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Utilizing Metal-based Nanoparticles as Nanopesticides for Pest Management

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Abstract

Metal-based nanoparticles (MNPs) are considered as a valuable ingredient of nanopesticides, as these new methods are offered to improve the pest control of the agriculture system and combat the ecological effects of conventional pesticides. Silver, copper, zinc, nickel, gold, iron, aluminium, titanium and other MNPs have peculiar nanoscale characteristics. These properties enable MNPs to be engineered to release under controlled and extended release which lowers the frequency of application and the environmental runoff. This mechanism is known to minimize the risks to the beneficial species and non-target animals as well as maximize the efficacy of pest management as per the principles and rules of sustainable crop protection. This review evaluates nanopesticides according to their specific targets. Additionally, examined are the mechanisms of action of metal-based nanoparticles, including chemical interactions, biological processes, and physical disturbance. The review also explains how MNPs damage membranes, denaturize proteins, interfere with DNA and damage mitochondria, all of which damage cellular integrity. Regardless of these advantages, there are still a lot of challenges to be solved, particularly in relation to the environmental impacts of MNPs, their influence on soil, potential harms to human health and ecosystem dynamics. A number of problems need to be fixed before MNPs can be used to their full potential in sustainable agriculture.

Keywords: Metal Nanopesticides, Green Synthesis, Conventional pesticides, Environmental risks.

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1. Introduction

According to report of Food and Agriculture Organization (FAO), average 40% crops were damaged due to pests in 2022, or around USD 220 billion [1]. By the end of 2050, there will be 9.9 billion people on the earth due to the present fertility rate [2]. Since the world's population is anticipated to increase by 48% by 2050, efforts are still being made to find novel ways to improve food production [3]. The production of food depends heavily on agriculture. Climate change, water scarcity and some biotic and abiotic pressures are examples of natural variables that might reduce crop output [4]. Through the employment of properly designed sensors, analytical systems, nanoscience and nanotechnology play a targeted and effective role in enhancing agricultural yields and assisting management decisions. The modern agricultural sector uses nanotechnology for pest control and diagnostics [5]. Smart farming has been made possible by the use of nanotools in the form of nanopesticides and fertilizers. Ag, Cu, Zn, Mo, Fe, Si, Mn, Ti, their oxides, carbon nanotubes and nanoformulations of conventional agricultural inputs including phosphate, urea, validamycin, azadiractina and sulphur tebuconazole have all been transformed into nanofertilizer and nanopesticides forms [6]. Using pesticides is one common strategy.

Any chemical, biological or combination of compounds meant to prevent, eradicate, or control pests or to promote the growth and development of plants is known as a "pesticide" [7]. Nanopesticides offer precision pest control by utilizing special qualities of nanoparticles. They are manufactured to save plants, boost leaf coverage, lower application waste, & simplify formulation [8]. Nevertheless, traditional pesticides also possess several weaknesses, including lack of selectivity, contamination of environment as well as resistance of pests. Nanopesticides, on other hand, release their active ingredients gradually, extending their effectiveness and reducing repeated applications [9]. Among different kinds of nanopesticides, some of common inorganic nanoparticles are metal-based nanoparticles (MNPs), like copper nanoparticles (CuNPs), nickel nanoparticles (NiNPs), silver nanoparticles (AgNPs), aluminium nanoparticles (AlNPs), titanium nanoparticles (TiNPs), zinc nanoparticles (ZnNPs), iron nanoparticles (FeNPs) and gold nanoparticles (AuNPs) [10]. These MNPs improve pest control effectiveness and minimize their environmental harm. Furthermore, these innovated inorganic formulations allow active chemicals dissolve more effectively, remain stable for long time, release in a controlled manner, lower evaporation, target pests more smartly, diminish damage to other creatures and environment, and lowers the pesticide's odor [11].

