmer and more humid climates of India.
18.	Ephestiaeulutella (Hübner)	Cocoa beans, tobacco, cereals, dried fruit & nuts, museum specimen and animalproducts.	Temperate species similar to P.interpunctella but populationincrease at 15˚C.
19.	Ephestiakuehniella (Zeller)	Cereal grains and flour	Found throughout the India.

In the realm of stored grains, a vast majority of insect-pestsbelonging to the orders Coleoptera, Lepidoptera, and mites, cause quantitative and qualitative losses (Table 1). These pests are classified as either primary or secondary based on their nature of damage. While primary pests infest sound or whole grains, secondary pests affect broken or already damaged grains. Various control methods, such as physical, mechanical, chemical, and biological practices, exist, but fumigation remains as a viable option due to its versatility under different storage conditions (Nguyen et al., 2015; Nayak et al., 2020). However, synthetic pesticides have been known to pose challenges due to their cost, ineffectiveness, and environmental and health hazards (Jallow et al., 2017; Poudel et al., 2020).Aluminium phosphide (AlP) emerges as a crucial fumigant for stored grain pest management, protecting bulk commodities effectively. The phosphine gas released by AlP easily penetrates grain bulks and dissipates through aeration, leaving no residues. Limited alternatives, such as methyl bromide and sulfuryl fluoride, exist, but concerns about fluoride residues have curtailed routine fumigation in developed countries (Bell, 2000; Oguntade, 2021). Insecticide resistance poses a global threat, with pests like the red flour beetle (*Triboliumcastaneum*), rice weevil (*Sitophilusoryzae*), and lesser grain borer (*Rhyzoperthadominica*) showing resistance to phosphine and other fumigants(Attia et. al. 2020).

3 NANO-BASED PEST MANAGEMENT: A NOVEL STRATEGY

Nanotechnology has been suggested for application across diverse sectors, encompassing biomass, food, nutrition, paint, sensing technology, paper, fertilizer, plant protection, and agrochemical industries. Nano-formulations of pesticides, incorporating nanoparticles like ZnO, Cu, Ag, and SiO_2, demonstrate a broad spectrum of effectiveness, lower water consumption, and diminished environmental impact compared to traditional insecticides. Zinc, an essential nutrient, not only fosters plant growth and development but also exhibits harmful effects on insect-pests. Silver, with its versatile potential, finds applications in medicine, living organisms, pest control, and plant management. Its efficacy against various agents, such as microbial, fungal, larvicidal, pesticidal, antibacterial, and antiviral, has been demonstrated through environmentally friendly methods. ZnO nanoparticles have been tested for their antifungal activity against the plant disease *Fusarium graminearum*, and the stability, smaller size, and eco-friendly byproducts of metal nanoparticles further enhance their appeal. Overall, nanoformulations emerge as a highly effective solution for combating insect infestations (Table 2).

Table 2: List of experimentally successful Nano-insecticide formulations for storage pest(Manna et al. 2023).

Bioactive component/Active ingredient	Formulation type	Target insect
β-cyfluthrin	NM	*Callosobruchusmaculatus*
SiO2 NP	M-NP	*Sitophilus oryzae, Rhizoperthadominica* *Triboliumcastaneum, Orizaephilussurinamenisis*
Ag-NP	M-NP	*Sitophilus granaries, Sitophilus oryzae* *Triboliumcastaneum, Callosobruchus maculatus* *Triboliumcastaneum*

Al2O3-NP	M-NP	*Sitophilus oryzae, Sitophilus zeamais*
ZnO-NP	M-NP	*Rhyzoperthadominica*
Bacillus thuringiensis	HNM	*Callosobruchus maculatus*
Chitosan NP	NS/NN	*Callosobruchus maculatus* *Callosobruchus maculatus*
Garlic essential oil	NN	*Triboliumcastaneum*
Mentha longifolia essential oils	NN	*Ephestiakuehniella*
Neem oil	NN	*Ephestiakuehniella,Sitophilus granaries Triboliumconfusum*
*Rosmarinus officinalis*essential oils	NE	*Triboliumcastaneum*
Carum copticum oil	NG	*Sitophilus granarius andTriboliumconfusum*
Cumin essential oil	NE/NG	*Sitophilus granarius andTriboliumconfusum*
Plantago major seed extract	NE	*Triboliumcastaneum*

Abbreviations:- HNM: Hybrid nano metal; NE: Nano encapsulation; NG: Nano gel; NM: Nano micelle; NN: Nano emulsion; NS: Nano suspension; SLN: Solid lipid nanoparticle; M-NP: Metal nanoparticle.

