Nanomaterials for Postharvest Management of Insect Pests: Current State and Future Perspectives

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Globally, between one quarter and one-third of total grains produced each year are lost during storage mainly through infestation of insect pests. Among the available control options such as chemical and physical techniques, fumigation with aluminum phosphide (AlP) is so far considered the best control strategy against storage insect pests. However, these insect pests are now developing resistance against AlP due to its indiscriminate use due to non-availability of any effective alternative control option. Resistance to AlP among storage insect pests is increasing, and its inhalation has shown adverse effects on animals and human beings. Nanotechnology has opened up a wide range of opportunities in various fields such as agriculture (pesticides, fertilizers, etc.), pharmaceuticals, and electronics. One of the applications of nanotechnology is the usage of nanomaterial-based insecticide formulations for mitigating field and storage insect pests. Several formulations, namely, nanoemulsions, nanosuspensions, controlled release formulations, and solid-based nanopesticides, have been developed with different modes of action and application. The major advantage is their small size which helps in proper spreading on the pest surface, and thus, better action than conventional pesticides is achieved. Besides their minute size, these have no or reduced harmful effects on non-target species. Nanopesticides can therefore provide green and efficient alternatives for the management of insect pests of field and storage. However, an outcry against the utilization of nano-based pesticides is also revealed. It is considered by some that nano-insecticides may also have hazardous effects on humans as well as on the environment. Due to limited available data, nanopesticides have become a double-edged weapon. Therefore, nanomaterials need to be evaluated extensively for their large-scale adoption. In this article, we reviewed the nanoformulations that are developed and have proved effective against the insect pests under postharvest storage of grains.

Keywords: nanotechnology, storage, insect control, nanopesticides, formulation

1 INTRODUCTION

Grain crops that are most widely grown worldwide include cereals (maize, wheat, millets, rice, etc.) (Awika, 2011; Ye & Fan, 2021); pulses (mung, beans, chickpea, cowpea, black gram, green gram, etc.) (Sharma et al., 2010; Liu et al., 2020); and oilseeds (soybean, sunflower, linseed, groundnut, etc.) (Attia et al., 2021). These crops form a crucial component of our diet as they are rich in proteins,
carbohydrates, fats, vitamins, minerals, and oils (Sarwar et al., 2013; Oso & Ashafa, 2021). Due to the presence of these nutrient elements, the grains of these crops are prone to infestation by insect pests during storage. The marketability of the food grains is hampered when insect pests feed on grains and make them unfit for human consumption, leading to huge monetary losses (Sharon et al., 2014; Sharma et al., 2016; Wang et al., 2021). Losses due to insect infestation under storage can go up to 50 to 60% under extreme situations (Kumar et al., 2017; Luo et al., 2020). Sometimes, the postharvest losses can surpass the losses that crops suffer in the field (Mesterházy et al., 2020). Direct losses occur in the form of direct consumption of kernels, while indirect losses include formation of webbing, exuviae, frass, and insect cadavers that significantly hamper seed quality and leave grains unfit for human consumption (Kumar and Kalita, 2017; Mesterházy et al., 2020). Changes in the grain storage environment due to insect infestation result in the formation of warm and moist "hotspots" which further lead to the development of storage fungi. The presence of fungi in stored grain can further increase the level of crop losses (Shankar and Abrol, 2012; Fones et al., 2020).

Storage insect pest species inflicting quantitative and qualitative losses during postharvest storage of grains mainly belong to two insect orders: Coleoptera (around 600 species), Lepidoptera (70 species), and mites (about 355 species) (Rajendran, 2002; Rajendran and Sriranjini, 2008). Insect pests of stored grains are of two types, namely, primary and secondary pests (Bang et al., 2020). Primary pests are those that damage sound or whole grains, while secondary pests damage broken or already damaged grains. Primary pests are further categorized into internal and external feeders based on the place of their attack (Deshwal et al., 2020) (Supplementary Table S1, S2). Several insect control options are available such as physical, mechanical, chemical, and biological practices, but fumigation is considered the most common method of pest control due to its wider application under various storage conditions such as bags, silos, warehouses, and mills (Nguyen et al., 2015; Nayak et al., 2020). However, synthetic pesticides are there in the market for the control of storage pests but these pesticides are costly, ineffective, and are harmful to the environment as well as to human health (Jallow et al., 2017; Poudel et al., 2020).

Aluminum phosphide (AIP) is the key fumigant among all the fumigants available for stored grain pest management as it gives higher grain and stored products protection (Daglish et al., 2002; Collins et al., 2005; Shin et al., 2021). Commodities in bulk quantity can be effectively protected against insect infestation by the usage of AIP. The phosphine gas released by AIP penetrates the grain bulks readily and eliminates rapidly from the grain via aeration leaving no residues. Moreover, there are very limited alternative fumigants available, for instance, methyl bromide and sulfuryl fluoride (Gu, 2020). But, routine fumigation of grains has been discouraged in developed countries since 2005 owing to the concerns of potential fluoride residues (Scheffrahn et al., 1989; Bell, 2000; Oguntade, 2021). Therefore, only dependence on phosphine for fumigation due to non-availability of other effective alternatives has inevitably resulted in insect resistance problems in many storage insect pests (Bengston et al., 1996; Chaudhry, 2000; Mills, 2001; Collins et al., 2002; Daglish et al., 2002; Hasan and Reichmuth, 2004; Pimentel et al., 2007; Wakil et al., 2021). The resistance to phosphine and other fumigants is observed in majority of stored grain pests such as red flour beetle Tribolium castaneum, rice weevil Sitophilus oryzae, and lesser grain borer Rhizopertha dominica which poses a very serious threat to postharvest grain produce around the globe (Dyte and Halliday, 1985; Badmin, 1990; Bell, 2000; Chaudhry, 2000; Valmas et al., 2008; Newman, 2010; Ali et al., 2013; Holloway et al., 2016; Collins and Schlipalits, 2018; Attia et al., 2020; Nayak et al., 2020; Collins et al., 2017). Thereby, insecticide resistance has become an issue of international importance (Champ and Dyte, 1977; Benhalima et al., 2004; Collins et al., 2005; Wang et al., 2006; Sparks et al., 2021). Conventional techniques for pest management in storage are now inadequate and new innovative management techniques are to be developed.

