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Production, Application, and Environmental Considerations of Nano Pesticides

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ABSTRACT

In recent years, due to the high importance of nanotechnology, this science has been used in various industries, including military, food, chemical, pharmaceutical, medical, and insecticides. Nano-insecticides are of great medical, health, and economic importance because they are used to fight against plant pests and vectors of important diseases such as malaria with greater effectiveness than their conventional types. So far, samples of Nano insecticides have been produced by different methods, but due to the serious need to expand this group of insecticides, it is essential to identify appropriate methods for preparing insecticide nanoparticles. Another issue that necessitates research and development in the field of Nano pesticides is the phenomenon of pest resistance to pesticides, which has seriously reduced the number of suitable pesticides, especially for health purposes. At the same time, further introducing the subject of Nano insecticides to researchers will boost research and development in this relatively new field. In this review, the issue of Nano pesticides was examined and their manufacturing methods were discussed. This study also introduces types of Nano-pesticides and discusses their environmental considerations and toxicity to mammals.

Keywords: Nano pesticides, Nanotechnology, Insecticides, Pesticides.

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INTRODUCTION

Nanotechnology is a field of research, development, and interdisciplinary industrial activity that has grown rapidly in the last decade. The word nanotechnology was first used by Richard Feynman in 1959, but it was officially used in 1974 by a Japanese scientist named Norio Taniguchi from the University of Tokyo, and a book published by him in 1986 provided appropriate information about Nanobiotechnology [1, 2].

Nanotechnology consists of four broad fields Nano medicine, nanomaterials, Nano measurement, and nanoparticle. The word "Nano" is taken from the Greek word meaning "small" and it is technically equivalent to a size of 9-10. In practice, nanoparticles used in nanotechnology have dimensions between 0.1 and 100 nm. Nanoparticles can be obtained either by shrinking large particles (Top-down) or by manipulating individual atoms and molecules to produce Nanoparticles and structures (Bottom-up) [1, 3, 4].

Some of the uses of nanotechnology include the biological restoration of the polluted environment, the release and controlled release of deodorants, antimicrobial substances, and antifungal substances on fabrics and fibers, aerospace, industrial, military, sanitary, medical, and pointed medicine [5, 6]. Nanomaterials are usually made during chemical processes. Determining the structure of nanoparticles made with the help of AFM (Atomic Force Microscope) and STM (Scanning Tunneling Microscope) is done, and due to the importance of STM in nanotechnology, the Nobel Prize was awarded to two inventors, Ann Binning and Rohrer, in 1986. In the body of living organisms, nanomaterials play a central role in the durability and survival of life. All the activities and interactions in the cells and tissues of living organisms are dependent on materials such as proteins and nucleic acids that have a Nanostructure [5, 7].

Nanoparticles inside the body of insects can be used as free Nanotechnology; in the same way, insects take advantage of the ferromagnetic nanoparticles, which act as receivers of Geomagnetic, in their lives. Especially insects use this property in orientation finding nests and feeding, and it plays an essential role in the life of social insects. Especially, these Nanoparticles are seen more in the eyes, head, and antennae. Unfortunately, the types of Nanoparticles that exist in the body of living organisms with free technology are not sufficiently exploited [1, 8, 9].

In recent years and with the advancement of nanotechnology, the production of different types of Nano pesticides was done in different ways and many groups of insects were tested with these substances. Considering the environmental problems and costs caused by the consumption of large amounts of conventional pesticides in nature, as well as the problems caused by the resistance of pests to these pesticides, research, and development in the field of Nano-pesticides is presented as a necessity. This article deals with the necessities, existing methods, and challenges facing the production and use of Nano pesticides.

Nano silica as a Nano biological pesticide

Silica is a very abundant substance in the earth. Natural silica such as quartz sand, rocks, and clay are used as raw materials for construction. To produce silica gel and other silica products, the above-mentioned raw materials are combined with chemicals. These materials are used in microelectronics, optical communications, and thin film technology, as well as in pharmaceuticals in the production of anti-cancer drugs [1, 5, 10].