Their minute size and great surface area enable enhanced contact with target organisms, including algae, bacteria, fungi, mites, weeds, insects, snails, birds, nematodes, viruses and larvae. Termites, fish, rats and other pests are targeted by them. The development of insect and mite eggs is also hindered by them, in certain situations [12]. The possible environmental hazards connected to nanopesticides have been highlighted by a number of recent studies, so it is appropriate to give an overview of the findings and future research opportunities. The benefits, prospects and difficulties associated with applying nanotechnology in agriculture have been covered in recent literature reviews [13]. In contrast to traditional pesticides, we focus on creating nanopesticides with better qualities or possible environmental hazards. It is also discussed on the existing problems and possible solutions to enhance the analysis of the benefits and environmental risks of nanopesticides. The current scientific development in the field of agriculture is reviewed in this paper, with an emphasis on Nanopesticides. The weaknesses of traditional pesticides were quickly addressed as well as the relevance of nanopesticide in crop protection and controlling pests, their efficacy against the target pests, the adverse effects on non-target organisms and other environmental aspects and existing risk analysis and governing standards. The paper mainly talks about advantages and disadvantages of using nanopesticides to control pests in agriculture.

2. Metal-Based Nanoparticles

Most well-known inorganic nanoparticles are metal-based nanoparticles (MNPs), which involves titanium nanoparticles (TiNPs), copper nanoparticles (CuNPs), nickel nanoparticles (NiNPs), silver nanoparticles (AgNPs), aluminium nanoparticles (AlNPs), zinc nanoparticles (ZnNPs), gold nanoparticles (AuNPs) and iron nanoparticles (FeNPs) [10]. These high inorganic formulations also make active chemicals dissolve more effectively, have longer shelf life, release in a regulated and controlled way, reduce evaporation, attack pests more specifically, reduce the harm of other organisms and the environment and reduce the odour of the pesticide [11]. MNPs have gradually been embraced as antimicrobial agents due to their anti-bacterial, anti-viral and anti-fungal properties [14]. By resolving the shortcomings of traditional pesticides, their inclusion into agricultural chemicals based on nanotechnology, such as nanoherbicides, nanoemulsions and nanofungicides has become more important in disease as well as pest management [14]. They offer novel strategies for precise nanoscale distribution, improved formulation and active component design [15]. MNPs have a numerous beneficial properties, including robust activity and more surface area-to-volume ratios [16]. AgNPs, for example, are extremely efficient against a variety of diseases due to their strong antibacterial characteristics [17]. CuNPs also show potential because of their fungicidal and bactericidal properties, which control plant diseases using low volumes and decrease environmental runoff. These characteristics indicate how MNPs can enhance pest control methods while decreasing harmful effects on environment.

3. Comparison of Conventional Pesticide and Nano-pesticide

3.1. Conventional pesticides

In order to prevent or eradicate a pest organism, conventional pesticides are manufactured artificially. They play a key role in disease control in modern agricultural practices [18]. The most well-known kinds of pesticides are organochlorine pesticides, carbamate pesticides, synthetic pyrethroids and organophosphates. They are separated into rodenticide, insecticide , herbicide, fungicide and bactericides based on the target such as weeds, insects, rodents, pathogens and fungi [19]. A significant amount of pesticides are lost after application as a result of photolysis, volatilisation and degradation and only about 0.1% of them are efficient against the targeted organisms. Additionally, conventional pesticides have poor biological activity and dispersibility [20]. Numerous studies have highlighted influence of pesticides on human health. For example, long term exposure to diazinon increases the risk of lung damage, cancer and cytogenetic effects in humans [21]. Breast milk is reported to contain hexachlorocyclohexane, heptachlor, hexachlorobenzene, methoxychlor, DDT, chlordane and endosulfan, all of which influence the health of infants [22]. Because of possible risks to human and environmental health, conventional pesticides are therefore discouraged. In order to increase crop output and control plant pests and diseases, there is a need for sustainable alternative methods utilizing modern & advanced technologies like nanotechnology.