Under the present scenario wherein agriculture today is facing major challenges of environmental contamination, pest resistance, bioaccumulation, and health hazards, nanotechnology is emanating as a highly attractive tool to achieve the target of lowering the quantity of pesticide used by offering new methods for the formulation and delivery of pesticide active ingredients, as well as novel active ingredients, collectively referred to as nanopesticides (Hayles et al., 2017; Shukla et al., 2019). The main advantage of nanopesticides usage is the reduction in the quantity of pesticide applied for a crop and or stored product protection. Nanotechnology deals with materials at the nanometer scale and is demonstrated to have a great potential in providing novel solutions to pest problems (Sasson et al., 2007; Kashyap et al., 2016; Unsworth et al., 2016; Kashyap et al., 2020). The use of nanotechnology will overcome the limitations associated with conventional pesticides by enhancing pesticide efficacy, improving stability of active ingredients, reducing the required pesticide dose, and conservation of agri inputs (Jasrotia et al., 2018; Rikta and Rajiv, 2021). However, new advanced nano-based formulations are expected to be target-specific, cost-effective, stable, and should have the ability to remain active under different application environments with a novel mode of action (Smith et al., 2008; Singh H et al., 2021). The concept of application of nanopesticides for storage pest management is new, and information related to their mode of action and application is lacking, which is hindering their usage under storage environment (Hischier et al., 2020; Kah et al., 2013; Kumar et al., 2018; Singh et al., 2020). However, many laboratory studies determining the efficacy of the nanomaterials have been conducted, but their large-scale application for postharvest management of insect pests is lacking (Hamel et al., 2020). Therefore, investigation of their behavior and ultimate fate in the environment is required that will aid in establishing a regulatory framework for their commercialization as well as will contribute to a sustainable grain protection (Nuruzzaman et al., 2016; Chhipa, 2017a; Bartolucci et al., 2020). This review documents the nanoformulations that have been evaluated for the management of storage insect pests until now and presents the research findings of laboratory studies and safety issues related to nanopesticides use. The article also
describes their advantages and limitations followed by conclusions and future perspectives.

2 ADVANTAGES OF NANOPESTICIDES

Pioneering nanotechnology has opened a new way for the development of nano-sized formulations that are highly effective for pest control with lesser residual toxicity and are environment-friendly (Yadav et al., 2021). These are chemically alterable particles consisting of a large surface-to-volume ratio, and their physical properties make them capable enough to target organisms (Madhuri et al., 2016; Mustafa & Hussein, 2020; Sahoo et al., 2021). Nanoparticles can be engineered in different forms, for example, a capsule acts as a physical shell and can better withstand degradation in the environment. Therefore, nanoparticles offer better long-lasting protection as compared to conventional pesticides (Sushil et al., 2021). Unlike conventional pesticide formulations, nanoformulations are specially designed to increase the solubility of insoluble or poorly soluble active ingredients and to release the biocide in a controlled and targeted manner (Margulis-Goshen & Magdassi, 2013; Ragaei & Sabry, 2014; Garg & Payasi, 2020). Therefore, a smaller amount of active ingredient per area is sufficient for application, and it can provide sustained delivery of active ingredients which may remain effective for extended periods (Singh et al., 2020). Thus, due to the reduced dose requirement, the cost of application is also reduced. Also, it is important for the controlled release formulations that they must remain inactive until the active ingredient is released (Shekhar et al., 2021).

The nanoscale application of agrochemicals in agriculture in the form of nanofertilizers, nanopesticides, nanosensors, and nanoformulations has changed the traditional agro-practices (Aouada and De Moura, 2015; Panpatte et al., 2016; Scott et al., 2018; Pirzadah et al., 2019; Singh R. P et al., 2021). In crop protection, different types of nanoformulations, such as nanoemulsion, nanosuspension, and nanoparticulate, are suggested to tackle the insect pests of field and storage (Islam, 2020; Kashyap et al., 2020; Yadav et al., 2021)). The amalgamation of botanicals with nanopesticides is one of the most powerful tools that provide eco-friendly control routes for insect pest control. Biological pesticides are already being used as an alternative to chemical pesticides (Qazi and Dar, 2020). On top of it, the synthesis of nanoparticles using botanicals has served many potential benefits to agriculture. Several surfactants, polymers, and metal nanoparticles in the nanometer size range are used in their production (Kah et al., 2013; Ragaei and Sabry, 2014; Shaban et al., 2020). These nanomaterials at the nanoscale exhibit some properties which are different from bulk materials, supporting their unique applications for different conditions (Elizabath et al., 2019; Mujtaba et al., 2020). Expansion of nanopesticides through plants, microbes, and their derivatives bring forth dominance of sustainable approach and environment-friendly control. Though nanopesticides have infinite potential, it is still a dream at the moment (Ditta, 2012; Aithal and Aithal, 2015) because of their environmental and ecological impacts (Scrinis and Lyons, 2007; Karn et al., 2009) (Figure 1).

3 MODE OF ACTION OF NANOPESTICIDES

Nanoparticles developed through various synthesis routes as novel pesticides have recently attracted high research attention. Various studies have been conducted to test their toxic potential against a wide number of insect pests; however, precise information on their mode of action against insects is lacking (Rai et al., 2014; Athanassiou et al., 2018). Only a few studies have been carried to study the toxicokinetics or toxicodynamics of nanopesticides against storage grain insect pests as these are relatively new materials and have not been studied in great detail. Toxicokinetics basically refers to the movement and changes an insecticide undergoes inside an organism: absorption, distribution, metabolism, and excretion, while toxicodynamics refers to the physiological, biochemical, and molecular effects of the compounds and the mechanisms in which they are involved (Alzogaray & Zerba, 2017). The mode of action of silica-, alumina-, silver-, and graphene oxide nanoparticle–based nanopesticides against insects has been studied in a few studies (Benelli, 2018). Silver nanopesticides decrease acetylcholinesterase activity leading to oxidative stress and cell death by affecting antioxidants and detoxifying enzymes. These are also reported to reduce protein synthesis and gonadotropin release, leading to developmental damages and reproductory failure by either up- or downregulating key insect genes (Nair and Choi, 2011). Metal nanoparticules reduce membrane permeability by binding to S and P in proteins and nucleic acids, respectively, leading to organelle and enzyme denaturation, followed by cell death. Gold nanoparticles can affect development and reproduction and also act as trypsin inhibitors (Patil et al., 2016; Small et al., 2016). Aluminum oxide and silicon dioxide nanopesticides act by binding to the insect cuticle, followed by physico-sorption of waxes and lipids, leading to insect dehydration (Debnath et al., 2011; Arumugam et al., 2016). Nanozeolite formulation acted by attaching itself to the body of T. confusum and then caused scratching and splitting of the cuticle that ultimately led to the dehydration and mortality of the insect (Ibrahim and Salem, 2019).stadler et al. (2017) reported the toxicity of nanostructured alumina and its mode of action against S. oryzae. The studies indicated that charged nanostructured alumina got attached to the beetle cuticle due to triboelectric forces, leading to insect dehydration through sorbing its wax layer by surface area phenomena (Figure 2).