3.1 Silver nanoparticles

Silver nanoparticles (AgNPs) stand out as highly researched and effective nanomaterials in the realm of insect pest management. Employed as carriers for agrochemicals, nanoparticles enable targeted delivery to specific sites(Gour et al. 2019). These compounds boast potent insecticidal, bactericidal, antifungal, and antiviral effects, showcasing significant potential against insect-pests. Additionally, they exhibit catalytic characteristics, antibacterial activity, enhanced chemical stability, and electrical conductivity, attracting increased interest from scientists in pest management research. Silver-based pesticide formulations, leveraging nanostructures, deliver elevated doses of active chemicals to target species compared to conventional pesticides. Importantly, these nanoformulations exhibit no toxicity to non-target organisms, ensuring their environmental safety. Notably, studies have demonstrated the successful inhibition of S. oryzae by silver nanoparticles. Plant-mediated green silver nanoparticles derived from Euphorbia prostrata and Avicennia marina have proven effective against S. oryzae, T. castaneum, and R. dominica. In one instance, the application of 1.00 g of silver nanoparticles per kg of seed resulted in an 83% mortality rate for adults and larvae of Callosobruchus maculatus. Biogenic silver and gold nanoparticles, extracted from Daphne mucronata and Monothecabuxifolia, respectively, have shown 100% effectiveness against T. castaneum, R. dominica, and Callosobruchusanalis. Silver nanoparticles, produced from silver nitrate and Moringa oleifera leaf extract, achieved 100% mortality against S. oryzae after a 15-day exposure period. Furthermore, silver nanoparticles derived from Azadirachta indica leaf extracts reduced egg production of T. castaneum and C. maculatus, and treating peach tree leaves with AgNPs and ZnNPs resulted in 100% mortality of rice weevil (S. oryzea) and lesser grain borer (R. dominica) through fumigation(Jasrotia et. al. 2022).

3.2 Aluminum Oxide Nanoparticles

Nanostructured alumina (NSA) dust or aluminum nanoparticles have demonstrated efficacy in safeguarding grains against infestation by stored insect-pests(Stadler et al. 2017). The pesticidal effectiveness of nanoalumina surpasses that of diatomaceous earth (DE) formulations when combating S. *oryzae*. Sabbour (2012) devised two entomotoxins utilizing Al_2O_3 and TiO_2 nanoparticles to combat S. *oryzae*. Notably, nano TiO_2 exhibited lower efficiency against S. *oryzae* compared to the aluminum-based toxin. Various sizes and morphologies of nanoalumina dust were tested against S. *oryzae* and R. *dominica*, with the highest mortality rate observed. However, it was discerned that the reduction in particle size and increase in surface area are not the sole determinants influencing pesticide efficiency. Application of nanoaluminum oxide at a rate of 2 g kg^{-}1 rice resulted in 100% mortality against rice weevils after 14 days, while utilizing nanostructured alumina dust (NSA) in 400 ml galvanized steel jars on S. *oryzae* yielded effective mortality rates. The use of aluminum oxide nanoparticles at a dosage of 1 g kg^{-}1 effectively eliminated 90% of S. *oryzae* within 4 days. Application of 400 mg kg^{-}1 to S. *paniceum* resulted in 100% insect mortality, followed by 80.64% for O. *surinamensis* and 79.41% for T. *confusum*. In wheat, aluminum oxide nanoparticles induced 100% mortality at a concentration of 8,000 mg/kg after 7 days of exposure. Over a span of 60 days, all tested Al_2O_3-NPs concentrations (1,000, 2,000, 4,000, and 8,000 mg/kg grain) significantly reduced S. *oryzae* offspring in a dose-dependent manner (Ismail et al., 2021).

