Nanopesticides: Promising Future in Sustainable Pest Management

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Abstract

Insects form the most successful and diverse group of animals present on earth today. Humans have shared a complex relationship with the insects. Though insects are indispensable as pollinators of crops yet at the same time they act as major destroyer of grains, pulses and fruits in the fields along with their post- harvest storage. Many of the dreadful diseases are also being transmitted by insect vectors to humans, livestock and other animals. Economic damage caused by insect pests is enormous. Adoption of advanced pest management strategies can alleviate the monetary losses substantially. Nanotechnological approach for pest control is an emerging and effective technique since it encompasses a wide range of objectives of an efficient pesticide like increased dispersion and solubility, slow release, controlled delivery system and protection against degradation. Newer formulations of pesticides with the intervention of nanotechnology are aimed to enhance their pesticidal properties. Insecticide formulations using nanomaterials as carriers of active ingredient have shown promising results for mitigation of pests of agriculture, storage and disease vectors. However, at present the knowledge is limited. There is a need for extensive evaluation of the toxicity of nanopesticides and the risks involved for humans and environment before their large-scale production and adoption. In this review article nanoformulations of pesticides with special emphasis on metal-based nanopesticides and their role as efficient alternatives in sustainable control of insect pests without much adverse impact on the environment has been summarized.

Keyword: Nanopesticides, Formulations,Nanotechnology, Pest management

1. Introduction

Agricultural sector is considered as one of the important industries in Indian economy which employs about 60% of Indian population and contributes approximately 18 % of the total GDP [1]. Around 19% population of the world is involved in agriculture and related activities. Almost 40% of the agricultural crops are damaged annually by pests all over the world which affects the food supply, economy of the country and poor rural communities. Huge amounts of pesticides are used to control insect infestation in the agricultural fields and afterwards during the storage of the grains. Use of pesticides is essential as it ensures to minimize the losses due to pest activity and maximize the yield of crops which is essential for food supply of animals and humans. Indiscriminate use of pesticides and lack of effective management have adversely impacted the environment as well as human health [2].

Environmental contamination exposes the human population to pesticide residues which are formed by physical, chemical and biological degradation of pesticides and find their way to water, air, soil and food [3]. Only about 1% of the pesticides utilized for control of pests reach the actual target while the major portion is lost via runoff, off-target deposition, spray drift and photo degradation which can affect the entire biodiversity adversely. [4].

There is a need for advanced research for the development of new technologies by which agrochemicals can be used more rationally for better yield and quality of agricultural produce along with least impact on the environment and economy. A balance has to be maintained between environmental concerns and economic realities. Among new technologies, nanomaterials represent an emerging trend in relation to pesticide use [5]. Nanocarriers and the new delivery systems could provide the development of safer and greener pesticides Advancement in nanotechnology and its application in the field of agrochemicals has led to innovation of nanopesticides which are more efficient in their action against insect pests [6].

2. Nanotechnology based pesticide formulations

Nanomaterials hold great promise with respect to employing them in formulation of nano-based pesticides owing to their small size, large surface area and target specific action. The effect of nanoformulations lasts for a much longer period with a lesser quantity of the pesticides and subsequently leaving less pesticide residue in the environment [7]. Nanoformulations help in improving the action and features of the pesticides such as dispersion, stability, solubility and delivery onto the target [8] thus, significantly increasing the efficacy of conventional pesticides [9].

The objectives of nanopesticide formulations are - 1. Increasing the solubility of otherwise less soluble active ingredients (AIs) to improve the bioavailability of pesticides 2. Release of AI in a slow, controlled manner and to protect the active ingredient against early degradation [10]. The controlled release of nanopesticides improves their effectiveness owing to their slow release and being active for a longer duration rather than a spontaneous release at a single stroke 3. Precise action against the target pest/pathogen [11]. Thus, nanoformulations provide selective, targeted and long-term controlled release of pesticides which is ecologically viable and safe.