4 CATEGORIES OF NANOMATERIALS

The word “nano” emerged from the Greek word “dwarf” (Bhattacharyya et al., 2010; Anandhi et al., 2020). Nanoparticles refer to materials having nanoscale external dimensions or internal structures. The nanoscale size generally has an upper limit of about 100 nm. Based on the particle size, nanoparticles were classified into three categories: 1) ultrafine
particles having a size less than 100 nm in diameter, 2) accumulation-mode particles having a size between 100 nm and 2.5 µm in diameter, and 3) coarse-mode particles having size greater than 2.5 µm in diameter (Sioutas et al., 2005; Kah et al., 2013; Kashyap et al., 2017; Kashyap et al., 2018; Yadav et al., 2021)). A nanosystem unit consists of two basic components: an active ingredient and a carrier. Based on their chemical composition, nanoformulations can also be classified into three basic categories including 1) inorganic-based, solid, and non-biodegradable nanoparticles (gold-, silver-, copper-, iron-, and silica-based nanoparticles), 2) organic-based biodegradable nanoparticles (liposomes, solid lipid, and polymeric nanoparticles), and 3) hybrid (combination of both inorganic and organic components) nanoparticles (Figure 3). For storage insect pest management, inorganic-based nanopesticides have been tested in more cases as compared to other categories. Also, plant-based nanoparticles have attracted more attention for stored grain pest control because these are environmentally safe and are easy to develop as compared to chemical-based nanopesticides (Goodsell 2004; Chen et al., 2019). Nanomaterials can also be developed using microbes or their bioactive compounds (Kashyap et al., 2018; Bazana et al., 2019). For stored insect pest control, various types of formulations have been suggested such as nanoemulsions, polymer-based nanopesticide formulations, and products containing engineered nanoparticles, for example metals and metal oxides (Mondal, 2020; Singh H et al., 2021). In this review, only metal-based nanoparticles, nanoemulsion, and polymer-based nanoformulations will be covered as these have been tested predominantly against storage insect pests. Moreover, a summary of nanopesticides evaluated against storage insect pests is given in Supplementary Table S3.
FIGURE 3 | Types of potential nanomaterials and nanoformulations suggested for insect pest management under storage.

FIGURE 4 | Types of polymer-nanoparticles formulations for delivery of pesticides via (A) adsorption on nanoparticle, (B) encapsulation within polymeric spheres (nanocapsule), (C) entrapment within polymeric nanoparticles (nanosphere), (D) attachment on nanoparticle by different linkers, (E) entrapment within polymeric micelles, and (F) branched and ordered polymeric molecules (dendrimers).
4.1 Metal-Based Nanomaterials

4.1.1 Silver nanoparticles

Silver nanoparticles (AgNPs) are so far one of the most tested and effective nanomaterials found for insect pest management. These nanoparticles are used carriers for delivering agrochemicals to the targeted site (Gupta et al., 2018; Gour et al., 2019). These exhibit well-built insecticidal, bactericidal, antifungal, and antiviral properties (Chen and Schluesener, 2008; Rai et al., 2014; Saratale et al., 2017) and are found to be very promising against insect pests. Additionally, they have catalytic properties, antimicrobial activity, higher chemical stability, and electrical conductivity that attracted more scientists for their use in pest management studies. The silver-based pesticide formulations deposit more dosage of active ingredients to the target species as compared to conventional pesticides (Ragaee and Sabry, 2014; Athanassiou et al., 2018). These nanoformulations have shown no toxicity to non-target organisms and are therefore considered safe to the environment (Jo et al., 2009; Oliveira et al., 2019).

Silver nanoparticles are reported to effectively control S. oryzae (Goswami et al., 2018; Zahir et al., 2012; Pathipati et al., 2021). The plant-mediated green silver nanoparticles using plant Euphorbia prostrata (Zahir et al., 2012) and Avicennia marina (Vijaya Sankar and Abideen, 2015) resulted in higher mortality of S. oryzae followed by T. castaneum and R. dominica. Silver nanoparticles application at the rate of 1.00 g kg⁻¹ of seed gave 83% mortality of adults and larvae of Callosobruchus maculatus (Rouhani et al., 2015). Vadlapudi and Amanchy (2017) developed silver nanoparticles (AgNPs) utilizing the leaf extracts of Myristica stachya wightiana that showed toxic effects against S. oryzae at concentration of 50 µg, and mortality of 29% ± 0.45 was obtained after 24 hrs. Nerium oleander plant extract–mediated AgNPs were found highly effective against larvae of T. castaneum and C. maculatus (Jafer and Annon, 2018). Rashwan and Abu-Zaied (2018) showed that AgNPs synthesized using rosemary executed 100% mortality for adults of S. granarius after 120 h, and the same efficacy of Laura and Cardamom was recorded after 14 h at 1 µg/ml concentration of AgNPs. High insecticidal efficacy was shown by the combination of silver nanoparticles and Malathion against T. castaneum (AS and Thangapandiyan, 2019). Silver nanoparticles fabricated using Annona reticulata leaf extract showed potent insecticidal properties against S. oryzae (Malathi et al., 2019). Clove, Syzygium aromaticum, essential oil-based AgNPs showed 71% repellency at 1% methanol extract concentration and 100% larvicidal mortality at 4% acetone concentration against T. castaneum (Selvaraj et al., 2019). Biogenic silver and gold nanoparticles synthesized from Daphne Mucronata (leaves, bark, and roots) and Monotheca buxifolia (leaves, seeds, and fruits) crude methanolic extracts are 100% effective against T. castaneum, R. dominica, and Callosobruchus analis (Shah, 2019). Silver nanoparticles prepared from silver nitrate using Moringa oleifera (Moringaceae) leaf extract gave the highest mortality (100%) against S. oryzae after 15 days of exposure (Rani et al., 2019). Silver nanoparticles extracted from leaf extracts of Azadirachta indica effectively reduced egg production of T. castaneum and C. maculatus to 85 eggs/female and 18 eggs/female, respectively, at a concentration of 2,000 ppm (Annon et al., 2020). Bio-prepared silver nanoparticles by Beauveria bassiana fungus showed 87.27% repellency and 97.56% mortality against C. maculatus at a concentration of 100% in 20 min soaking period (Al Jubury et al., 2021). Datura stramonium EO–coated silver nanoparticles gave highest mortality of 41.40% against Trogoderma granarium at 300 ppm, and the highest range was 67.89% at 15% concentration of D. stramonium (Gulzar et al., 2020). Silver nanoparticles achieved 100% killing at a concentration of 5,000 ppm within 72 h of application against O. surinamensis (Salman and Hameed, 2020). Silver nanoparticles prepared using ethanolic and hot aqueous extract of leaves of the Damas, Conocarpus lancifolius, showed the maximum sterility index among the stored date moth, Ephesia cautella, and was most effective at 1,500 ppm concentration (Abbood and Ali, 2020). Silver nanoparticles of Camellia sativa extract gave mortality of 60.1% against O. surinamensis and 46.2% against S. granarius at a concentration of 500 ppm after an exposure period of 72 h (ur Rehman et al., 2021). Silver nanoparticles synthesized using extract of Spirogyra hyalina as a capping and reducing agent showed 30% mortality against T. castaneum at 500 ppm (Al Radai et al., 2021). Curry leaves–mediated silver nanoparticles provided minimum seed damage (38.67%), minimum seed weight loss (0.78%), and absolute mortality (100%) of Callosobruchus chinensis at 70 ppm concentration on seventh day after treatment (Yerragopu et al., 2019). Plant-based silver nanoparticles from Ricinus communis and Citrus paradise gave highest repellency against T. castaneum in the range of 67.89% at 15% concentration of R. communis, and lowest was 28.31% at same concentration of the C. paradise oils (Shahzadi et al., 2019). Green silver nanoparticles prepared with peel extract of sweet orange, Citrus sinensis (L.), caused 83–77% mortality of T. confusum (Sedighi et al., 2019). Silver nanoparticles (AgNPs) at a concentration of 20% using an aqueous extract of hyperpigmented tomato skins resulted in 52% mortality of adults cowpea weevil (C. maculatus) (Carbone et al., 2020). Leaves extract taken from peach tree treated with AgNPs and ZnNPs showed 100% mortality of rice weevil (S. oryzae) and the lesser grain borer (R. dominica) by the fumigation method (Mosa et al., 2021).