3.2. Nanopesticides

Pesticides that are bound to a hybrid substrate, embedded in a matrix, or on functionalized nanocarriers activated by external stimuli or enzymes are referred to as nanopesticides. Because of their unique shape and characteristics, nanosized particles are believed to examine pesticide activities in novel nanocarrier formulations on basis of variety of materials, including silica, polymers, lipids, copolymers, metal, carbon, ceramic and others [23]. In comparison to conventional pesticides, these nanoparticles have several advantages, including high level of efficiency, low level of environmental degradation, level of resistance, monetary gains and sustainability financial assistance. Due to these qualities, they are better alternatives to efficient and sustainable crop production of agricultural products. Due to an increased ratio of surface area to volume, nanopesticides are capable of reacting with target organisms better than regular pesticides. Due to this higher efficacy, environmental pollution is reduced since lower doses of nanopesticides can be employed at reduced doses to obtain same or even higher results [25]. Also, nanopesticides allow active substances to be more stable against degeneration and ensure a more consistent and extended release in agricultural sector [26]. This reduces exposure to environment and removes necessity of using many applications of nanopesticides. Nanopesticides minimize effects of nontarget organisms, including useful insects and microorganisms, since it targets pests directly [27]. This property goes a long way in reducing toxicity of whole ecosystem and guaranteeing well-being of human beings & ecosystem. Nanopesticides facilitate farmers and agricultural industry with financial advantages by enhancing agricultural productivity & quality (Figure 1)[24].

3.3. Merits of nanopesticides in contrast to conventional pesticides

Before spraying the target crops or the surrounding area, conventional pesticide formulations with various additives are typically diluted with water. The effectiveness of the active ingredients may be reduced by hydrolysis, photolysis or degradation brought on by different environmental factors. The regulated release of the active compounds from nanocarriers has the ability to enhance the exposure of the target organisms and in this way, decreases the dosage required for plant protection [25]. In other words, Nanopesticides can show more stability and controlled release in contrast to conventional pesticides, so they are capable to increase exposure time and control or handle efficacy to the target organisms (Table 1).

4. Mechanism of Action of Nano pesticides

NPs can make weakly water-soluble pesticides more soluble so that pests can absorb them more readily [26]. By adding molecules (ligands) that bind to particular receptors, proteins, antibodies, or peptides on the target pest, nanopesticides are meant to be more functionally specific and target particular plant tissues or pests. Pesticide side effects are reduced by this procedure [27]. The smaller size of nanopesticides guarantees their direct delivery to intracellular targets and more efficient penetration of biological barriers like plant cell walls or insect cuticles when compared to traditional pesticides [28]. Active chemicals can be released in a controlled and regulated way because NPs encapsulate them and shield them from environmental deterioration [29]. Release of active compounds is stimulated by environmental factors like pH and temperature, guaranteeing proper timing and location [30]. Nanopesticides have the ability to enter pest cells through endocytosis. Nanopesticides are also able to deal with drift and leaching which are some of the greatest problems of conventional pesticides due to their low volatility and solubility. Some nanopesticides are also programmed to break down to harmless byproducts after release of its active ingredients [35]. Nanopesticides are usually supplemented with adjuvants and synergists to enhance the number and total pesticidal effect on the target organisms [36].

4.1. Mechanism inside pest cell

Some of the ways that nanopesticides can act in pest cells include membrane disordering, mitochondrial variation, DNA destruction and protein degradation. On getting into a cell, nanopesticides cause several cytotoxic effects disrupting normal cellular activities. Besides binding DNA and triggering genotoxic effects potentially causing mutations or genomic instability, they also affect membrane integrity which causes structural damage and changes in permeability. Disruption of ATP production leads to dysfunction of the mitochondrion which impacts cellular metabolism. More so, nanopesticides promote protein degradation which leads to loss of biological activity and morphological integrity. Their presence results in free radical image and cellular stress by promoting the formation of ROS which degrades proteins, lipids and nucleic acids. All these effects together lead to abnormal functioning of the cells and may culminate in cell death either by necrotic or apoptotic processes (Figure 2).

