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The Role of Nanopesticide Formulations in Agricultural Bioeconomy

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Abstract

The reckless use of conventional pesticide formulations leads to many problems on the environment. So, using new approach in pesticide formulation production can be reduced these harmful effects. Furthermore using this approach can be reduced the cost of pesticide production, improving the pesticide properties and increase the national income especially, in developing countries. This strategy can be called the bioeconomy. The bioeconomy expression means the use of new biological resources sustainably to obtain the food, energy and industrial goods. Nanopesticide formulations are the new trend in pesticide production that can be decreased the production cost of pesticide, decreases environmental pollution and increases the potency of pesticides against target pests. With this strategy, it is possible to use one-tenth the amount of pesticides to achieve the same effect as with the traditional quantity. Therefore, this strategy is very important for the economies of developing countries. This approach aims to achieve maximum output with minimal resources.

Keywords: Nanopesticides; Bioeconomy; Management

1.WHAT IS BIOECONOMY?

Bioeconomy expresses to the optimal use of new tools to obtain the vital necessities of life, such as food and energy. On the other hand, Birner [1] stated that the bioeconomy is an economy that relies on new innovations in vital fields, especially the life sciences to meet essential human needs. The bioeconomy is also defined as the economic activities that rely on the invention, development, production and use of biological products and processes [2]. So, the bioeconomic is always concerned with bioactivities. According to FAO bioeconomic is defined as the best use of biological resources, including innovation, science, nanotechnology, data analysis, processes, products, and services to all economic parts with the aim of moving towards a sustainable economy.

2.THE RELATION BETWEEN BIOECONOMY AND AGRICULTURE

There is a very close relationship between the bioeconomy and nanotechnology in the field of pesticides. Agriculture is considered one of the most important and the largest components of the bioeconomy [3,4], with a high importance for biodiversity, rural employment, farmer's income, greenhouse gas emissions, the best method used of agricultural lands and agrochemical (pesticides and fertilizers) application as well as the major and minor elements. Therefore, in the future, bioeconomy agriculture must be updated and persisted. This means that agricultural production should be increased to produce sufficient amount of food and biomass is supplied to meet the sharp increasing of world population. At same time we preserve the ecosystem and biological diversity (environment) [5]. With the beginning of green revolution in the world; the food production was increased to double amount in the past 50 years. From 1960 until now (2025), the human population was sharply increased and reached to approximately seven billion. It expected in 2050, the world population is increased by 30 % to reach at 9.2 billion [6]. Furthermore, more arable land must be increased to produce this increasing

of population and meets the principal goods such as green fuel or fiber instead of food. So, it was badly need to increase the land production to face the rising of costs and rising standards of human and environmental health, the best combination of available technologies has to be used.

Pesticides are considered the main component of agricultural development. Due to the side effects of the conventional formulations of pesticides it's dire need for a new strategy in pesticide production to reduce this harmful effect of the conventional formulations. Nanotechnology can be resolving this problem. Nanopesticide formulations are the new approach to pesticides production and could be the magic solution to this problem. The relation between national economy and nanoagrochemical (nanofertilizers and nanopesticides) was discussed [7]. The results found that the nanoformulations greatly increased the crop production, ensure food security, decreased the socioeconomic obstacles.

The total world area of arable land suitable for agriculture is approximately 1.5 billion hectare. The global annual crop production from this area is 3 billion ton. To obtain this production we need to 187 million ton of fertilizers, 4 million ton of pesticides, 2.7 trillion cubic meters of fresh water and over two quadrillion British thermal units. Over time, you will need to double these quantities. So, alternative resources must be obtained to resolve this problem.

3. PESTICIDES PRODUCTION AND BIOECONOMY

It's known that, agricultural crops are infested with more than 30,000 species of weeds, 3,000 species of worms and 10,000 species of plant-eating insects. These pests not only existed in the fields but also existed in storage such as bugs, molds and rodents. All these pests can cause huge damage in storage crops. Using of pesticides can protect the crops and prevent these losses with the post-harvest pests such as weevil and beetles. The pesticides and other agrochemicals market consists of the sales of pesticides and other agricultural chemicals by entities (organizations, sole traders or partnerships) that formulate and synthesis agricultural and household pest control agents (except fertilizers). The pesticides and other agrochemicals market involve insecticides, fungicides, herbicides and other pesticides. The Food and Agriculture Organization of the United Nations (FAO) determined that; annually losses of global crop production caused by agricultural pests are ranged between 20 to 40 %. This damage means around \$220 billion. Synthetic pesticides are widely used especially in the developing world. The global pesticide demand is increasing due to the current system of crop production, which gives high agricultural yields. Global food consumption has increased greatly, especially with population growth to double in the past 50 years [8]. The food and agricultural organization (FAO) determined that 35 % of potential crop yield is lost by infesting of pre-harvest pests [9]. It's known that increase the world population means increasing the world demand for food. So, crop production, pest's management and trade volumes will have to meet the increasing of world population. Additionally, farmers and commercial farming companies will increase acquisitions in arable land to increase crop production. This leads to increase the demand for pesticides (insecticides, herbicides and fungicides in the forecast period). So, using pesticides has a great role in reducing the food losses by management the agricultural pest's population. The outcome of the pesticides using provides evidence that pesticides will continue to be an important agents in the diverse range of technologies that can sustain and improve living standards for the people of the world [10].