4.1.2 Aluminum Oxide Nanoparticles (Al₂O₃NPs)

Nanostructured alumina (NSA) dust or aluminium nanoparticles are found to protect the grains from stored insect pest infestation (Stadler et al., 2017). Stadler et al. (2012) showed that pesticidal activity of nanoalumina is more effective than diatomaceous earth (DE) formulation against S. oryzae. Sabbour (2012) synthesized two entomotoxins made from nanoparticles of Al₂O₃ and TiO₂ against S. oryzae. Among these, aluminum-based toxin was found more effective against S. oryzae as compared to nano TiO2. Nanoalumina dust of different size and morphology was tested against S. oryzae and R. dominica, and the higher mortality was recorded. But at the same time, it was concluded that reducing the size of the particle and
increasing the surface area were not the only dominant factors that influence the effectiveness of insecticides.

Nanoalumina can be a good alternative to harmful dust formulations based on diatomaceous earth. Abo-Arab et al. (2014) reported that alumina oxide nanoparticles caused 95.33% mortality of S. oryzae and 91.66% mortality of S. zeamais at a concentration of 1 g kg−1 within 21 days of treatment. Similarly, Nasr (2015) proved the efficacy of Al2O3 nanoparticles against S. oryzae. Nanoaluminium oxide showed mortality of 100.0% when applied at the rate of 2 g kg−1 of rice, after 14 days against rice weevil (El-Bendary et al., 2016). López-Garcia et al. (2018) tested nanostructured alumina dust (NSA) in 400 ml galvanized steel jars on S. oryzae, and it gave effective mortality rates. Comparably, Das et al. (2019) confirmed that treating S. oryzae with tested nanoparticles such as aluminium oxide at a dosage level of 1 g kg−1 killed 90% S. oryzae within 4 days. The insecticidal activity of NSA as seed protectant was evaluated against three insect pests; OrYZaeophilus surinamensis, Stegobium paniceum, and Tribolium confusum. The insect mortality was found to be 100.00% when applied at the rate of 400 mg kg−1 for S. paniceum followed by 80.64% in O. surinamensis and 79.41% in T. confusum (Belhamel et al., 2020). Aluminum oxide nanoparticles showed 100% mortality at 8,000 mg/kg of wheat after 7 days of exposure; in addition, after 60 days of exposure, all tested Al2O3-NPs concentrations (1,000, 2000, 4,000, and 8,000 mg/kg grain) significantly decreased the number of S. oryzae offspring in a dose-dependent manner (Ismail et al., 2021).

4.1.3 Titanium Dioxide Nanoparticles (TiO2NPs)
These nanoparticles have low toxicity and minimal non-target biological effects (Ziental et al., 2020). The effectiveness is dependent on the chemical and physical characteristics including size, crystal structure, and photo-activation (Skocaj et al., 2011). The main advantage of using titanium dioxide formulations in storage is lesser ecological harm to non-target species (Norman and Chen, 2011). Abo-Arab et al. (2014) showed that titanium dioxide nanoparticles killed 61.66% of S. oryzae and 60.66% of S. zeamais at a dosage of 1 g kg−1 within 21 days Das et al. (2019) confirmed that treating S. oryzae with tested nanoparticles of titanium dioxide at a dosage level of 2 g kg−1 killed 90% S. oryzae within 14 days Sabbour (2012) demonstrated the toxicity of two NPs, TiO2 and Al2O3, against S. oryzae, both under lab and storage conditions in Egypt. Nano Al2O3 was found more effective than nano TiO2. A high concentration of TiO2 nanoparticles recorded high cumulative mortality of T. castaneum after exposure time 1, 3, and 5 days from treatments (15.30, 23.57, and 29.85%, respectively) (Hilal et al., 2021).

4.1.4 Zinc Oxide Nanoparticles (ZnONPs)
Zinc oxide nanoparticles have been used for developing pesticides because of their remarkable antimicrobial, physical, and optical properties (Akbar et al., 2020; Akintelu and Folorunso, 2020). Different methods can be utilized for their synthesis such as vapor transport and precipitation hydrothermal (Raoofi, 2013). The utilization of plant extracts for the purpose of developing ZnONPs is gaining popularity these days as these are quite safe and eco-friendly. Zinc oxide–based nanoformulations have been found effective in controlling S. oryzae and T. castaneum with higher mortality rates (Hamza 2012; Salem et al., 2015). Nasr (2015) performed a screening test to compare the effects of ZnO nanoparticles with pirmiphos methyl on S. oryzae. The results proved nano ZnO as an alternative to pirmiphos methyl which has harmful effects on human beings. Bacillus thuringiensis–coated zinc oxide nanoparticles (Bt-ZnO NPs) reduces fecundity, total development period, and causes 100% mortality of pulse beetle, C. maculatus, at 25 µg/ml (Malaikozhundan et al., 2017). ZnONPs exhibited a significant toxic effect against S. oryzae and C. maculatus at the highest concentration while T. castaneum showed high resistance (Haroun et al., 2020). Zinc oxide nanoparticles of size 100 nm at a concentration of 1,000 ppm showed 100% mortality of C. maculatus (Mohammed and Aswd, 2019), while in a more updated test, zinc oxide nanoparticles at 200 ppm gave the highest mortality of 100% and lowest egg production against the same pest in green gram (Lakshmi et al., 2020). ZnO nanoparticles in combination with Ricinus communis, Jatropha curcus, and Citrus paradise leaf powder showed 66.32% mortality of T. castaneum and 49.51% of T. granarium (Haider et al., 2020). ZnO prepared using the extract of E. globulus showed 80.5% mortality of R. dominica at 600 ppm after 15 days exposure (Siddique et al., 2021). Similarly, Hilal et al. (2021) concluded that a high concentration of ZnO nanoparticles recorded high cumulative mortality of T. castaneum after the exposure time 1, 3, and 5 days from treatments (20.42, 27.08, and 33.96%, respectively). Chitinase from Lactobacillus coryniformis–incorporated ZnONPs gave 100% mortality of maize weevil, Sitophilus zeamais, at a concentration of 6 mg/L, and the average death rate was 2.4 days (Dikbaş et al., 2021).