Generally, nanoformulation of a pesticide involve mainly two components: Nano Carrier NC and the Active Ingredient of the pesticide AI. Pesticides are generally nanoformulated by loading the nanoparticles with the active ingredient of pesticides through a number of ways like encapsulation, adsorption, entrapment, attachment via covalent linkages or by formation of nanoemulsions or nanosuspensions [12]. The carrier particles added in the formulations are generally inert materials which may function as solvents, diluents, surfactants or stickers [13]. the nanocarriers mostly used are natural polymers or polysaccharides or lipids which degrade easily or non-biodegradable metals or metal oxides [7]. Nature of nanoformulation varies with the type of nanomaterial used which can be categorized as 1. Inorganic, non-biodegradable metal-based nanoparticles 2. Organic, biodegradable, polymer, lipids and liposome-based nanoparticles 3. Hybrid nanoparticles formed as a combination of organic and inorganic nanoparticles [14]. The efficacy of any insecticide and its utility as a management tool can be altered according to the nature of its constituents - active ingredient and carrier material, their physical and chemical characteristics and the target plants or organisms.

Nanoformulations fabricated with metal nanoparticles and their applications in controlling the pests responsible for damage to agricultural crops, stored food grains and health of humans and their livestock have been discussed in details in this review.

3.Metal based nanopesticides

These are considered **as** green, safe and efficient alternative for the management of insect pests in the field conditions and even under storage. Metal nanoparticles have been found to be effective in the control of many agricultural and medical pests including insects and plant pathogens too and are therefore used in preparation of novel formulations of the pesticides. Nanoparticles of metals such as silver, gold, copper, zinc, iron oxide, titanium oxide and silica are currently used in pesticide formulations [15]. These nanoparticles can also be fabricated from phytoextracts by green synthesis which is an easy, single step process without the use of high pressure, energy and toxic chemicals. Green synthesized metallic nanoparticles are eco-friendly and an inexpensive alternative to other frequently used chemical pesticides [16].

3.1 Silver nanoparticles -. Ag NPs are one of the most researched and preferred nanoparticles due to their application in major areas of human interest like agriculture, medicine, human health and biomedical industries owing to their antioxidative, antimicrobial, anticancer and insecticidal properties [17,18]. Ag NP based formulations of pesticides are able to transfer higher doses of active ingredients to the target organisms and are non-toxic to non-target organisms in comparison to conventional pesticides [19,20] and hence therefore considered safe and environment friendly [21]. Silver nanopesticides reduce the acetylcholinesterase activity in the target organism which affects antioxidants and enzymes responsible for detoxification finally leading to cell death. They also act on insect’s prime genes responsible for protein synthesis and reproductive hormones, disrupting the development and sexual maturity of the insect pests [22].

3.2 Aluminium oxide nanoparticles (Nanostructured alumina NSA) - Aluminium oxide dust has been in use as a contact insecticide since ages for the control of insects by causing mechanical injury to insect cuticle. NSA provides a more effective alternative to conventional insecticides due to its unique properties like electric charges, nanosized particles, large surface area and high sorptive potential [23]. NSA is considered as a potential pesticide in the field of agriculture, stored products protection and wood preservation [24].

NSA shows potent insecticidal property by a two-step action mechanism which involves physical and electrostatic phenomena. Insects have positive electric charges on their bodies which are generally increased with the movements like flying or walking [25,26]. This leads to strong adherence of oppositely charged particles to their bodies. NSA is a nanoformulation of Aluminium oxide where the nanoparticles carry fixed negative electric charges. When the insect comes in contact with NSA, these negatively charged particles get bound to the cuticle of the insect having positive electrostatic charge. NSA particles cause abrasion of cuticle, sorption of waxes present in the cuticle finally leading to insect dehydration and mortality [27]. In addition, ingestion of these particles also contributes to the insect mortality over a long period of exposure. It has been found that NSA exert its effect on several species of stored grain insect pests and leaf cutting ants [28].

3.3 ZnO nanoparticles - Zinc oxide is a versatile material with unique physical and optical properties and can be exploited in nano dimensions with possible future applications [29]. There is a vast scope for developing eco-friendly and potent zinc oxide nanoparticles for their application in the fields of agriculture and biomedical sciences. They can be synthesized by several chemical methods. Green synthesis of zinc oxide nanoparticles by using different plant extracts is also feasible, economical and safe as there is no formation of harmful chemical by-products. Zinc oxide nanoparticles owing to their antimicrobial action against many bacteria and fungi have also been recommended for their use in agriculture pest control.