5. Nanoparticles' Potency as Nanopesticides

Increased water solubility, increased stability, lower dosages, release behavior of active ingredients, smart targeting, protection against degradation and overall productivity are just a few benefits of using nanoparticles as pesticides.

5.1. Solubility

The greatest quantity of pesticide which can dissolve in every solvent at particular pressure and temperature circumstances is known as the pesticide's solubility [31]. Low solubility is a common problem for conventional insecticides, which reduces their efficacy [32]. Because smaller nanoparticles have high surface area exposed for interaction with solvents, MNPs in particular show enhanced solubility with decreasing particle size. MNP solubility is a complicated process that is impacted by ambient factors and physicochemical characteristics.

5.2. Stability

The preservation of particular nanostructural traits, such as opposition to aggregation, anti-clumping, crystallinity, coherence(compositional integrity), morphological stability (size and shape) and surface chemical properties is referred to as "nanoparticle stability" in general [33]. It has been demonstrated that nanopesticides are more stable and active than traditional pesticides in all environmental conditions [34].

5.3. Controlled Release

Active chemicals may usually be released by nanopesticides in a controlled way. By maintaining a steady concentration of the pesticide throughout time, this controlled release technique enhances its effectiveness and lowers the possibility of overdosing. To put it briefly, controlled release could be adjusted to provide desired results in predetermined amounts of time [35].

5.4. Target Specificity

In order to minimize incidental to beneficial species and lower the likelihood of resistance or opposition development, nano delivery systems can be designed for targeted delivery to organisms [36].

5.5. Efficiency

Nanopesticides typically require lower dosages than conventional pesticides due to their unique physicochemical properties and high surface area-to-volume ratio[32]. Nanopesticides are 31.5% more effective than traditional pesticides [24].

6. Environmental harms and Compliance of nanopesticides

Because of their rising production and use, engineered nanoparticles are released into the environment more frequently [37]. The usage of nanopesticides in agriculture will naturally increase.