However, zinc oxide nanoparticles are found to be less effective in controlling the storage pest’s population as compared to other nanoparticles such as silver, aluminum oxide, and titanium dioxide (Raduw and Mohammed, 2020; Wazid et al., 2020). In a study, Das et al. (2019) evaluated aluminum oxide, titanium dioxide, and zinc oxide nanoparticles against S. oryzae. Nanoaluminium oxide gave 90% mortality at 1 g kg−1 after 4 days, whereas nano zinc oxide and titanium dioxide achieved this level at 2 g kg−1 after 14 days. Therefore, it justifies the fact that zinc oxide nanoparticles are less effective in controlling storage pests. Still, due to its antimicrobial properties, it is recommended for usage in agricultural pest control.

4.1.5 Copper Nanoparticles (CuNPs) and Iron Oxide Nanoparticles (FeNPs)
Biotransformed CuNPs using Pseudomonas fluorescens MAL2, which is almost similar to Pseudomonas fluorescens DSM 12442T DSM, act as a great warrior against T. castaneum (El-Saadony et al., 2020). CuO-NPs fabricated by harnessing metabolites of Aspergillus niger strain (G3-1) gave a mortality percentage of 55–94.4% and 70–90% against S. granaries and R. dominica, respectively (Badawy et al., 2021). A combination of iron oxide nanoparticles and aqueous extract of Anthocephalus cadamba
exhibits 100% mortality against *S. granarius* (Sivapriya et al., 2018).

### 4.2 Silicon Dioxide Nanoparticles (SiO₂NPs)

These are also known as silica nanoparticles and have higher thermal stability, low toxicity, and excellent biocompatibility with a range of molecules and polymers (Rahman and Padavettan, 2012; Huang et al., 2019). These can act as excellent nanocarriers for different agrochemicals due to their mesoporous property (Rastogi et al., 2019). Silica has a wider applicability because of its shape, size, porosity, and crystallinity which can be precisely manipulated. These can act as excellent nanocarriers for the delivery of biopesticides, pheromones, fungicides, and growth promoters (Barik et al., 2008; Cáceres et al., 2019).

Nanotubes reported with aluminosilicate have the capacity to attach to plant surfaces and hair of insects through which they enter into the insect body and affect their body functions (Patil et al., 2009). Silica-based nanoformulation was tested against red flour beetle *T. castaneum* and gave effective control of the pest (Debnath et al., 2011). SiO₂ gave 100% mortality of cowpea weevil, *C. maculatus*, when applied at the rate of 2.06 g kg⁻¹ (Rouhani et al., 2013). Chlorypryflos-loaded silica nanoparticles (Ch-SNPs) effectively control *R. dominica* and *T. confusum*, and it was found that mortality increased with increased concentration (Babamir-Satehi et al., 2017). Similarly, Kallur and Patil (2019) reported that nano-SiO₂-based nanoparticles extracted from *Alstonia scholaris* showed higher toxicity with a LC₅₀ of 0.8 mg/ml and LC₉₅ of 1.95 mg/ml against *R. dominica*. Silver nanoparticles in combination with plant oil *Ricinus communis* showed 67.89% repellency at 15% concentration and 28.31% repellency at the same concentration in combination with *Citrus paradise* oil against *T. castaneum* (Shahzadi et al., 2019). SiO₂ nanoparticles showed a strong defensive response against *Caryedon serratus* in groundnut at 0.67 mg/kg and 1.7 mg/kg, and it was observed that mortality increased with time of exposure (Diagne et al., 2019). Inorganic nanosilica killed 50% of adults *T. castaneum* at 0.90% concentration after 10 days of treatment (Khalil, 2019). SiO₂ nanoparticles act as a strong defensive tool against *Caryedon serratus* in groundnut at 0.67 mg/kg and 1.7 mg/kg, and mortality increased with time of exposure (Diagne et al., 2019). Rouhani et al. (2019) proved that silica nanoparticles (SNPs) are highly effective against *S. granarius* causing 100% mortality after 2 weeks. Fumed silica (aerosil 200) nanoparticles at a concentration of 1.5 and 2 gm/kg caused 100% mortality of *T. granarium* and *Stegobium paniceum* after 5 and 2 days of treatment (Abdelfattah and Zein, 2019).

Silica nanoparticles prepared with the help of sol-gel technique effectively controlled *R. dominica*, *T. castaneum*, and *O. surinamensis* (El-Naggar et al., 2020). Fumigation of maize grains with SiO₂-NPs proved very effective against four common stored grain pests, namely, *S. oryzae*, *R. dominica*, *T. castaneum*, and *Orizaephilus surinamensis* (El-Naggar et al., 2020). Silica nanoparticles along with neem leaf extracts effectively reduced egg production of *T. castaneum* and *C. maculatus* to 58 eggs/female and nine eggs/female, respectively, at a concentration of 2,000 ppm (Anon et al., 2020). Ziaee and Babamir-Satehi (2020) loaded nanosilica with three ingredients deltamethrin, pyriproxyfen, and chlorypryflos and tested it against the larvae of *T. granarium* feeding on stored wheat using mosaic and galvanized steel surfaces. Deltamethrin, followed by chlorypryflos, was found to be the most effective against larvae of *T. granarium*, and the mortality was significantly higher in galvanized steel than the mosaic ones. Green silica nanoparticles (1,500 ppm) synthesized using spinach leaves, tuli leaves, and paddy husk proved to be an alternative to Malathion against storage pests (Wazid et al., 2020). Three silica forms, that is, Aerosil 200, chemical, and bio-silica in the form of nanoparticles were tested against *C. maculatus*, *R. dominica*, and *T. confusum*. All the tested materials caused mortality of adult and offspring of the three tested insects, and mortality increased with the increase of concentration and exposure period. The adults *C. maculatus* were more susceptible followed by *R. dominica* and *T. confusum* with the three tested materials at all concentrations used (Saleem, 2020).

Insect proof nets coated with silica nanoparticles showed absolute mortality against *S. oryzae* (Agrafioti et al., 2020). Nanosilica of 30 nm size at a concentration of 0.5 g per kg of rice showed mortality rate of 80 and 97.4% against *S. oryzae* after 7 and 14 days, respectively (Kar et al., 2021). Nanosilica prepared from sugarcane bagasse ash (SCBA) and used as an additive to the diatomaceous earth (DE) enhanced the insecticidal activity of Mamaghan DE, and after 14 days of exposure, the adult mortality was more than 86 and 95% for *T. confusum* and *R. dominica*, respectively (Saed et al., 2021).