3.3 Titanium Dioxide Nanoparticles

Nanoparticles display minimal toxicity and limited unintended biological effects. Skocaj et al. (2011) observed that their efficiency is influenced by chemical and physical factors, including size, crystal structure, and photo-activation. The utilization of titanium dioxide formulations in storage helps mitigate the ecological impact on non-target species. Abo-Arab et al. (2014) reported that titanium dioxide nanoparticles, administered at a dose of 1 g kg^{-}1 over 21 days, eliminated 61.66% of S. *oryzae* and 60.66% of S. *zeamais*. Furthermore, a dosage of 2 g kg^{-}1 effectively eradicated 90% of S. *oryzae* within 14 days. In Egypt, under laboratory and storage conditions, the toxicity of TiO_2 and Al_2O_3 nanoparticles against S. *oryzae* was investigated. Nano Al_2O_3 demonstrated greater efficacy than nano TiO_2. Elevated concentrations of TiO_2 nanoparticles resulted in increased cumulative mortality of T. *castaneum* at 1, 3, and 5 days of exposure, with percentages of 15.30, 23.57, and 29.85, respectively.

3.4 Zinc Oxide Nanoparticles

The effectiveness of zinc oxide nanoparticles as insecticides stems from their antibacterial, physical, and optical characteristics. Various synthesis methods, such as vapor transfer and hydrothermal precipitation, can be employed to create these nanoparticles. There is a growing trend towards utilizing plant extracts in the production of ZnONPs, driven by their safety and environmental advantages. Zinc oxide-based nanoformulations exhibit notable efficacy in suppressing S. *oryzae* and T. *castaneum*, resulting in higher mortality rates for these pests(Salem et al. 2015). Nonetheless, when compared to silver, aluminum oxide, and titanium dioxide, zinc oxide nanoparticles demonstrate reduced success in controlling storage pests. In a study conducted by Das et al. (2019), aluminum oxide, titanium dioxide, and zinc oxide nanoparticles were evaluated against S. *oryzae*. Nanoaluminium oxide achieved a 90% mortality rate at 1 g kg^{-}1 within 4 days, whereas nanozinc oxide and titanium dioxide reached the same level at 2 g kg^{-}1 after 14 days. This discrepancy elucidates the relatively lower efficacy of zinc oxide nanoparticles in managing storage pests. Despite this limitation, the inherent antibacterial properties of zinc oxide make it a viable option for agricultural pest control.Similarly Gindaba et al. (2023) reported that using leaf extract to synthesize nanoparticles is an eco-friendly method. Their study investigated the synthesis of zinc oxide nanoparticles (ZnO NPs) from the leaf extract of *Clausenaanisata*Hook.f. ex Benth., using zinc nitrate hexahydrate (Zn(NO3)2·6H2O) as the zinc source. Characterization of the nanoparticles was conducted using ultraviolet-visible (UV-Vis) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). XRD revealed the crystalline structure of the nanoparticles, while SEM confirmed their morphology, allowing for predictions about the size of the ZnO NPs. These nanoparticles were tested for efficacy against *Sitophilus zeamais* adults, with mortality assessments conducted over 14 days. All three dosages (0.2 g, 0.4 g, and 0.6 g) effectively killed *S. zeamais*, and there was a significant reduction in the emergence of F1 progeny compared to the untreated control. Additionally, maize seeds treated with ZnO NPs successfully germinated.

3.5 Copper Nanoparticles and Iron Oxide Nanoparticles

The combination of iron oxide nanoparticles and aqueous extract from *Anthocephalouscadamba* demonstrates complete effectiveness, resulting in 100% mortality against S. *granaries*. Additionally, biotransformedCuNPs containing *Pseudomonas fluorescens* MAL2, a strain akin to *Pseudomonas fluorescens* DSM 12442T, effectively counter T. *castaneum*. CuO-NPs, derived from *Aspergillus niger* strain (G3-1), exhibit mortality rates of 55-94.4% and 70-90% against S. *granaries* and R. *dominica*, respectively, as reported by Badawy et al. in 2021.A mixture of iron oxide nanoparticles and the aqueous extract of *Anthocephalus cadamba* demonstrates 100% mortality against *S. granarius* (Sivapriya et al. 2018).