3.4 Cu nanoparticles - Copper is an easily available metal, not very expensive and used in various nanopesticide formulations. Copper is one of the most essential elements required by the plants for their growth and development. Copper nanoparticles have the potential to protect the plants both from fungal and bacterial infection and to act against insect pests and therefore can be used in the formulation of nanopesticides, nanoherbicides and nanofertilizers. These nanoformulations are effective in very less quantities and thus minimise the toxic effects on environment and human health. Copper nanoparticles can help in the target delivery of pesticides and can be stabilized with polyvinyl pyrrolidone done to enhance their antimicrobial activity [19]. They are quite popular for their broad-spectrum antimicrobial action also. Many studies have been conducted to explore their potential as pesticides for the control of mosquitoes and stored grain pests.

3.5 TiO2 nanoparticles - Titanium oxide nanoparticles have the potential to protect the agriculture products from insect pest as well as from the attack of microbes. They are effective due to their chemical and physical characters such as structure of the crystal and photoactivation [30]. Titanium oxide based nanoformulations of pesticides are very safe to use for storage pests as they show minimal toxic effects to non-target organisms [31]. Use of nano titanium oxide is preferred in agriculture sector as they do not show adverse effects on plant growth.

3.6 Silicon dioxide or Silica nanoparticles - Silica nanoparticles are excellent nanocarriers for agrochemicals due to their specific physical characteristics like shape, size and porosity which can be easily manipulated [32]. They are very stable at high temperatures and can be fabricated along with a variety of molecules and polymers to create novel nanoformulations of pesticides [33]. Silica nanoparticles are also used as a carrier for their efficiency in controlled release and target specific application of insecticides [34]. Biological control agents like pheromones, growth regulators and biopesticides can be specifically delivered to target organisms with silica nanoparticles as carriers. Silicon dioxide nanoparticles just like NSA attack the insect cuticle leading to dehydration and finally the death of the insect [35].

4. Applications of Metal based nanopesticides

4.1 As insecticides for pests of Agricultural crops in field conditions

Metal NPs have a great potential to be used as safe pesticides/alternative in crop protection in place of chemical insecticides. Biopesticide like antifeedants delivered through nanoformulations show enhanced efficacy. The terpenes Alpha-pinene, Linalool, Nerolidol and Carene act as antifeedants in several lepidopteran insects and lead them to death due to starvation [36]. However, their use in the agricultural fields is restricted as their persistence and shelf life is very low due to their volatile nature. These terpenes were formulated with silica nanoparticles to enhance their bioavailability and antifeedant activity against S*podoptera litura* and *Achaea janata*. Shelf life of these compounds was enhanced by more than 6 months. Such nano-biocomposites are eco-friendly than the present synthetic pesticides, therefore hold a scope in future pest management programmes [37].

Aphis nerii, the oleander aphid is a common and serious pest of many important ornamental plants worldwide. Nanoparticles of silver and silver-zinc were tested on *Aphis nerii*. Results showed the potential of these nanoparticles for their use as an effective control agent for *A. nerii* [38]. Nanopesticide CNAP- HMS-PDAAM prepared by using adhesive and porous silica nanoparticles as carrier of cyantraniliprole (CNAP) was tested against *Chilo suppressalis* (Walker) and *Cnaphalocrocis medinalis* (Guenee) in the rice fields. This novel formulation showed efficacy for long-term control due to its anti-washing property and sticking on rice leaves and its sustained release effect. The nanocarrier silica particles had no adverse effect on the growth of rice and showed good biocompatibility thus ensuring their use in agricultural applications [39].

Spodoptera littoralis, an important pest on a wide range of host plants like cotton, tomatoes, cabbage, squash has acquired resistance to many insecticides. Shaker suggested a new control strategy for *Spodoptera* by the application of TiO_2 nanoparticles. Second and fourth instar larvae fed on the leaves treated with TiO_2 NPs for 2 days succumbed to death after 15 days of application. TiO_2 NPs affected biological aspects of *Spodoptera* like larval period, formation of pupae, adult emergence, sex ratio and life span of adults. They also caused body malformations in all stages of life cycle, decreased the egg laying and hatching [40].

