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Nano Pesticides: Production, Use, and Environmental Impact

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ABSTRACT

Recent advances in nanotechnology have led to its widespread application in several industries, including food, military, chemicals, pharmaceuticals, medicine, and pest control. Nano-insecticides have attracted considerable attention due to their effectiveness in combating plant pests and disease vectors, such as malaria, and providing more efficient solutions than traditional pesticides. Various methods have been developed for the production of nano-insecticides, but with the increasing demand for this category of insecticides, it is crucial to identify optimal approaches for the synthesis of insecticidal nanoparticles. Another important factor driving the need for innovation in nano-pesticides is the growing problem of pest resistance, which has reduced the availability of effective pesticides, especially for health-related purposes. Expanding research on nano-insecticides will further promote development in this emerging field. This review explores nano-pesticides and describes their production methods, types, environmental impacts, and potential toxicity to mammals.

Keywords: Pesticides, Nanotechnology, Nano pesticides, Insecticides

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Introduction

Nanotechnology has rapidly advanced over the past decade as an area of research, development, and industrial application. The term "nanotechnology" was initially introduced by Richard Feynman in 1959 but was officially coined by Japanese scientist Norio Taniguchi in 1974 at the University of Tokyo. His book published in 1986 provided a detailed understanding of nanobiotechnology [1, 2].

Nanotechnology encompasses four main areas: nanomedicine, nanomaterials, nano-measurement, and nanoparticles. The term "nano" originates from the Greek word for "small," and refers to a scale of 10^{-9} meters. Typically, nanoparticles used in nanotechnology range from 0.1-100 nm in size. These particles can be created through two primary methods: the top-down approach, which reduces the size of larger particles, or the bottom-up method, which builds nanoparticles by manipulating individual atoms and molecules [1, 3, 4].

Nanotechnology has a wide range of applications, such as in environmental restoration, controlled release of substances like deodorants, antimicrobials, and antifungals in fabrics, as well as in aerospace, industrial, military, medical, and targeted therapies [5, 6]. Nanomaterials are primarily produced through chemical processes, and their structures are analyzed using tools like the Atomic Force Microscope (AFM) and Scanning Tunneling Microscope (STM). The development of STM earned inventors Ann Binnig and Heinrich Rohrer the Nobel Prize in 1986. In living organisms, nanomaterials play an essential role in life preservation and functionality, as the activities within cells and tissues rely on nanostructures like nucleic acids and proteins [5, 7].
Nanoparticles present within the bodies of insects can be considered a form of free nanotechnology, similar to how insects utilize ferromagnetic nanoparticles to detect geomagnetic fields. These nanoparticles play a crucial role in various insect behaviors, particularly in navigation, locating nests, and feeding. This phenomenon is especially significant in the lives of social insects, with nanoparticles primarily found in the head, eyes, and antennae. However, the potential of these naturally occurring nanoparticles in living organisms, as part of free technology, has not yet been fully harnessed [1, 8, 9].
With recent advancements in nanotechnology, various types of nano-pesticides have been developed and tested on different insect species. Given the environmental concerns and the high costs associated with the excessive use of conventional pesticides, as well as the increasing resistance of pests to these chemicals, further research and development in the field of nano-pesticides has become essential. This article discusses the requirements, current methods, and challenges in the production and application of nano-pesticides.