3.6 Silicon Dioxide Nanoparticles

Silica nanoparticles exhibit thermal stability, low toxicity, and compatibility with various molecules and polymers. In a study by Rastogi et al. (2019), mesoporous nanocarriers made of silica were identified as effective transporters for a range of agrochemicals. The precise manipulation facilitated by silica's shape, size, porosity, and crystallinity makes it versatile. These nanocarriers have demonstrated effectiveness in delivering biopesticides, pheromones, fungicides, and growth promoters. Aluminosilicate nanotubes have the ability to attach to plant surfaces and insect hair, enabling entry into the body and influencing its functions. A nanoformulation based on silica proved successful in controlling the red flour beetle T. *castaneum*. Additionally, SiO_2 resulted in 100% mortality of the cowpea weevil C. *maculatus*at a rate of 2.06 g kg^{-}1. Chlorpyrifos-loaded silica nanoparticles (Ch-SNPs) effectively controlled R. *dominica* and T. *confusum*, with mortality rates increasing at higher concentrations. Furthermore, nano-SiO_2–based nanoparticles derived from *Alstoniascholaris* exhibited higher toxicity, with an LC_{50} of 0.8 mg/ml and LC_{95} of 1.95 mg/ml against R. *dominica*. Silver nanoparticles, when combined with *Ricinus communis* oil, demonstrated 67.89% repellency at a 15% concentration and 28.31% repellency with Citrus paradise oil against T. *castaneum*. Insect-proof nets coated with silica nanoparticles completely eliminated S. *oryzae*. Nanosilica (30 nm) at a concentration of 0.5 g per kg of rice resulted in mortality rates of 80% and 97.4% against S. *oryzae* after 7 and 14 days, respectively. The addition of nanosilica from sugarcane bagasse ash (SCBA) to diatomaceous earth (DE) enhanced its insecticidal activity, leading to over 86% and 95% adult mortality for T. *confusum* and R. *dominica*, respectively, after 14 days of exposure (Saed et al., 2021).

3.7 Nanoemulsions

Numerous nanoemulsions have undergone testing for the management of stored grain pests. The utilization of nanoemulsion formulations has proven to enhance the efficacy of botanical insecticides for commercial applications, specifically targeting particular insects. The addition of adjuvants and surfactants has been shown to augment the efficiency of these formulations. Their cost-effectiveness stems from high water solubility and the ability to readily dissolve hydrophilic and lipophilic compounds, necessitating fewer active ingredients and inert materials. Moreover, these formulations exhibit substantial storage stability over a broad temperature range (-10 to 55℃). Recent research has indicated a potential issue of habituation when employing essential oil nanoformulations against storage pests. A study evaluating nanoemulsions of fennel (*Foeniculum vulgare*), mint (Mentha x piperita), and sweet orange (*Citrus sinensis*) essential oils against R. *dominica* discovered habituation in the instances of M. *piperita* and C. *sinensis* (Giunti et al., 2021). Among the tested formulations, cold aerosol and gel nanoemulsions derived from *Allium sativum* oil exhibited the highest toxicity, while nanoemulsions formulated with *Pimpinella anisum* were found to be the most effective repellent against T. *confusum*. Notably, exposure to a nanoemulsion containing *Achillea biebersteinii* essential oil at 10 µL/L air resulted in the complete elimination of the second larvae of T. *castaneum* after a 4-day period (Almadiy, 2021).