Silica nanoparticles show the potential to control insect pest of beans and soybeans even in the cultivated field. They reduced the population of three insect pests with different feeding patterns - the Cowpea aphid - *Aphis craccivora*, American serpentine leaf miner - *Liriomyza trifolii* and Cotton leaf worm - *Spodoptera littoralis*. There is an immediate dropping down effect on aphids after the spray of silica nanoparticles [41]. Tomato psyllid, *Bactericera cockerelli* Sulc. is a serious pest of potatoes, tomatoes and other solanaceous plants in parts of America, Canada and Mexico. Insecticidal effects of Zn O nanoparticles or TiO_2 nanoparticles and their combination was shown against *Bactericera cockerelli* in laboratory and greenhouses [42].

Spodoptera frugiperda, a serious pest of maize has developed resistance to synthetic chemical insecticides. Innovations in nanotechnology offer alternative target specific tool of pest management. The larvae were fed on food dipped in different concentrations of zinc oxide nanoparticles under lab conditions. Exposure to zinc oxide nanoparticles cause body deformities in all stages of the life cycle from larvae to adults along with decreased fecundity, oviposition and hatchability of eggs. Zinc oxide nanoparticles have been shown to act a potent insecticide in control of *Spodoptra frugiperda* and other species without the risk of developing resistance [43].

4.2 As Insecticides for Control of Stored Grain Pests

There are a number of insects that destroy the stored grains or depreciate their value in storage. The losses caused by them in storage may sometime exceed the losses caused in the fields. Most of the insect pests of stored grains are beetles, members of order Coleoptera. Many other species of insects are serious pests of food grains causing quantitative and qualitative losses to these grains under stored conditions. The quality of grains is affected to such an extent that it becomes unfit for human consumption [44]. Fumigation is the most preferred technique of controlling the stored grain pests. Most of the chemical pesticides used as fumigants are quite costly and harmful for the human health also [45]. Majority of stored grain pests have developed resistance to commonly used fumigants such as phosphine and there is a need for the development of alternative methods of pest control. Metal based nanopesticides have been tested extensively for the postharvest management of storage insect pests.

Numerous reports are available to prove effectiveness of Ag NPs against stored grain pests. Recent researches support the use of Ag based nanopesticides for control of major stored grain pests like *Sitophilus oryzae, Sitophilus granarius, Tribolium castaneum, Callosobruchus maculatus* etc. Ag NPs fabricated by using the extract of leaves of *Camelina sativa* (Tea) applied at a concentration of 500 ppm resulted in 46.2 % mortality of *S.granarius* and 60.1 percent mortality of *O. surinamensis* after 3 days of exposure period [46]. Rani et al., 2019 developed Ag NPs with the leaf extract of *Moringa oleifera* causing 100% mortality of *S.oryzae* after 15 days of exposure. Ag NPs prepared with leaf extract of *Azadirachta indica* reduced the egg laying capacity of *Callosobruchus maculatus* and *Tribolium castaneum* [47]. Silver nanoparticles when applied at a dosage of 1 g per kg of grains caused more than 80% mortality of larval stages and adults of *Callosobruchus maculatus* [48].

Nanoalumina has been recommended to be used as an insecticidal dust as its effect on *S.oryzae* was more pronounced than commercial diatomaceous earth formulations [25]. Nanostructured alumina dust is used to protect the seeds or grains from the infestation by the pests of storage. Nano aluminium oxide is reported to cause more than 95% mortality of *S. oryzae* at a dosage of 1 gm/ kg within 21 days of exposure [49] whereas a double increase in dose i.e. 2 gm/ kg caused 100% mortality after just 14 days of exposure [50]. The efficacy of NSA applied at the rate of 400 mg/kg measured in terms of mortality varied from 79% in *Tribolium confusum* ,80% in *Oryzaephilus surinamensis* and 100% in *Stegobium penicillium* [51].

Aluminium oxide nanoparticles bind to the insect cuticle causing sorption of waxes present in the cuticle finally leading to insect dehydration and mortality [25] in *S. oryzae*. Aluminium oxide nanoparticles are considered a safe and better alternative to chemical insecticides used in the control of *Tribolium castaneum* [52]. However, Ismail et al, 2021 [53] reported the toxic effects of Aluminium oxide nanoparticles on *S.oryzae* as well as on the rats, the non- target organisms. Therefore, there is a need for further research to develop new and safer nanoformulations of aluminium oxide.