Nano-silica with surface charge and changed hydrophobicity can be successfully used to control a wide range of plant pests as well as external parasites of animals. Hydrophobic or lipophilic surface-modified Nano silica can be well used in the treatment of fowl malaria. These substances absorb excess cholesterol from the host's serum, which is used by the malaria parasite, especially the blood cycle. Nano silica particles can be used in the fight against domestic insects, flies, and internal and external parasites of animals, fungi, worms, etc. Amorphous silica gel is another dehumidifier that is used to control pests such as mites, bed bugs, and other pests that nest in the seams and cracks of the house, attic, and household items [5]. The increase in environmental risks and the phenomenon of resistance to insecticides [11-15], as well as the restriction of the use of many chemical pesticides and the reduction in the production of new types of low-risk pesticides [16], have led to the expansion of research in the field of biological pesticides. Pests use some types of cuticular waxes as protective barriers against the loss of water in their bodies, but nano silicas are absorbed in this fat barrier and cause the death of the insect. Also, nanosilicas do not change gene expression in insect chips, so they can be used as nanobiological pesticides [5].

Nano photocatalyst insecticides

One of the appropriate technologies in the field of reducing the harmful environmental effects of pesticides is the production of their degradable types with the help of nanotechnology. One of these methods is the use of Nanoparticles that increase the photo degradability of pollutants. For example, titania nanoparticles such as TiO_2 are one of the most widely used photocatalyst compounds, which are cheap, stable, non-toxic, and effective. Nanoparticles of imidacloprid insecticide produced by layer-by-layer technique

(LDL) or sodium alginate had higher degradability than normal imidacloprid [11]. Chlorofenapyric is a broad-spectrum insecticide and acaridae that is used against many insects and mites, especially those that are resistant to carbamate, organophosphate, and parathyroid insecticides. This substance is a pro-insecticide that becomes the main insecticide due to decomposition in the insect's stomach. The mode of action of this insecticide is to disrupt the flow of proton transfer in the mitochondrial membrane and inhibit the production of ATP from ADP, thus causing cell death. Because old chlorophene has no effect on predatory mites and has relatively low negative effects on the environment, it is a good option for producing Nano formulations [17, 18].

In another study, the surface property of Ag/TiO2 was changed from hydrophilic to hydrophobic by acid etching. Ag/TiO2 modified Ag/TiO2 insecticide, suitable additives were mixed to produce chlorfenapyr Nano insecticide formulation. The average diameter of the particles of this formulation is 100 nm. This insecticide is completely stable in the dark, but it is about 8 times more unstable in front of light, especially UV light than the original insecticide. Such formulations can reduce its accumulation in the environment and its harmful effects while maintaining the short-term effectiveness of the insecticide [19]. On the other hand, contrary to popular belief, the Nano formulation of chlorfenapyr has relatively less toxic effects than its normal type, and different amounts of these two types of formulations were injected intraperitoneally into mice, and micronucleus and Comet tests showed that similar DNA damage in blood lymphocytes Environmental and chromosomal damage was caused in bone marrow cells. Of course, the severity of these damages was higher than normal chlorfenapyr. Tests performed by flow cytometry on the liver cells of rats showed that the amount of cell death induced by normal and Nano chlorfenapyr is not significantly different [20].

The Nano formulation of pirimiphos-methyl insecticide was prepared with the help of Nano TiO2, Nano TiO2 modified with SDS, and Nano TiO2 produced in situ. These formulations are well stored in the dark and are stable, but their decomposition increases strongly in front of UV light. The degradation of pirimiphos-methyl Nano formulation was 69%, 90.5%, and 51.9% under three days of sunlight and 95%, 99.5%, and 7.6% after three hours under UV. While the rate of decomposition of conventional insecticide was equal to 9.1% and 6.9% in the mentioned conditions [21]. The USEPA has expressed its concerns about Nano-compounds such as Nano-silver and Nano-scale pesticides, but so far it has not proposed any measurement criteria for possible Nano-pesticide contamination or a specific control framework for Nano-formulation pesticide compounds. One of the reasons for this concern is the high penetration and absorption of Nano-formulated compounds into the body of mammals, including humans, which may pose risks during use and after [22].

Nano formulation of extracts from plants

One of the other methods and formulations in pest control, especially types resistant to common pesticides, is the preparation and use of Nano formulations of extract extracted from plants. The very thin layer formed by the Nano formulation of the active substances of the plants causes longer-term repelling effects [23].