3.8 Polymer-based nanoformulations

Formulations employing polymers for the controlled release of insecticides, herbicides, and fungicides are under development as part of pest management programs aimed at safeguarding light-sensitive active ingredients. These polymer-based delivery systems disperse active components in aqueous environments, establishing a protective reservoir that facilitates controlled release. The gradual release of these active ingredients is contingent upon the degradation characteristics of the nanocarrier, the bonding between the carrier and active ingredients, and prevailing weather conditions. Recent advancements in polymer nanoformulations encompass various structures such as nanocapsules, nanospheres, nanogels, micelles, nanofibers, and formulations based on chitosan. The widespread use of polymeric nanomaterials for encapsulating active ingredients is driven by their environmentally friendly and biodegradable properties. These polymers play a crucial role in safeguarding and stabilizing active ingredients, including essential oils and plant secondary metabolites that may otherwise be susceptible to degradation or evaporation when exposed to light, water, air, or elevated temperatures. Among the essential properties of a polymer, biodegradability currently holds paramount importance. Nanotechnology has demonstrated its ability to enhance the efficacy of essential oils in controlling storage pests, addressing challenges that were previously insurmountable. In a study by Jesser et al. (2020), the insecticidal properties of essential oil-loaded polymeric nanoparticles (EOPN) were investigated, considering post-application temperature. Palmorosa exhibited exceptional effectiveness in contact toxicity bioassays and demonstrated efficacy in fumigant bioassays, especially when combined with peppermint oil. Importantly, no significant impact of environmental variations was observed. Utilizing polyamidoamine dendrimer-coated carbon nanotubes (PAMAM-CNT-dsRNA) for delivering dsRNA has proven to enhance RNA interference in T. *castaneum*, contributing to increased gene knockdown in red flour beetles. Ikawati et al. (2021) reported a high mortality rate against T. *castaneum* using polyethylene glycol nanoparticles loaded with clove essential oil (*Syzygium aromaticum*). These findings highlight the promising potential of polymer-based formulations in advancing effective and environmentally sustainable pest control strategies.

3.9 Chitosan-Based Formulations

Chitosan, a bioactive polymer obtained through the deacetylation process of chitin, a prevalent natural polysaccharide, has been the subject of limited research regarding its efficacy against storage insect-pests. A nanogel incorporating Myristic acid-chitosan (MA chitosan) and *Carum copticum* (L.) essential oil (EO) demonstrated effectiveness in combatting S. *granarius* and T. *confusum*. The toxic impact increased over time, and chitosan nanoparticles, when infused with peppermint oil (PO), exhibited high toxicity against S. *oryzae*. In a study by Upadhyay et al. (2019), the nanoencapsulation of *Melissa officinalis* essential oil in a chitosan matrix amplified fumigant activity (LC_{50} ~ 0.048 µL/ml air) and antifeedant activity (EC_{50} ~ 0.043 µL/ml) against T. *castaneum*. Furthermore, essential oil nanoparticles derived from R. *officinalis* and *Zataria multiflora*, encapsulated in chitosan and polycaprolactone, proved effective in controlling the confused flour beetle.

3.10 Nanocapsules

A week-long application of a nanoencapsulated formulation containing polymerized C. *cyminum* oil/water emulsion on rust-red flour beetles produced an LC_{50} value of 16.25 ppm, surpassing the efficacy of the oil alone. The nanocapsules with R. *officinalis* essential oil demonstrated effectiveness against T. *castaneum*. *Albizia procera* cysteine protease nanocapsules (ApCP) at concentrations of 7.0 and 3.5 mg/g achieved complete eradication of *Sitotrogacerealella*. In a study by Emamjomeh et al. (2021), nanoencapsulated essential oils of *Eucalyptus globulus* and Z. *multiflora* proved to be successful in controlling E. *kuehniella*. Nanoparticles containing *Artemisia haussknechtii* essential oil induced 100% mortality at 166 ppm, and nanoencapsulated*Cuminum cyminum* essential oil, in combination with reduced phosphine, effectively managed 50% of S. *granarius* and T. *castaneum* populations at concentrations of 42.51 and 78.99 µL/L, respectively. Additionally, *Lavendula angustifolia* demonstrated comparable efficacy to cumin oil.

4 MODE OF ACTION OF NANOPESTICIDES

Nanoparticles have garnered attention as innovative pesticides owing to their varied synthesis methods. While numerous studies have investigated their toxicity against insect-pests, information regarding their mode of action remains limited. Research on the toxicokinetics and toxicodynamics of nanopesticides against storage grain insect-pests is scarce due to their novelty and insufficient exploration. Toxicokinetics encompasses the movement of insecticides within an organism, involving processes like absorption, distribution, metabolism, and excretion. On the other hand, toxicodynamics focuses on the physiological, biochemical, and molecular effects of compounds and their underlying mechanisms. Silica, alumina, silver, and graphene oxide nanoparticle-based nanopesticides have been subjects of several studies exploring their efficacy against insects.