Results and Discussion

Nano silica as a Nano-biological pesticide

Silica, an abundant compound on Earth, is commonly found in natural forms such as quartz sand, clay, and rocks, which are used in construction. To manufacture silica gel and other silica-based products, these raw materials are treated with chemicals. Silica compounds are utilized in various fields, including microelectronics, optical communications, and thin film technology, as well as in the pharmaceutical industry, particularly in the production of anti-cancer medications [1, 5, 10].
Nano-silica, with modified surface charges and altered hydrophobicity, has proven effective in managing a variety of plant pests and animal external parasites. Lipophilic or Hydrophobic surface-modified nano-silica is particularly useful in combating fowl malaria. These particles absorb excess cholesterol from the host's serum, which is crucial for the malaria parasite, especially during the blood stage. Nano-silica particles can also be applied to control domestic pests, such as flies, as well as internal and external animal parasites, fungi, and worms. Amorphous silica gel serves as a dehumidifier and is used to manage pests like bed bugs, mites, and other insects that reside in the crevices and seams of homes, attics, and furniture [5].
The growing environmental risks, along with the increasing resistance to conventional insecticides [11-15], as well as the limitations on the use of many chemical pesticides and the reduction in the development of new low-risk pesticides [16], have prompted a surge in research focused on biological pesticides. Certain types of cuticular waxes are utilized by pests as protective barriers to prevent water loss, but nano-silicas penetrate these fat barriers, leading to the insect's demise. Additionally, nano-silicas do not alter gene expression in insect cells, making them a viable option as nanobiological pesticides [5].

Nano photocatalyst insecticides

An effective approach to mitigating the harmful environmental impact of pesticides involves the development of biodegradable versions using nanotechnology. One such method involves the use of nanoparticles that enhance the photodegradability of pollutants. For instance, titanium dioxide (TiO_2) nanoparticles are widely utilized as photocatalysts due to their low cost, stability, non-toxicity, and effectiveness. Nanoparticles of imidacloprid, when produced using techniques like the layer-by-layer method or sodium alginate, exhibit higher degradability compared to standard imidacloprid [11].
Chlorfenapyr, a broad-spectrum insecticide, and acaricide, is used to control a variety of insects and mites, particularly those resistant to carbamates, organophosphates, and pyrethroids. It is a pro-insecticide that converts to its active form in the insect's stomach. Its mode of action involves disrupting proton transfer across the mitochondrial membrane and inhibiting ATP production from ADP, ultimately leading to cell death. Chlorfenapyr

is advantageous for nano-formulation production due to its minimal effects on predatory mites and relatively low environmental impact [17, 18].

In another study, the surface properties of Ag/TiO_2 were modified from hydrophilic to hydrophobic through acid etching. The modified Ag/TiO_2 was then combined with suitable additives to produce a chlorfenapyr nano-insecticide formulation. The particles in this formulation have an average size of 100 nm. While this insecticide remains stable in the dark, it is approximately eight times more unstable when exposed to light, particularly UV light, compared to the original version. These formulations help reduce environmental accumulation and toxicity while preserving the insecticide's short-term effectiveness [19].

Contrary to common belief, the nano-formulation of chlorfenapyr exhibits relatively lower toxicity than the conventional form. When both versions were injected intraperitoneally into mice, micronucleus and Comet assays indicated similar DNA damage in blood lymphocytes and chromosomal damage in bone marrow cells. However, the severity of these damages was more pronounced with the conventional chlorfenapyr. Flow cytometry tests on rat liver cells revealed no significant difference in cell death between the normal and nano versions of chlorfenapyr [20].

The nano-formulation of pirimiphos-methyl insecticide was developed using nano TiO_2, SDS-modified nano TiO_2, and in situ-produced nano TiO_2. These formulations are stable and well-preserved in the dark, but they undergo significant decomposition when exposed to UV light. Under 3 days of sunlight, the degradation rates of pirimiphos-methyl nano-formulations were 69%, 90.5%, and 51.9%, and after three hours of UV exposure, the degradation reached 95%, 99.5%, and 7.6%, respectively. In comparison, the conventional insecticide only showed degradation rates of 9.1% and 6.9% under similar conditions [21].

The US Environmental Protection Agency (USEPA) has raised concerns about the use of nano-compounds such as nano-silver and nano-scale pesticides. However, the agency has not yet established specific criteria for measuring potential contamination from nano-pesticides or developed a regulatory framework for controlling nano-formulated pesticide compounds. One of the primary concerns is the enhanced ability of nano-formulated compounds to penetrate and be absorbed by mammalian bodies, including humans, which could pose risks during and after their use [22].

Nano formulation of extracts from plants

Another approach to pest control, particularly for species resistant to conventional pesticides, is the creation and use of nano-formulations derived from plant extracts. The ultra-thin layer formed by these nano-formulations of plant active compounds results in longer-lasting repellent effects [23].