Silica nanoparticles have a good potential for its use as a protectant of stored seeds and better alternative to synthetic insecticides when applied with proper precautions [54]. Silica oxide nanoparticles did not show any adverse histopathological effects on non-target organisms like male mice, thus considered as safe and eco-friendly nanopesticide [55]. El Naggar et al. [56] reported the effectiveness of silica oxide nanoparticles as a fumigant for maize grains against serious storage pests like *T.castaneum*, *R dominica*, *O. surinamensis* and *S.oryzae*. Botanical nanopesticides synthesized using *Azadirechta indica*, tulsi leaves, spinach leaves and paddy husk along with silica nanoparticles have proved to be very effective, green alternative to synthetic chemical insecticides for the protection of storage pests [57-58]. Biosynthesized copper nanoparticles show more toxicity against *T. castaneum* than chemically synthesized nanoparticles [59].

ZnONPs have been found effective against the storage pests namely *S.oryzae* ,*T.castaneum* and *C. maculatus*. Zn-Cu nanoparticles incorporated with leaf powder of *Jatropha curcas*, *Citrus paradise* and *Ricinus communis* result in high mortality of *T. castaneum* and *T.granarium* [60]. Nanoparticles of ZnO fabricated with extract of *E. globulus* are highly effective against *Rhizopertha dominica* [61]. However, ZnONPs are less effective in comparison to other NPs such as silver, aluminium oxide and titanium oxide in management of many insect pests of stored grains [58].

Titanium dioxide nanoparticles recorded high mortality of *Sitophilus oryzae, S. zeamais* and *T. castaneum* under storage as well as in lab conditions [62]. Nano-zinc oxide and titanium dioxide were effective in ptotection of stored produce from *S. oryzae* as well as microbial infections [30].

4.3 As Pesticides for Control of disease vectors

A large number of plant synthesized metal nanoparticles have been reported to show toxic action against ticks and mosquitoes which are responsible for spread of many diseases [63]. Nickel nanoparticles can be used for killing of larval forms of blood sucking parasites. They show larvicidal property against the larvae of cattle ticks *Rhipicephalus* and *Hyalomna*, 4th instar larvae of *Anopheles subpictus, Culex quinquefasciatus* and *Culex gelidus* [64].

Many of metal NPs have the potential to be used as environmentally safe ovicides, larvicides, pupicides and adulticides [65] for mosquito control which are responsible for the spread of malaria, dengue and filaria etc. Silver nanoparticles tested on *Culex quinquefasciatus* caused high larval, pupal mortality and reduction in pupae formation and adult emergence [66]. Zinc oxide nanoparticles show promising activity against *Aedes aegypti* by decreasing their egg laying activity and increasing the mortality. Zinc oxide nanoparticles may be used as an effective control tool against mosquito larval populations and have potential application in biomedical field [67].

Green nanopesticides synthesized from the extract of various plant species using different plant parts and nanoparticles of metals like Ag, Zn, Co, Cu, Ti, Au etc.have been found to be effective for the management of mosquito populations [68]. According to a number of studies, green synthesized metallic nanoparticles are toxic to mosquitoes and may also cause morphological and histological malformations during their development [65]. Third instar larvae of *Aedes aegypti* exposed to green encapsulated zinc oxide nanoparticles resulted in shrunken abdominal region, change in thoracic shape, damaged midgut and loss of anal gills and lateral hairs [69].

Kabtiyal et al. 2022 [70] have reported that silver nanoparticles synthesized with the phytoextracts showed high larvicidal action on all the important mosquito species of *Anopheles, Culex* and *Aedes*. Moreover, LC_{50} and LC_{90} values of silver nanoparticles were much less than that for the crude plant extract. Mosquito populations can be controlled with the use of least possible dosages which is cost effective and eco-friendly Silver nanoparticles synthesized with leaf extracts of *Leucas asper* and *Hypetis suaveoleus* showed 100% mortality of larvae of *Aedes aegypti*, *Anopheles stephensi* and *Culex quinquefasciatus* [71]. Nanoparticles of zinc oxide synthesized with phytoextract of *Cipadessa baccifera* caused high larval mortality in *Anopheles stephensi, Aedes aegypti and Culex quinquefasciatus* [72]. Bimetallic nanoparticles of silver and cobalt synthesized with root extract of *Palmyra palm* caused high larval mortality of *Culex quinquefasciatus* [68].