Economically speaking, it is well known that every dollar spent on pesticides yields four dollars in increased production. This explains to us the importance of pesticides in agricultural production as one of the essential inputs for sustainable farming. Therefore, using smaller quantities of pesticides with maintaining their effectiveness against pests would be one of the most important economic aspects of pesticide use.

Recently, the global pesticides consumption reached at four million tons are used annually, herbicides is the most type used (50 %), followed by insecticides (30 %), fungicides (18 %) and other types such as rodenticides and nematicides (Fig 1).

This quantities increased in 2020 to 6.6% compared with 2019 related to the pesticide volume (975 000 tons); 5.8 % in terms of revenue; and 8.0 % in terms of application area (1.6 billion ha), of which 2.0 % referred to new agricultural areas [11]. China was the most consumers followed by the USA, Argentina, Thailand, Brazil, Italy, France, Canada, Japan and India (Fig 2). According to a report by the firm reports and data, the global pesticide market is expected to reach at 96.96 billion US dollars by 2027. Using of pesticide formulations in agriculture the total production of main crops (rice, cotton,

wheat, etc.) increased to 50 % between 2000 and 2018, to 9.1 billion tons in 2018, slightly below the record high of 2017.

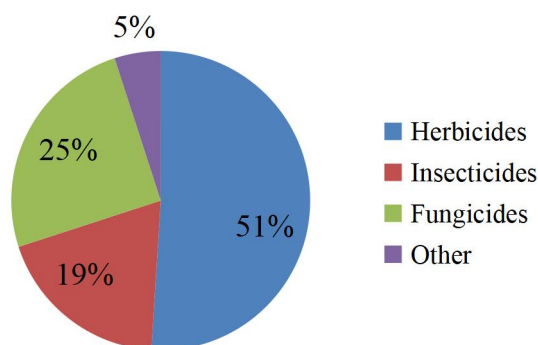


Fig 1. Pesticides world production

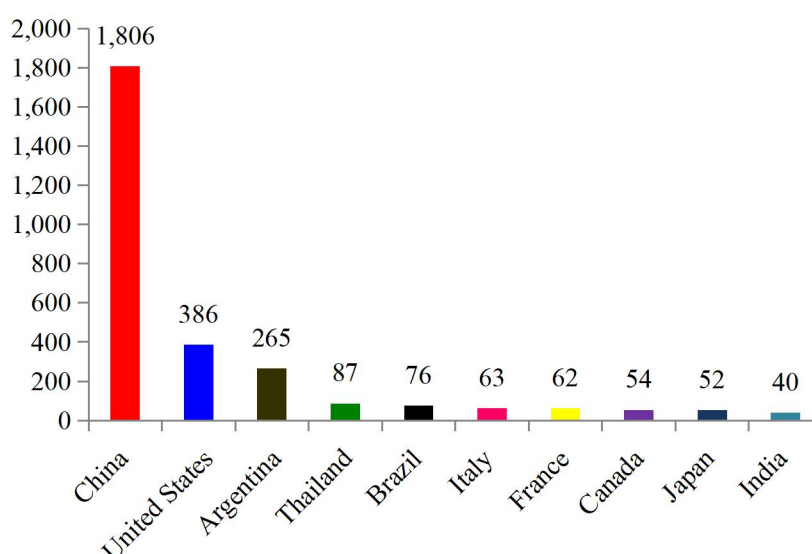


Fig 2. Pesticides world consumption, 2020

Recently, the world agrochemical market (pesticides and fertilizers) is expected to increase from \$80.27 billion in 2020 to \$84.82 billion in 2021 at a compound annual growth rate (CAGR) of 5.7%. This increasing is mainly due to the company's competition and recovering from the COVID-19 impact, which had earlier led to restrictive containment measures involving social distancing, remote working, and the closure of commercial activities that resulted in operational challenges. The world pesticides market may be increased to \$109.75 billion in 2025 at a CAGR of 7%.