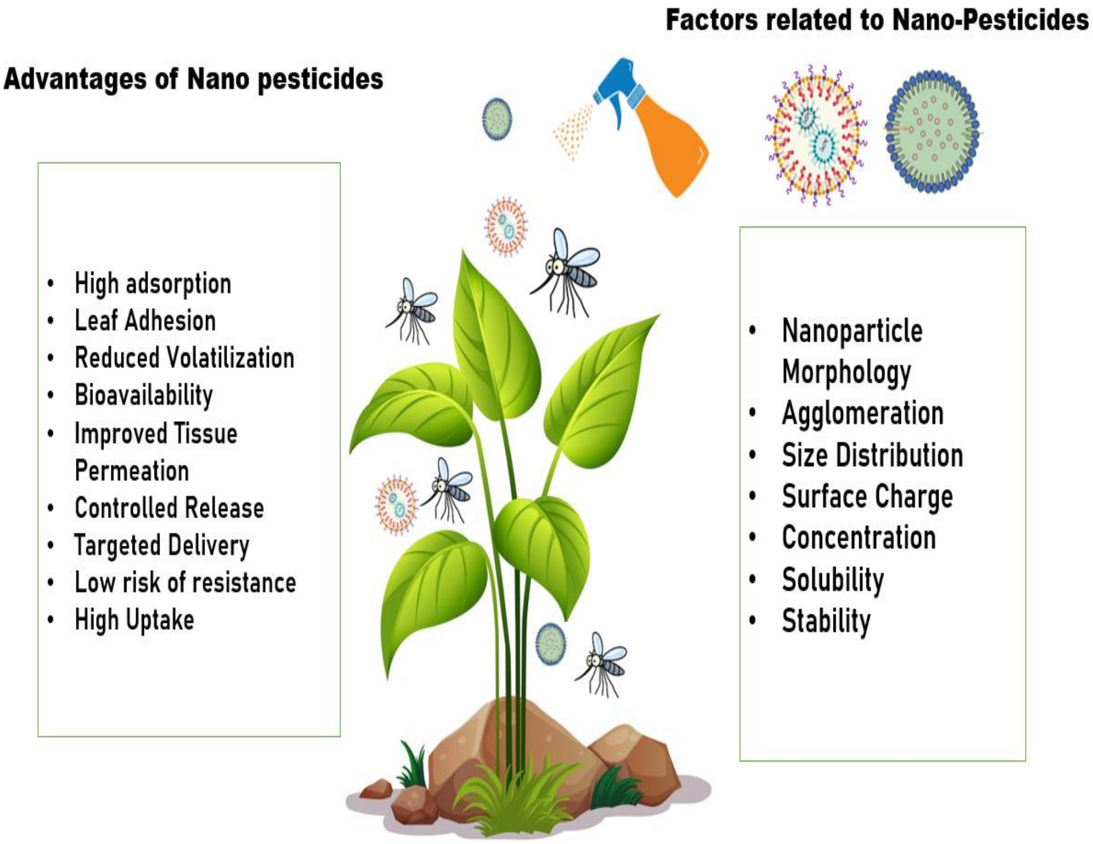

Figure 1. Nanopesticides in Pest Control

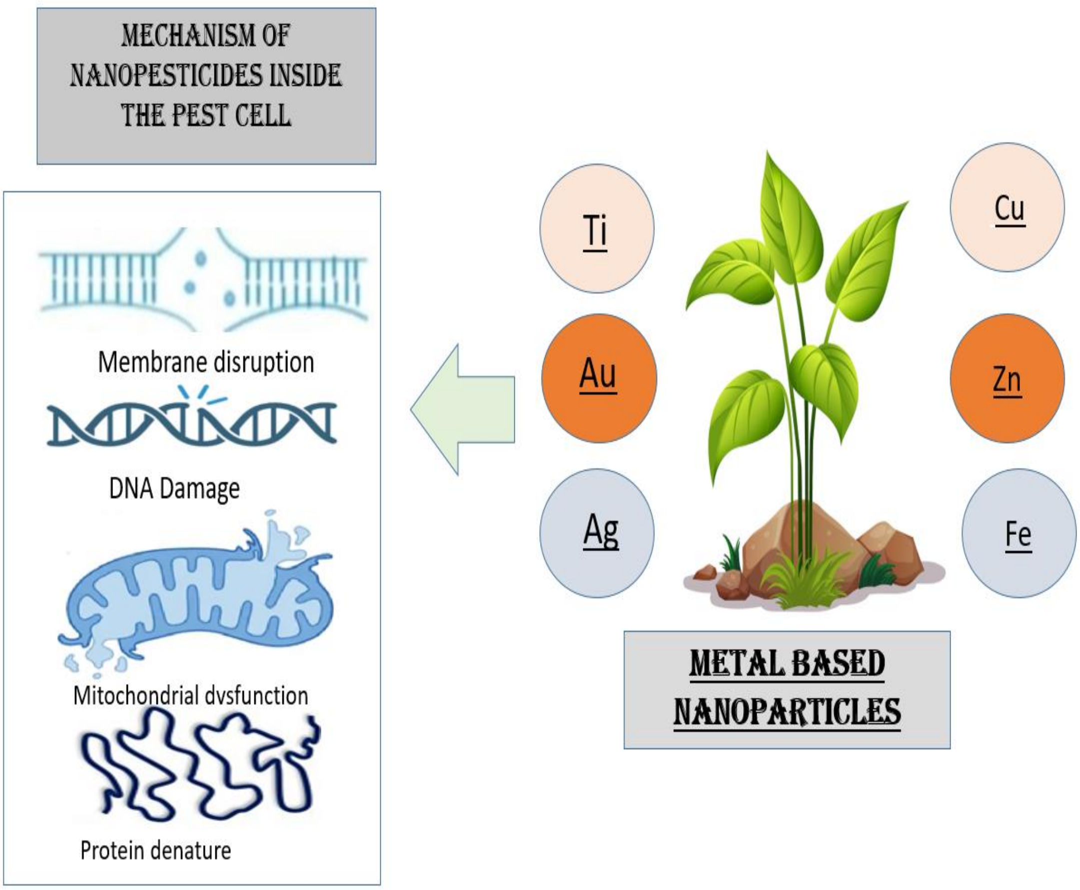

Figure 2. Action Mechanism of nanopesticides [46]