In a separate study, silver nanoparticles derived from Heartleaf moonseed extract showed strong efficacy against head lice and malaria vector mosquito larvae. These silver nanoparticles were found to be about five times more effective in combating head lice than the normal plant extract [24]. Santhoshkumar *et al*. evaluated the impact of silver nanoparticle coatings made from Nelumbo nucifera extract on malaria and filaria vectors. Their findings revealed that the silver nano-formulation exhibited nearly ten times greater larvicidal activity than the regular extract [25]. Similarly, silver nanoparticles synthesized using Annona squamosa leaf extract demonstrated notable effectiveness against mosquito larvae of species such as *Culex quinquefasciatus*, *Anopheles stephensi*, and *Aedes aegypti* [25].

The nano-formulation of *Eclipta prostrata* extract displayed significantly stronger larvicidal effects against malaria and filarial vectors when compared to the regular plant extract. In this case, the nano-formulation had 4-5 times the larvicidal impact on mosquito larvae [26]. Furthermore, silver nanoparticles from the aqueous extract of Mimosa pudica showed exceptional larvicidal properties against malaria, filaria vectors, and ticks. This nano-formulation proved to be more than five times more effective as a pesticide than the traditional plant extract formulation [27].

Nano formulation prepared by microorganisms

Various microorganisms, including fungi and bacteria, are frequently utilized for the biological control of insects. Nanotechnology can enhance the ability of these organisms to penetrate insect bodies. For instance, silver nanoparticles derived from *Cochliobolus lunatus* extract exhibit potent anti-larval effects against *Aedes aegypti* and *Anopheles stephensi*. Notably, these formulations didn't show toxicity to *Poecilia reticulate* at the concentrations used, which are commonly found in the environment, suggesting that they have a minimal environmental impact [28].

Gold and silver nanoparticles produced using the fungus *Chrysosporium tropicum* are effective against *Aedes aegypti* larvae. Among these, silver nanoparticles proved to be 3 times more effective than gold nanoparticles. This research demonstrated that the use of fungal nanoparticles for mosquito control is not only an environmentally friendly approach but also effective in targeting various stages of mosquito larvae. These nanoparticle-fungus formulations enter insect bodies via the cuticle and effectively kill them [29].

The advantages of using Nano formulations of pesticides

A key advantage of nano-formulated pesticides is their ability to achieve the same level of effectiveness as conventional formulations but with significantly lower quantities of active ingredients. This reduces concerns over potential toxic effects on mammals and lessens the environmental impact by minimizing the use of harmful substances. To further decrease the consumption of active ingredients in nano-pesticides and alleviate related concerns, two strategies can be employed: 1) Developing new formulations with alternative materials and techniques to enhance efficacy, and 2) Incorporating synergists into nano-pesticide formulations. The second approach involves creating formulations with layered pesticides and synergists, which can reduce the necessary amounts of active substances while maintaining effectiveness against pests.

An emerging issue is the reuse of pesticides that pests have developed resistance to. The theoretical explanation behind this centers on how insecticides are metabolized in pest bodies and the role of synergists in enhancing the effectiveness of insecticides. For example, pyrethroid insecticides are broken down by oxidase enzymes [30, 31], and before reaching their target site, some of the insecticide molecules are decomposed. The remaining molecules can reach the target area and, if present in sufficient quantities, can kill the pest. The required initial amount of insecticide depends on the enzyme levels in the pest's body, ensuring that enough insecticide remains after metabolism to cause death.

Synergists like piperonyl butoxide (PBO) work by inhibiting the action of oxidase enzymes, preventing insecticides from being broken down, thus allowing smaller amounts to achieve the desired effect on pests. This principle can also be applied to pesticide-resistant insects. In these insects, such as those resistant to pyrethroids, increased gene expression of enzymes, including oxidases, is a contributing factor. By preparing layered pesticide formulations combined with synergists, it is possible to overcome resistance by inhibiting the enzymes responsible for insecticide breakdown. Consequently, adding synergists to nano-pesticide formulations can not only reduce the amount of insecticide needed for sensitive pests but also improve their effectiveness against resistant insects. This is particularly critical for sanitary insecticides, which have received less research attention and development [32, 33]. Due to resistance to pests and limited incentives for pesticide producers to develop new types of sanitary pesticides, only a few options are available in the field of health. Without continued research into these formulations, the reliance on higher quantities of existing pesticides could increase, leading to the known harmful effects documented in various studies.