In another study, silver Nanoparticles of *Heartleaf moonsead* extract have very good effects against head lice and larvae of malaria vector mosquitoes. In this study, silver nanoparticles prepared from plant extract have about 5 times more anti-head lice effect [24]. In the study of Santhoshkumar *et al*., the effects of coating the formulation of silver nanoparticles of *Nelumbo nucifera* extract on malaria and filaria vectors were evaluated. In this study, silver nanoformulation of plant extract compared to its normal extract has almost 10 times the larvicidal effects [25]. Silver nanoparticles prepared by reduction reaction using *Annona squamosa* leaf extract had good effects against *Culex quinquefasciatus*, *Anopheles stephensi*, and *Aedes aegypti* mosquito larvae [25].

The nanoparticle formulation of *Eclipta prostrata* extract has much greater larvicidal effects against malaria and filarial vectors compared to the normal plant extract. So, in comparison, nanoformulation has a 4-5 times stronger effect on mosquito larvae [26].

Silver nanoparticles of aqueous extract of *Mimosa pudica* plant have very good larvicidal effects on malaria filaria vectors and ticks. In this study, the nanoformulation has more than 5 times the pesticide effect compared to the conventional formulation of the above plant extract [27].

Nano formulation prepared by microorganisms

Several groups of microorganisms, such as bacteria and fungi, are commonly used in biological control of insects. Using nanotechnology, it is possible to facilitate the entry of these factors into the body of insects. Silver nanoparticles made from *Cochliobolus lunatus* extract have strong anti-larval effects against *Aedes aegypti* and *Anopheles stephensi*. These formulations did not have a toxic effect on *Poecilia reticulate* in the amounts used, which are abundant in the environment, which indicates the acceptable environmental effects of these substances [28].

Nano particles of gold and silver using the fungus *Chrysosporium tropicum* are effective against *Aedes aegypti* larvae. In these tests, silver nanoparticles were three times more effective than gold nanoparticles. This study showed that the use of nanoparticles of this mushroom to control mosquitoes, besides being an environmentally compatible method, is effective in controlling the different stages of these larvae. These nanoparticles containing fungi enter the body of insects through the cuticle and kill them [29].

The advantages of using Nano formulations of pesticides

One of the advantages of Nano-formulations of pesticides is that they are as effective with lower amounts of effective insecticides as conventional formulations with high effective amounts. This issue, regardless of the concern of toxic effects on mammals, because it causes less consumption of effective substances, it also causes less adverse effects on the environment. Theoretically, the methods that may cause a further reduction in the consumption of effective substances in the Nano-formulation of pesticides and as a result reduce the aforementioned concerns can be operationalized in two ways: 1- Finding formulations with different materials and techniques for More effect, 2- Adding substances such as synergists to the formulation of Nano pesticides. In the recent method, formulations containing different layers of pesticides and synergists can further reduce the amounts of effective substances required for a proper effect on pests in the insecticide formulation.

A new issue is raised under the title of reuse of pesticides to which resistance has occurred in pests. The theoretical explanation of this issue depends on the effect of insecticides and their metabolism in the body of pests, as well as the effect of synergists in applying synergistic effects. For example, pyrethroid insecticides are decomposed by oxidase enzymes [30, 31] so after using insecticides and entering the body of living organisms, before the insecticide molecules reach their main site of action reach, some of them are decomposed by these enzymes, and the rest of them reach the place of effect, if enough, they cause the death of the insect. Depending on the level of expression of these enzymes, the initial amounts of insecticides needed to control insects are defined so that after some amount is broken down by the enzymes, they remain in the body of the target insect enough to cause their death.

By using synergists such as piperonyl butoxide (PBO), which inhibits oxidase enzymes, insecticide molecules are not broken down in the body of the target insect; therefore, smaller amounts of it cause the desired effect on insects. The same theory holds for pesticide-resistant insects. In resistant insects, for example, pyrethroids, one of the mechanisms is an increase in gene expression of various enzymes, including the most important ones, oxidases. Therefore, the preparation of layered secondary formulations of pesticides and synergists can make them more effective in resistant insects by inhibiting the enzymes that decompose insecticides. Based on this, adding synergists to the Nano-formulation of insecticides can be used for resistant insects in addition to reducing the amount of insecticides used against sensitive insects. This issue is especially important in the case of sanitary insecticides that have been less researched and produced [32, 33]. In other words, due to the resistance of pests to sanitary pesticides on the one hand and the lack of motivation and incentives (especially of the economic type) in pesticide production companies to produce new types of sanitary pesticides, a very small number of pesticides are available for use in the field of health. If such research is not done, common pesticides should be used with a higher amount, the harmful effects of which have been reported in various studies.