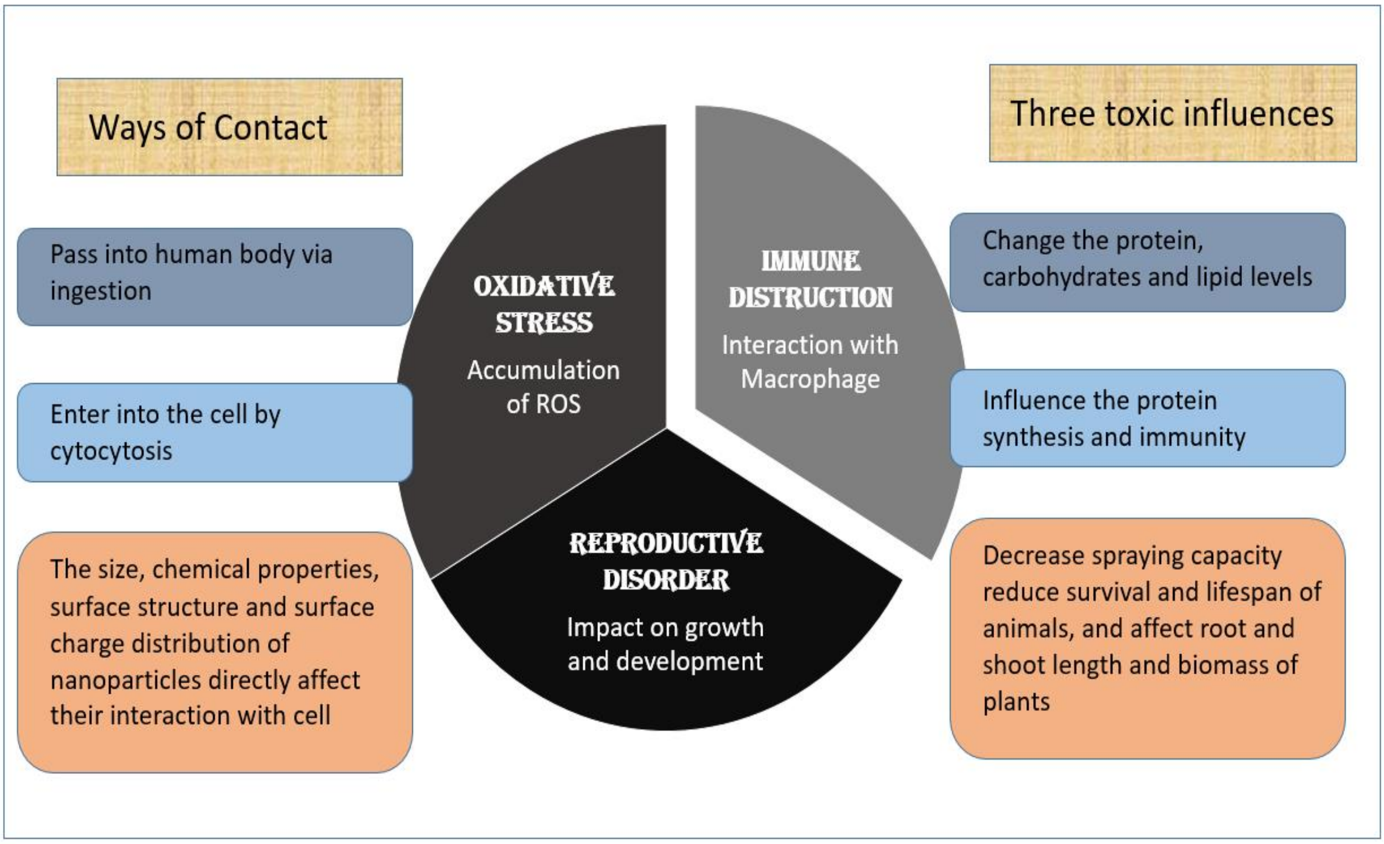

Figure 3. Toxicological effects of Nanopesticides

Table 1. Comparison of Conventional pesticides and Nano-Pesticides

Characteristics	Conventional Pesticides	Nanopesticides
Organic solvent content	More	Low or not required
Solubility	Less	High
Dispersibility	Low	High
Dosage requirement and frequency	More	Low
Efficiency	Reduced	Increased uptake/Efficacy
Bioavailability	Less	High
Degradation in soil and plant	Slower	Faster Degradation
Regulated release	Low	High
Harm to target organisms	Present	Enhanced harm to target organisms
Toxicity to non-target organisms	Present	Yes (comparatively low)
Bioaccumulation	High	Moderate or low
Natural threat assessment methods	Available	Partially available
Regulatory Guidelines	Present	Partially available (under development)

According to Li et al. (2019), these compounds maybe harmful or risky to organisms that are not targets to be intented, assembled or collected through transport and bioaccumulation and engage with other environmental contaminants and dissolved organic matters to further harm the environment [38]. Nanoparticles can immediately stack up in a food chain and have an impact on plant growth, which may lead to human and animal exposure. Even though research has shown that nanoparticles pose a harm to the environment, environmental remediation has shown a great deal of interest in them [39]. Metal-based nanoparticles have some beneficial impacts on plants, but they can also have some harmful ones. Many studies examine toxicity of metal-based