Environmental concerns and Nano pesticides

The development of environmentally friendly pesticide formulations is increasingly essential in modern times, especially those that offer controlled release, low toxicity to mammals, high efficacy, and compatibility with hydrophilic systems. Traditional fat-soluble pesticides are often presented in highly concentrated forms or emulsions, thick suspensions, and similar formulations, with particle sizes around one micron. To be effective against target insects, large amounts of these conventional insecticides must be used, which can have harmful effects on non-target organisms and the environment [34].

However, research has demonstrated that formulations with nano-scale dimensions can significantly improve bioavailability due to their small size and large surface area, leading to more efficient interactions with the target [35]. That said, the increased permeability that comes with nano-size particles also raises biological and environmental concerns that require careful investigation and management [34]. One example is a nano-formulation of permethrin, which was created by evaporating oil microemulsion solvent in water (a mixture of an aqueous phase and an organic phase). This formulation has particles ranging from 27-151 nm and is amorphous in X-ray diffraction images. The larvicidal effects of this water-dispersible nano-permethrin formulation are far more potent than the conventional permethrin [34].

Pests such as ticks, mosquitoes, and human lice, which cause significant economic and health-related damage to humans and livestock, are often controlled using chemical pesticides. However, these substances can have a destructive impact on the environment and non-target organisms, while also contributing to the rise of pesticide resistance because of their excessive use. As a result, there is an urgent need for new, eco-friendly pesticides. Among the various nanocomposites, inorganic materials like TiO_2 and SiO_2, which are rendered into nano-formulations, have gained considerable attention. These materials are insoluble in water, which may make them less toxic than ZnO, which is water-soluble. Furthermore, since zinc is an essential element for living organisms, its toxicity to humans and livestock is relatively low [36].

Zn nanoparticles can exhibit toxicity in two primary ways: 1) through the release of harmful ions and 2) by inducing stress or irritation due to the particles' surface, shape, or size. These effects can disrupt biological processes or interfere with the intracellular biological environment in their nano form. Toxicity studies on Zn oxide nanoparticles revealed that their LD50 is between 1.3 and 1.4 times that of zinc oxide. Consequently, this research demonstrates that smaller quantities of nano-formulated pesticides can produce pesticide effects similar to those achieved with larger amounts of conventional pesticides. This is particularly significant for managing resistance, as it suggests that resistant arthropods could potentially be controlled using doses comparable to those of traditional pesticides [31].

Conclusion

While considerable research has been conducted on the preparation and characterization of industrial pharmaceuticals, studies focusing on nano-pesticides are still limited. Two main methods have been employed in the production of pesticide nanoparticles: (a) the creation of nanocapsules by encapsulating pesticides using organic compounds, and (b) the evaporation technique of oily microemulsion solvent in water, which combines an organic and an aqueous phase. For instance, permethrin nanoparticles were successfully synthesized using the latter method and tested on various mosquito groups [34]. Similarly, imidacloprid, a model lipophilic insecticide, can be produced through nanoprecipitation and solvent evaporation of oily microemulsion with chitosan [16].

Research in nanotechnology is advancing rapidly, with numerous potential applications for nanomaterials. The utilization of nanoparticles across different sectors continues to expand, showing great promise for the future. In many instances, these materials are more efficient and economical than their conventional counterparts. Given the limited number of insecticides available for health applications, particularly against disease vectors like malaria, and the ongoing decline in research and development coupled with pesticide resistance, the development of new insecticides through nanotechnology is crucial. However, as research and innovation in this area continue to grow, it is equally important to assess the environmental and toxicological impacts of the products being created.

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