### 4.3 Nanoemulsions

Numerous nanoemulsions have been tested for controlling stored grain pests. These nanoemulsion formulations can improve the effectiveness of botanical insecticide for commercial use and are target-specific (Frederiksen et al., 2003; Anjali et al., 2012). The effectiveness of these formulations can be increased by using adjuvants and surfactants. These are relatively cheaper because their water solubility is high and can solubilize hydrophilic and lipophilic compounds easily, thus requiring less amount of active ingredients and inert material. Moreover, storage stability is quite high under a broad range of temperatures (~10–55°C) (Pavoni et al., 2019). Essential oil nanoformulations have been tested as an alternative for synthetic pesticides. Using such formulations can help in overcoming the problems such as poor water solubility, degradation, and volatility (Martin et al., 2010). These types of formulations are anticipated to be more productive than bulk substances (Anjali et al., 2010, 2012). In the past 10 years, essential oil-based nanoemulsions have proved their strong potency in the management of storage pests (Pavoni et al., 2019). For instance, eucalyptus oil nanoemulsion comprising of Karanja’s and Jatropha’s aqueous filtrate at concentrations of 300 and 1,500 ppm resulted in 88–100% mortality of *T. castaneum* adults within 24 h duration (Pant et al., 2014; *Pimpinella anisum* L. (Apiaceae) essential oil–based nanoemulsion consisting of 81.2% of (E)-anethole showed the toxicity of (LC₅₀ = 9.3% v/v) and significantly decreased progeny.
of rust-red flour beetle (Hashem et al., 2018; Mohammed and Nasr, 2020). Tested essential oil nanoemulsion of eucalyptus oil of a particle size of 8.57 nm was found to have higher insecticidal activity against *T. castaneum*. Similarly, eucalyptus oil nanoemulsions were passed across centrifugation, thermodynamic stability, heating and cooling, and freezing and thawing experiments and tested at lethal concentrations (LC_{50}) of 1:2 and 1:2.5 against *T. castaneum*, that is, 0.56 and 0.45 μL/cm² and were proved to be highly toxic (Adak et al., 2020). Nenaah (2014) showed that nanoemulsions of *Achillea biebersteinii*, *A. santolina*, and *A. mellifolium* essential oils are effective against both larvae and adults of *T. castaneum*. Furthermore, *A. biebersteinii* EO nanoemulsion exhibits some additional efficacy against the adults of red flour beetle. Some more essential oil nanoformulations that proved effective against stored insect pests are *Jojoba* (*Simmondsia chinensis*) nanoemulsion (Sh et al., 2015); *Purslane* oil nanoemulsion (Sabbour et al., 2016); and oregano and thyme essential oil–based nanoemulsion (Hossain et al., 2019).

Nanoemulsion developed from sweet orange (*Citrus sinensis*) EO formulation was reported to be acutely toxic to confused flour beetle and flat grain beetle (Giuini et al., 2019). Dhivya et al. (2019) studied the potential of sweet flag oil (*Acorus calamus*) nanoemulsion (spontaneous emulsification) against *S. oryzae*. *Mentha spicata* L. and *Mentha pulegium* essential oils nanoformulations showed mortality of 95.47 and 86.03%, respectively, against *T. castaneum* (Heydarzade et al., 2019). Nanoemulsion made from neem oil (Azadirachta indica A. Juss) was 85–100% effective against *S. oryzae* and 74–100% effective against *T. castaneum* (Choupian et al., 2017). *Hazomalania voyronii* essential oil–based nanoemulsion (HVNE) resulted in 92.1, 97.4, and 100.0% mortality against *T. confusum*, *T. castaneum* larvae, and *T. molitor* adults, respectively, at 1,000 ppm concentration in 7 days (Kavallieratos et al., 2021a). Similarly, Kavallieratos et al. (2021b) developed isofuranodiene-based NE 3% (w/w) derived from *Smyrnium olsatum* essential oil (EO) that exhibited high adulticidal effects against *T. molitor* and larvicidal activity against *T. castaneum* and *T. confusum*, reaching 98.6, 97.4, and 93.5% at 1,000 ppm after 7 days of exposure, respectively. Cumin essential oil (*Cuminum cyminum*) nanoemulsion was found to be highly toxic to *T. castaneum* (Hashem and Ramadan, 2021). Larvae of *E. kuehniella* were killed with nanoformulation in the form of emulsion using a botanical extract of *M. longifolia* having a particle range of 14–36 ppm (Louni et al., 2018). Similarly, the same formulation of *M. longifolia* had higher fumigant toxicity against *C. maculatus* and was successful in killing 50% egg population at a concentration of 9 μL/L in 4.7 days (Louni et al., 2019). Nanoencapsulated Janesville oil was found more effective against *T. confusum* and *T. castaneum* than coriander or black seed oil. (Sabbour et al., 2020a). Nanoformulations of the Tasmanian blue gum (TBG) EO effectively controlled the population of *C. maculatus* (Ya-Ali et al., 2020). Nanoemulsions prepared by extracting essential oils of *Anise* (*Pimpinella anisum*), *Artemisia* (*Artemisia vulgaris*), fennel (*Foenicum vulgare*), garlic (*Allium sativum*), lavender (*Lavandula angustifolia*), mint (*Mentha piperita*), rosemary (*Rosmarinus officinalis*), and sage (*Salvia officinalis*) showed considerable toxicity against *T. confusum*. However, the highest toxicity was observed by the application of garlic oil nanoemulsion, and the best repellent was found to be *P. anisum* (Palermo et al., 2021).

Very recently, a new study indicated that continuous use of essential oil nanoformulations against storage pests could give rise to habituation. A test conducted against *R. dominica* by using nanoemulsions of fennel (*Foeniculum vulgare*), mint (*Mentha x piperita*), and sweet orange (*Citrus sinensis*) essential oils showed that habituation occurred in the case of *M. piperita* and *C. sinensis* application (Giunti et al., 2021). Cold aerosol and gel nanoemulsion formed using Allium sativum’s oil showed the highest toxicity, and the best repellent was nanoemulsion of *Pimpinella anisum* against *T. confusum* (Palermo et al., 2021). Nanoemulsion prepared with *Achillea biebersteinii* essential oil at 10 μL/L air caused 100% mortality of the second larvae of *T. castaneum* after 4 days of exposure (Almady, 2021).