nanoparticles in particular, including the toxicity of gold nanoparticles [40], silver nanoparticles [41], zinc oxide nanoparticles [42], copper nanoparticles [43], nickel nanoparticles [44], magnesium oxide nanoparticles [45], titanium dioxide nanoparticles and iron nanoparticles. Additionally, there are five primary ways that nanoparticles interact with biological systems: (i) mechanical effects resulting from their firm and specific interfaces; (ii) chemical effects of dissolving metal ions in solution; (iii) catalytic activities occurring on surfaces; (iv) changes in chemical environment or conditions, such as pH changes [47] and (v) surface effects from protein binding, either covalently or non-covalently, as well as oxidative effects. Additionally, nanoparticles have the ability to interface with cell membranes, changing their permeability and structure. Such interference may negatively impact the emergence of seedlings as well as the general growth of plants by impairing cellular integrity, nutrient incorporation and ion transport systems. Some nanoparticles can induce genotoxicity by breaking DNA of plant cells. The mutations, hereditary stability and chromosomal disorder may affect plant growth and fecundity (reproductive output). The intake of AgNP disequilibrates process of water and small molecules, stops the production of chlorophyll, reduces rate of photosynthetic activities and enhances generation of reactive oxygen species. This ROS excessive load destroys chloroplasts and may lead to slow growth or even plant death [54].