Environmental concerns and Nano pesticides

The preparation of environmentally friendly formulations of pesticides is one of the necessities of the present century, which have the characteristic of controlled release with high efficacy, low toxicity for mammals, and compatibility with hydrophilic formulations. Conventional fat-soluble pesticides often come in highly concentrated solutions and additives in the form of emulsion formulations, thick emulsions, thick suspensions, etc. These formulations have a particle size of about one micron, and the use of these conventional formulations of insecticides requires the use of amounts that are effective on the target insects. These concentrations have adverse effects on non-target organisms and the environment [34].

However, it has been shown that the formulation in NATO dimensions can significantly increase the bioavailability, which is due to the very small size and, as a result, the very large contact surface [35]. However, there are certain environmental and biological concerns precisely because of the increased permeability due to Nano-size that must be studied and managed [34]. Permethrin Nano formulation was prepared by evaporation of oil microemulsion solvent in water (which is obtained by mixing an organic phase and an aqueous phase). This formulation has a particle size of 151-27 nm and is amorphous in X-ray refraction photographs. The larvicidal effects of this water-dispersible Nano-permethrin formulation are far more than the usual type of permethrin [34].

Very important pests such as ticks, human lice, and mosquitoes, which have caused great economic and life losses to humans and livestock, are often controlled by chemical pesticides, which in addition to the destructive effect on the environment on organism's untargeted living has many negative effects. In addition, with the high use of these substances, regardless of the adverse effects on the target animals such as livestock and humans, the phenomenon of resistance to pesticides, which has become very common due to their excessive use, has decreased their effectiveness. Meanwhile, new and environmentally friendly pesticides are much needed. Among the nanocomposites, inorganic materials that have become Nano, such as TiO_2 and SiO_2, have received much attention. These materials are not soluble in water, so they may have lower toxicity compared to ZnO which is soluble in water. In addition, Zn is one of the elements required by the body of living organisms, so its toxicity for humans and livestock seems to be less [36].

Zn nanoparticles exert their toxic effect in two ways: 1) chemically by releasing toxic ions and 2) causing stress or irritation caused by the surface, size, or shape of nanoparticles. These stimulations can inhibit biological processes or have an inhibitory interaction with the intracellular biological environment in its Nano form. Biometric tests of Zn oxide nanoparticles showed that the LD_{50} of zinc oxide nanoparticles is between 1.3 and 1.4 of zinc oxide. Therefore, the results of this research show that smaller amounts of Nano formulation of a pesticide can have appropriate pesticide effects and are comparable to larger amounts of conventional pesticides. This issue plays an important role in the management of resistance because it may be possible to control resistant arthropods by using doses similar to conventional pesticides [31].

CONCLUSION

Although there has been a great deal of research on various methods for the preparation and characterization of industrial pharmaceuticals, very few such studies have been conducted on Nano pesticides. The two methods that have been used in the production of pesticide nanoparticles are a) the production of Nanocapsules containing pesticides by encapsulating the pesticides using organic compounds and (b) the evaporation method of oily microemulsion solvent in water (which is a mixture of an organic phase and an aqueous phase). For example, permethrin nanoparticles were successfully prepared by the recent method and tested on several groups of mosquitoes [34]. Imidacloprid insecticide as a model lipophilic pesticide can be produced by nanoprecipitation and solvent evaporation of oily microemulsion using chitosan [16].

It can be concluded that research and development in the field of nanotechnology are progressing rapidly and a wide range of applications are envisaged for nanomaterials. The use of nanoparticles in various fields is expanding day by day and seems to be very promising for the future. These materials are in many cases better in terms of efficiency and economy than similar conventional materials. Due to the small number of insecticides suitable for health purposes and to fight against the vectors of diseases such as malaria and due to the decrease in research and development and the phenomenon of resistance to insecticides in vectors, the production of new types of insecticides with the help of nanotechnology is important. However, it seems that in parallel with the expansion of research and development in this field, the examination of environmental considerations and toxicology of manufactured products is also of particular importance.

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