### 4.4 Polymer-Based Nanopesticide Formulations

The development of controlled release formulations of insecticides, herbicides, and fungicides using polymers for pest management programs is presently being given major attention keeping in mind the protection of the photo-labile active ingredients (Neri-Badang and Chakraborty, 2019). Polymer-based delivery systems increase the dispersion of active ingredients in aqueous media and act as a protective reservoir covering that leads to a controlled release of active ingredients (Kalia et al., 2020) *(Figure 4).* Slow release of active ingredients depends on nanocarrier’s degradation properties, bonding between active ingredients and the carrier, and the weather factors (Kumar et al., 2019). A number of polymer nanoformulations such as nanocapsules, nanospheres, nanogels, micelles, nanofibers, and chitosan-based nanoformulations have recently been developed. Polymeric nanomaterials are most commonly used for encapsulation of active ingredients mainly due to their eco-friendly and biodegradable nature (Kumar et al., 2017; Ramasamy et al., 2017). The benefit of using polymers is their protection and stability against active ingredients such as essential oils and plant secondary metabolites that have stability issues. These compounds get degraded and evaporated when they come in contact with light, water, air, and high temperatures. According to the current scenario, biodegradability is the most important property that a polymer must have.

Polymer-based nanoformulations can provide improved efficiency of active ingredients with minimized lethal effects on the ecosystem due to reduced use of organic solvents and surfactants in the formulations (Li et al., 2018). Due to polymer-based controlled formulations spatial and temporal doses are reduced and stability and effectiveness are improved (Chen and Yada, 2011). They are also attractive to researchers due to their complex delivery systems by incorporating multiple active ingredients with different modes of action, biocompatibility, and biodegradability (Tong et al., 2017). The
polymers deployed for nanopesticide formulations consist mainly of polysaccharides (e.g., chitosan, alginates, and starch) and polyesters (e.g., poly-ε-caprolactone and polyethylene glycol) (Kashyap et al., 2015; Rani et al., 2017; Kumar et al., 2018). Nowadays, there has been an increased trend of using eco-friendly and biodegradable natural materials such as lecithin and corn oil (Nguyen et al., 2012; Kashyap et al., 2015) and cashew gum (Abreu et al., 2012).

Polyethylene glycol–based amphiphilic copolymers exhibit biodegradability, easy processing, and other well-explored properties (Torchilin, 2006). Therefore, they are considered the most attractive polymers. In addition, PEG-based formulations are considered superior in comparison with other commercial products for the purpose of insect pest as well as nematode control (Loha et al., 2012; Pankaj et al., 2012). Polyethylene glycol (PEG)–coated nanoparticles loaded with garlic essential oil effectively control red flour beetle, T. castaneum (Herbst) (Yang et al., 2009). A comparative toxicity study between nanostructured alumina (NSA)- and Protect-It diatomaceous earth (DE)–based products showed that NSA is much more effective in killing R. dominica than Protect-It® (Stadler et al., 2012). Therefore, NSA is an alternative to diatomaceous earth (DE)–based products as it decreases significant percentage of progeny production and can be used for future formulations of pesticides. Vadlapudi and Amanchy (2017) developed a moderate control of R. dominica by the formation of silver nanoparticles (AgNPs) and leaf extracts of Myristachya wightiana (essential oil). Likewise, nanoemulsion of Eucalyptus essential oil with a particle size of 8.57 nm and polydispersity index (PDI) 0.28 effectively controlled R. dominica as compared to essential oil alone, which shows a great potential of nanoformulation-based products (Mohammed and Nasr, 2020). Very recently, citronella oil, moringa oil, and goatweed extracted from (Ageratun conyzoide) were converted into nano-oils via polymerization technology and were tested at the concentration of (0.5%) on the third instar larvae of R. dominica showed a highest accumulative mortality (99.0%, 89, 87%, respectively) (Sabbour et al., 2020b). In many studies, essential oils that were not much effective in controlling storage pest attack have been proved as a strong product for controlling the same when formulated with nanotechnology. Likewise, Jesser et al. (2020) studied the relationship between insecticidal activities of EO or essential oil–loaded polymeric nanoparticles (EOPN) and also kept notice on post-application temperature in the research. In contact toxicity bioassay, palmorosa proved to be the most efficacious, while in a fumigant bioassay, palmorosa along with peppermint oil were found to be effective. In addition, no effect of environmental variation was noticed. Delivering dsRNA by the utilization of polyamidoamine dendrimer–coated carbon nanotubes (PAMAM-CNT-dsRNA) help in raising the level of RNA interference in T. castaneum (Edwards et al., 2020). Thereby, PAMAM-CNT-dsRNA increases the efficacy of gene knockdown in red flour beetle. Clove essential oil (Syzygium aromaticum)–loaded polyethylene glycol (PEG) nanoparticles shows high rate of mortality against T. castaneum (Ikawati et al., 2021).

4.5 Chitosan-Based Formulations

Chitosan is a bioactive polymer formed by the deacetylation of chitin, which is one of the most abundant natural polysaccharides (Badawy et al., 2011). Only a few studies have been carried out on the efficacy of the chitosan-based formulations against storage insect pests. Myristic acid–chitosan (MA chitosan)–based nanogel loaded with Carum copticum (L.) essential oil (EO) was found effective against S. granarius and T. castaneum, and the studies indicated that toxicity effect increased with the increasing exposure time (Ziaee et al., 2014). Peppermint oil (PO)–encapsulated chitosan nanoparticles were found highly toxic against S. Orzyze (Rajkumar et al., 2020). Melissa officinalis essential oil nanoencapsulation in the chitosan matrix improved fumigant activity (LC50 = 0.048 μL/ml air) and acted as a strong antifeedant (EC50 = 0.043 μL/ml) against T. castaneum (Upadhyay et al., 2019). Likewise, chitosan- and polycaprolacton-encapsulated R. officinalis and Zataria multiflora essential oil nanoparticles effectively controlled confused flour beetle (Ahsaei et al., 2020).

4.6 Nanocapsules

Nanoencapsulated Cymunum cuminum polymerized oil/water emulsion (using poly(urea-formaldehyde)) when sprayed on rust-red flour beetle continuously for 7 days resulted in LC50 value of 16.25 ppm, which is lower than the value of oil tested alone (Negahban et al., 2012). Nanoencapsulation of R. officinalis essential oil–loaded formulation found effective against T. castaneum (Khoobdel et al., 2017). Cysteine protease nanocapsule of Albizia procera (ApCP) resulted in 100% mortality of Sitotroga cerealella at 7.0 and 3.5 mg/g concentrations (Batool et al., 2021). Likewise, nanoencapsulated Eucalyptus globulus and Z. multiflora essential oils were found effective for the control of E. kuehniella (Emamjomeh et al., 2021). Nanoparticles encapsulated with Artemisia haussknechtii essential oil showed 100% mortality at 166 ppm (Khanahmadi et al., 2017). The combination of nanoencapsulated form of Cuminum cuminum essential oil with reduced amounts of phosphate controlled 50% population of S. granarius and T. castaneum at a concentration of 42.51 and 78.99 μL/L, respectively, and Lavandula angustifolia can also be used as it is on par with cumin oil (Bayramzadeh et al., 2019).