The NPs react with plants through many different chemical and physical reactions which signals transduction pathways that lead to the production of ROS [55]. By producing ROS like hydrogen peroxide, superoxide radicals, and hydroxyl radicals, nanoparticles can cause oxidative stress in plants. Lipids, proteins and DNA are among the biological components that are harmed by excessive ROS generation, which results in cell death and stunted growth. Oryza sativa was poisoned by high concentrations (1000 µg mL−1) of silver nanoparticles(25nm), which damaged vacuoles and cell walls when they penetrated the roots [48]. By preventing the absorption of nutrients and water, high quantities of nanoparticles can have a direct impact on seed germination. Poor initial growth and decreased seedling emergence result from this. Research have proved that nanotechnology has been used extensively in various applications such as in the agriculture, industry and medical field. Nevertheless, because of the possible toxicology influence of the nano particles and the deficiency of the current study models, we itemize some of the scientific issues towards the wholesome approach to the nano particles toxicology and nanotechnology which can be the common concerns in the next 10 years as well.

The toxicological events involving the response to nano particles are usually complicated. The following conditions might exist, one is the fact that one type of nano particles can cause several body systems damages, another is that several types of nano particles can result in single body system damage or the damage of several organs. The future study should be more concerned with this consideration (Figure 3) [49]. Few studies have been published on how nanopesticides interact with other pollutants or environmental toxins. Therefore, further research on this topic is necessary to properly comprehend nanopesticides and their relationship to the environment. Understanding the several facets of nanoformulations, such as how the active ingredients' behaviour changes in nanoformulations and how pure active ingredients compare to both traditional formulations and nanoformulations is equally crucial [50]. Since nanopesticides can enter the environment unintentionally or on purpose, just like conventional pesticides, ecological compartments like water, soil and air have their own complications that call for particular concerns of risks posed by nanopesticides [51].

Concerns about the fate, decomposition and toxicity of nanopesticides as well as methods for assessing environmental risk are being highlighted by the increased interest in their use [52]. On the other hand, increased use of nanomaterials in farming methods or their possible integration into food could raise exposure levels and alter the ratio of advantages to disadvantages. It is difficult to assess and quantify the significant elements of cytotoxicity and genotoxicity as well as to characterise the biological safety of nanopesticides due to the complexity of nanostructures, such as reactivity, shape, electric charge and size [8]. The mechanisms by which nano-enabled strategies achieve their goals, such as how nanomaterial characteristics like charge, shape, size and hydrophobicity affect interactions with plant physiology [53].Regulations pertaining to engineered nanomaterials in agricultural food safety are developing in the European Union, but they are difficult to implement because of the design variables of nanomaterials and the complexity of agricultural systems, including biotic and abiotic elements [13].

7. Conclusions and Future prospects

Nanotechnology shows potential in agricultural productivity, while nanopesticide formulations have shown potential influence in pest control and management. Regardless of the advantages of nanotechnology, changes in environment have occured. Since the use of nanotechnology in agriculture and the food business is still in its early stages, a comprehensive understanding of interactions between plants and nanomaterials is required. MNPs offer novel approaches to enhance yield, improve nutrient delivery and control pests, all of which carry significant practice implications for modern agriculture. Their distinct characteristics, such as specificity to target, greater solubility and controlled release allow more effective utilization of agrochemicals, which reduces costs and reduces their environmental effects. MNPs allow farmers to produce more efficiently and make the agriculture process more sustainable. Nevertheless, the important issues such as possible toxicity, impact on the environment in long term, cost-effectiveness and regulatory approval, will have to be conquered before MNPs can be widely used in agriculture.

Studies indicate that these nanoparticles can deal with microorganisms in the soil, which has an impact on the nutrient cycling and the health of plants. There is also a need to monitor in the long run since there is a concern about accumulation of nanoparticles in the soil and water and the possibility of resistance being developed by the pests. It is evident from earlier studies that exposure to nano-based pesticides at larger concentrations or for longer periods of time can negatively impact non-target creatures, such as both plants and animals. Large-scale field-based research is necessary to assess the effectiveness or potency of nanopesticides in practical application with safe and efficient delivery method for sustainable agriculture. To examine the possible harm of nanopesticides and implement regulatory measures, risk assessment and management techniques must be developed. Achieving and maintaining global food security and safety will depend on the environmentally benign development of nano-enabled agriculture.

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