Vivekanandhanam et al [73] showed that *Metarhizium robertsii* mediated synthesized copper nanoparticles are highly toxic to the larvae of *Anopheles stephensi, Anopheles aegypti, Culex quinquefasciatus* and *Tenebrio molitor* causing significant mortality. A low toxicity was observed on non- target organisms like *Artemia salina, Artemia nauplii, Eudrilus eugeniae* and *Eudrilus andrei*. CuNPs synthesized with seed extract of *Annona squamosa* displayed significant larvicidal activity against *Anopheles stephensi* ,the vector for spread of malaria..

Attempts have been made to evaluate the use of metallic nanoparticles as acaricides for the control of different species of ticks which are important ectoparasites of livestocks and responsible for spread of some dreadful diseases among them [74]. ZnO nanoparticles have been used for the control of tick, *Hyalomma sp*. which is a vector for transmission of many bacterial, viral, protozoan and rickettsial diseases in humans and animals. Sprays of zinc oxide nanoparticles in the concentration of 250 mg per ml cause 100% mortality of ticks at all exposure times and 125 mg per ml at exposure time of 30 minutes in vitro conditions [75]. However, there is a need for *in vivo* studies to evaluate the efficacy of zinc oxide nanoparticles as an acaricide. Titanium oxide nanoparticles also show remarkable acaricidal activity. These particles synthesized from the extract of *Calotrophis gigantea* flowers act against the adult of *Haemaphysalis bispinosa* and larvae of *Rhipicephalus microplus,* two very important tick parasites of many mammals in the world [76]. Experiments with silver chloride nanoparticles have proved their antitick activity against *Rhipicephalus microplus. Hyalomna anatolicum and Haemaphysalis bispinosa* [77].

5. Future Perspective: Safety and risks associated with nanopesticides

Application of nanoparticles as pesticides provides numerous advantages but also could result in unintentional spread of engineered nanoparticles into the environment. The enhanced activity of nanopesticides can result in unique benefits to agroecosystems and humans but may also pose new unexpected risks to the environment [78-79]. There is a concern about the long-term effects of nanopesticides as some of these nanostructured materials may flow into the soil-water systems and get incorporated in the food chains [80-81].

The fate of nanopesticides and biosafety issues associated with their release in the environment are still unclear. Behaviour of nanopesticides and their fate in the environment is dependent upon the functional features of the carrier and stability of carrier-active ingredient complex [82]. Most of the studies for assessing the impact of nanopesticides on the environment have been conducted in laboratories while more comprehensive experimental work will fill this knowledge gap [7]. The future research should be focused on assessment of activity of nanoformulations under field conditions, ecotoxicity and finally regulatory and legislative framework for the introduction of new formulations of nanopesticides in agriculture, safe storage of grains and disease vectors [83]. Evaluation of their potential impact on the safety of non-targets should be made mandatory before the implementation of nanotechnology in developing nanopesticides for commercial usage [9].

Current knowledge about the ecotoxicological behaviour of nanopesticides is not sufficient to assess the risks associated with their application at a large scale [84]. Further research for better designing of nanopesticides, their risk assessment and regulations for mass production and employability as environmentally safe agrochemical will pave the way for a sustainable future.

6.Conclusion

The arena of agriculture and health are facing pertinent global challenges like climatic changes, environment degradation which become more important in the face of increasing population, food scarcity and spread of diseases. There is an urgent need to implement new technologies for promising solutions to these problems. Field applications of well researched nanopesticides can accelerate the sustainable agriculture and vector control by their multifaceted attributes: less dosage application, lower treatment frequency, higher efficacy; henceforth low cost/ economical and least adverse environmental impact. However, nanotechnology is still in a nascent stage of development. There may be many unforeseen effects of the long-term usage of nanomaterials in the environment. Advanced research is required to bring the nanopesticides to the level of a game changer in sustainable pest management.

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