5 CONCERNS ABOUT NANOPESTICIDES USAGE

One of the considerations for favoring nanopesticides over conventional pesticides is that these lessen environmental contamination through the reduction in pesticide application rates and losses (Jasrotia et al., 2018; Luiz de Oliveira et al., 2018). Conversely, these may pose a new problem of longer persistence and higher toxicity. A small droplet size may also lead to early evaporation of the nanodroplets before reaching the target. The interaction of nanoformulations with microorganisms, plants, and other animals at different trophic levels is another major area requiring investigation. Moreover, the environmental fate of
pesticide nanoformulations on soil, groundwater, and non-target organisms is unknown. The properties of the nanocarriers and the dispersion of the active ingredient within the nanoformulation matrix determine the release of the active ingredients into the environment. It has been reported that delayed release of nanoparticles over an extended period of time may affect non-target organisms (Kah et al., 2013). Nanocarriers mostly used in nanoformulations are either natural polymers or polysaccharides or lipids, which degrade easily but very little concern has been raised toward the use of non-biodegradable nanocarriers such as metal and metal oxides (Kah and Hofmann, 2014). Moreover, most of the synthesized nanocarriers are for controlled release that may cause human body exposure of nanoformulations in a restricted manner (Gahukar and Das, 2020). Conventional formulations require use of harmful organic solvents in developing pesticidal nanof ormulations, and these solvents are highly toxic to the environment.

Regulations for the registration and introduction of nanoproducts into the market are lacking. There is an urgent need to develop standard guidelines for the evaluation of nanochemicals before registration and commercialization as it is pertinent to understand their behavior, efficacy, toxicity, physicochemical properties, and environmental effects. The research studies regarding comparison of nanopesticides with their conventional analogues in all aspects are necessary to guide future research regarding the environmental risks of nanopesticides using the life-cycle analysis. This analysis should take into consideration all the steps of nanoformulations production, application, incorporation levels into food chain, and possible effects on agrosystem conditions that may influence hazardous properties and risk characterization nanomaterials. There is a growing concern in the scientific community about toxicity and impact of nanopesticide formulations on the ecosystem due to their widespread applications, which requires more investigation and research in these areas. Therefore, more efforts should be made to search and find out the way for the development of safer and smarter nanoformulations.

6 REGULATIONS OF NANOPESTICIDES

The increasing trend of usage of nanomaterials in various fields is on the rise in today's hi-tech world. However, at the same time, environmental risk assessment of nanomaterials such as nanopesticides is very essential before a product can be placed on the market worldwide. Risk assessment of nanomaterials, their persistence, behavior, and fate in the environment should be determined prior to their release. The regulatory and legislative bodies around the globe are required to ensure to account for their safe usage and successful risk assessment. Nanoparticles, because of their characteristic features such as size, surface area, and catalytic properties, require additional testing beyond guidelines for setting their toxicity levels (Singh et al., 2020). Various national and international regulatory bodies are trying to ensure safety of nanomaterials. In some regions including Asia, Africa, and Oceania, heterogenous methods are used for the regulation of nanoproducts and these methods vary country-wise (Kookana et al., 2014). For instance, recently in India, guidelines for the evaluation of nano-agri input products and nano-agriproducts have been framed that defined nanomaterials either as a nanofertilizer or nanopesticide (Naqvi and Flora, 2020). The Scientific Advisory Panel of the US Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) has contemplated pesticides made of nanometals/or metal oxides and has recommended that potential health and environmental risks of such nanomaterials should be taken into consideration before their market release (Grillo et al., 2021). Furthermore, in Europe, plant protection products (PPPs) are mainly regulated by Regulation (EC) No 1107/2009 in which prior authorization is required from the government (Villaverde et al., 2014; Cao et al., 2020). The official control of nanomaterials' residues in the food is regulated under (EC) No 396/2005 (European Food Safety Authority et al., 2019), and labor safety from these chemicals is covered by the REACH Regulation (EC) No 1907/2006, which gives information to manufacturers and importers about the risks associated with their usage (Tranfo et al., 2020). The Australian Pesticides and Veterinary Medicines Authority (APVMA) also framed regulations for the release of nanomaterials (Bowman & Hodge, 2009; Walker et al., 2017). Priorities in R&D sector of countries around the globe must focus on reducing ecotoxicity of nanopesticides by standardization of testing guidelines for nanopesticides; a better understanding of hazards posed by nanopesticides and their degradation products; increasing time of exposure of nanopesticides tests against particular organisms; and identification of nanopesticide that comes under boundaries for regulatory coverage.

7 CONCLUSION AND FUTURE DIRECTIONS

Even after countless efforts, food security is still challenging because of limited resources and rising population. The smart nanopesticides can have advantages over conventional agrochemicals such as lower dose requirement, higher solubility, and targeted delivery of active ingredient leading to higher eco-protection with lesser environmental ill-effects (Dubey and Mailapalli, 2016). Despite several advantages, nanoparticles also pose serious drawbacks such as low selective toxicity, low biodegradability of inorganic nanoparticles, and development of pesticide resistance in non-target organisms, if used in an indiscriminate way. Some nanosystems are at their beginning stage or are under development. Moreover, the data concerning the environmental fate of these nanoparticles and their possible negative impact on non-target organisms is scarce, and there is lack of knowledge in this regard. Increased attention must be paid toward the possible impact and reverberations that nanomaterials can have on the environment, non-target organisms, and development of ecologically safer nanopesticides. Scientists need to dwell deeper into research related to precautions to be taken, mutations in food due to nanostructured materials (NSMs), and nanoparticles toxicity in
human cells and their environmental impacts (Chhipa et al., 2017b; Sahoo et al., 2021). Only the research community can decide nanotechnology can bring more positive impacts than potential risks. The concept of “green nanotechnology” that is being posed as one of the benefits of nanoproducts need to be assessed by investigating the potential risks involved with their use. The sustainability of these products in addition to their safety and risks should be also need to be assessed, including the cost of production, environmental impact, and renewability of all material used for synthesis and production (Watson et al., 2011; Chowdappa and Gowda, 2013).

Future research in nanotechnology should be focused on 1) development of smart nanopesticide formulations to combat the limitations of conventional formulations, 2) development of environmentally sustainable green nanopesticides chemistry, 3) development of technologies for cheap and commercial nanopesticides production, 4) activity comparison of nanoformulations with conventional analogues at the field level to determine their practical utility, 5) ecotoxicological assessment of nanopesticides, and 6) establishment of legislative and regulatory framework for the safe introduction of nanopesticides in agriculture. Except minuscule limitations, nanomaterials have immense potential of transforming crop protection practices from environment harming to an environment favoring. It makes agriculture cost-effective too. This kind of development will improve the food life, storability, and security and in turn both the costumers and producers will receive more profit.

**AUTHOR CONTRIBUTIONS**

PJ: conceptualized the topic of the review and wrote the article; MN: collected and compiled all the literature; CM, AS, SK, and UK: assisted in the writing of the manuscript; AB, PK, SK, and GS: assisted in writing, reviewing, and finalized the article for submission.

**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fnano.2021.811056/full#supplementary-material

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