Silver nanopesticides have been observed to diminish acetylcholinesterase activity, inducing oxidative stress and cell death by impeding antioxidants and detoxifying enzymes. Research by Nair and Choi (2011) indicates that these chemicals can hinder protein synthesis and gonadotropin release, leading to developmental damage and reproductive failure through the up- or downregulation of key insect genes. Metal nanoparticles interact with sulfur (S) and phosphorus (P) in proteins and nucleic acids, decreasing membrane permeability. This, in turn, results in organelle and enzyme denaturation, ultimately causing cell death. Gold nanoparticles exhibit impacts on development, reproduction, and trypsin inhibition.

Nanopesticides such as aluminum oxide and silicon dioxide bind to insect cuticles, inducing dehydration through physicosorption of wax and lipids. According to Ibrahim and Salem (2019), a nanozeolite formulation attached to the body of T. *confusum*, leading to scratching and splitting of the cuticle, ultimately causing dehydration and insect mortality. In the case of nanostructured alumina, a study on its toxicity mechanism against S. *oryzae* revealed that charged nanostructured alumina adhered to the beetle cuticle through triboelectric forces, inducing dehydration by absorbing the wax layer via surface area phenomena.

5 ADVANTAGES OF NANOFORMULATIONS

The nanotechnology-based technologies such as nanofertilizers, nanopesticides, nanosensors, and nanoformulations have significantly transformed traditional agricultural systems. Nanoformulations, including nanoemulsions, nanosuspensions, and nanoparticulates, prove to be effective for safeguarding crops against insect-pests both in the field and during storage. The utilization of nanotechnology has revolutionized the creation of highly efficient pest control formulations that exhibit low residual toxicity and environmental compatibility. These chemically modifiable particles boast a significant surface-to-volume ratio, enabling precise targeting of organisms. Various engineered forms of nanoparticles, such as capsules with robust physical shells resistant to environmental degradation, have been developed. Nanostructures provide prolonged protection, surpassing the durability of conventional pesticides. In contrast to traditional pesticide formulations, nanoformulations enhance the solubility of active ingredients that are insoluble or poorly soluble, facilitating controlled and targeted biocide release.The application of minimal amounts of active ingredients per unit area ensures sustained delivery and prolonged effectiveness over time (Singh et al., 2020). The reduction in required doses translates to lower application costs. Controlled release formulations remain inactive until the release of active ingredients(Shekhar et al. 2021).

The integration of botanicals with nanopesticides emerges as a highly effective strategy for eco-friendly insect-pest management. Furthermore, the use of botanicals for synthesizing nanoparticles holds promising advantages for agriculture. The production involves surfactants, polymers, and metal nanoparticles with nanoscale dimensions, leveraging the unique properties of nanomaterials suitable for diverse applications. The distribution of nanopesticides through plants, microbes, and their derivatives aligns with a sustainable and eco-friendly approach to insect-pest management. However, the environmental and ecological concerns due to usage of nanopesticides need to be addressed for their wider usage and exploit full potential(Karn et al., 2009).

6 CONCERNS ABOUT NANOFORMULATIONS

Nanopesticides are favored over traditional pesticides due to their reduced application rates and losses, leading to decreased environmental contamination. However, concerns arise regarding heightened toxicity and prolonged persistence. The potential evaporation of nanodroplets before reaching their intended target is linked to small droplet sizes. Comprehensive research is essential to comprehend the interactions between nanoformulations and microorganisms, plants, and animals across various trophic levels. Moreover, the environmental repercussions of pesticide nanoformulations on soil, groundwater, and non-target organisms remain uncertain. The release of active ingredients hinges on nanocarrier properties and their dispersion within the nanoformulation matrix, with nanoparticles posing a threat to non-target organisms if released gradually. While natural polymers, polysaccharides, and lipids are commonly employed as nanocarriers due to their easy degradation, limited attention has been given to non-biodegradable nanocarriers such as metals and metal oxides. Nanocarriers are typically engineered for controlled release, minimizing human exposure to nanoformulations (Gahukar and Das, 2020). In contrast, conventional formulations for pesticidal nanoformulations rely on toxic organic solvents, posing environmental risks. A comprehensive comparison between nanopesticides and their conventional counterparts is imperative for future research on the environmental hazards associated with nanopesticides, including life-cycle analysis. This analysis should encompass production, application, and incorporation of nanoformulations into the food chain, while also considering potential effects on agrosystem conditions that may impact the hazardous properties and risk characterization of nanomaterials. The widespread adoption of nanopesticides has sparked concerns about their toxicity and ecological impact, necessitating further research to address these issues. A focused effort on developing safer and more intelligent nanoformulations is crucial for sustainable agricultural practices.

Enhancing the efficacy of insecticides through nano-formulation is advantageous, although the safety of commercially available nanoparticles is not guaranteed. Thus, a thorough assessment of potential adverse effects stemming from nanoparticle use in agriculture is imperative. While nanomaterials can offer plants nutritional benefits and protection against pests, they also have the potential to induce stress in non-pest species and present ecological hazards. The emergence of "nanotoxicology" as a distinct field underscores the need to scrutinize the toxic effects of nanomaterials. Notably, the mobility of nanoparticles may elevate the risk they pose to living organisms compared to larger particles. Recent research by Paramo et al. (2020) highlights the detrimental impact that nanoparticles can have on nano-insecticides.

7 REGULATORY ASPECTS

Nanomaterials are increasingly employed across diverse sectors, particularly within advanced industries. Yet, it is imperative to evaluate the environmental repercussions of nanomaterials, including nanopesticides, prior to their introduction into the global market. Conducting a comprehensive assessment of their environmental risks, encompassing persistence, behavior, and fate, is crucial. Global regulatory and legislative bodies play a pivotal role in ensuring a thorough and effective risk assessment. The distinct size, surface area, and catalytic properties of nanoparticles necessitate additional testing to ascertain their toxicity levels. National and international regulatory bodies are committed to ensuring the safety of nanomaterials, although regulatory approaches for nanoproducts vary across regions such as Asia, Africa, and Oceania. In India, guidelines for evaluating nano-agricultural inputs and products classify nanomaterials as either nanofertilizers or nanopesticides. The Scientific Advisory Panel of the US Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) recommends evaluating pesticides containing nanometals or metal oxides for potential health and environmental risks prior to market release. In Europe, plant protection products (PPPs) are subject to Regulation (EC) No 1107/2009, mandating government authorization. European regulations also address nanomaterial residues in food through EC No. 396/2005, while the REACH Regulation (EC) No. 1907/2006 informs manufacturers and importers about associated risks. The Australian Pesticides and Veterinary Medicines Authority (APVMA) has instituted regulations governing the release of nanomaterials. To mitigate the ecotoxicity of nanopesticides, nations should standardize testing guidelines, enhance understanding of nanopesticide hazards and their degradation products, extend exposure periods for specific organisms, and identify nanopesticides meeting regulatory criteria.

8 CONCLUSION AND FUTURE DIRECTIONS

In spite of numerous endeavors, the challenge of ensuring food security persists due to limited resources and a growing population. Smart nanopesticides present advantages over traditional agrochemicals, such as reduced doses, enhanced solubility, and precise delivery of active ingredients, resulting in heightened eco-protection with diminished environmental impact. However, nanoparticles carry both merits and demerits, encompassing low selective toxicity, poor biodegradability, and the potential for pesticide resistance in non-target organisms if used imprudently. Several nanosystems are in early stages or under development, with scant data available on the environmental impact of nanoparticles on non-target organisms, contributing to a knowledge gap. As nanomaterials can exert adverse effects on the environment and non-target organisms, the imperative is to craft ecologically safer nanopesticides to alleviate these concerns. Further investigation is required to address precautions, potential food mutations induced by nanostructured materials (NSMs), nanoparticle toxicity in human cells, and overall environmental ramifications. Future strides in nanotechnology research should be directed towards formulating intelligent nanopesticides, advancing environmentally sustainable green nanopesticide chemistry, devising cost-effective and commercially viable nanopesticide production technologies, comparing the efficacy of nanoformulations with conventional counterparts in real-world settings, and evaluating ecotoxicity. The transformative potential of nanomaterials in revolutionizing crop protection practices from harmful to environmentally beneficial underscores the shift towards more cost-effective agriculture. This development enhances food longevity, storability, and security, ultimately leading to increased profits for both consumers and producers.

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