4. NANOPESTICIDE FORMULATIONS AS A NEW STRATEGY

The word nanopesticides are used to describe any tiny pesticide particles that include entities in the nanometer size range (recently up to 100 nm and under 1000 nm). By this definition the nanopesticides include many types of formulations (nanoparticles, nanocapsules, nanosuspension, nanoemulsion, etc.) which are described in detail subsequently. Nano-sizing was first undertaken in the medical field during the 1970s. The first document on synthetic nanopesticides was made by Speiser and co-workers from ETH in Zurich during this period [12].

One of the critical threats in the agricultural processes is the need to resolve any problem related to pesticide's use such as environmental pollution, bioaccumulation, and in-crases in pest resistance, which needs to reduce in the pesticides concentrations used for agricultural crop and stored product protection. Nanotechnology can resolve these issues as a highly attractive trend to achieve this target by using new shapes and size for the pesticide formulations and delivery of active ingredients pesticide used, as well as novel nanoactive ingredients, collectively referred to as nanopesticides [13,14]. Recently, there are more than 232 nano-enabled products are synthesized by 75 international companies in 26 countries all over the world [15]. Nanotechnology has taken a big step forward, and

this is converted in the money invested in development and research in the nanopesticides field. Approximately of \$27 billion was spend by the United States National Nanotechnology Initiative (NNI) in the year 2019 [16].

The main target of using nanopesticides in agricultural development is increasing productivity and decreasing of the pesticides quantity and environmental contamination.

5. MECHANISM OF ACTION OF NANOPESTICIDES

Using nanopesticide formulations made it possible to increase of the pesticide penetration through the plant tissues in leaves, roots and fruits, and consequently raises the systemic activity compared to the conventional formulations [17]. Nanopesticides are growing in popularity, as they appear able to make the same results as conventional pesticides and more when applied at lower concentrations. However, regulatory and ecotoxicological research gaps still need more investigation and researches to find a final decision to use nanopesticides in a wide range. Scientific researchers now may be reduced these gaps, and suggests the roles and registrations needed to enable sustainable nanopesticide use on a worldwide scale. Nanoparticles formulations can make the difference by increasing the stability of a pesticide when applied or expedite its slow release over time for good control under field conditions (nanocapsule formulations). Such nanopesticide formulation have been shown to improve the efficacy of some herbicides (weed-control), nematicides (worm-control), acaricides (mite- and tick-control), bactericides (bacteria-control) and fungicides (fungi-control) formulations and decreasing the crop losses caused by agricultural pests and the costs to the crops production. Further research is needed, however, to ensure that these substances are used in an environmentally sustainable manner. Some nanopesticide formulations with either higher efficacy or ecofriendly to environmental profile are already used in the fields. For example, a turf fungicide based on water-based (non-petroleum) nano/microemulsion technology has been synthesized with several good advantages. According to the product formulation, the nano/micron-sized particles prevent rapid accumulation of the emulsion formulations, do not need to continued stirring, stop plucking of filters nozzle in spray equipment and make the formulation stable for a long time compared with the conventional formulation of pesticides. Furthermore, the nanoformulations increase systemic properties, which are intended to decreasing the product washing off easily especially in the rain conditions. However, more than 90% of conventional pesticide formulations run off into the environment and establish in agricultural products in the process of application as a result of the disadvantages of conventional pesticide formulations, such as the use of a dust drift, poor dispersion, harmful solvent, etc. Recently, using of nanotechnology to develop new formulations has shown good potential in improving the efficacy and safety of pesticides used in agricultural ecosystem. The development of nano-based pesticide formulations aims at the slow release of main and sufficient amounts of their active ingredients in responding to environmental inducer and biological system through controlled release mechanisms [18].

6. NANOPESTICIDES CLASSIFICATION

The mixing of nanotechnology as a means for nanopesticides is in the early phase of development. The main idea behind this mixing is decreasing the use of conventional pesticides to be in line with safe environmental applications. Nanopesticides can make this decreasing the amount of pesticides used. Encapsulated pesticides (as a main class of nanopesticide formulations) can provide controlled release of active ingredient, while efficiently increasing of permeability, stability, and solubility. Furthermore, it can increase the pest-control efficiency over extended durations by preventing the premature degradation of active ingredients (AIs) under harsh environmental conditions.

6.1. Advantages of Nanopesticides Use

There are many advantages of nanopesticides used such as:

- 1- Stability of active ingredient against UV, sun, heat and rain
- 2- Highly penetrating and deliver to the target pests
- 3- Prolong the effective duration (persistence)
- 4- Reducing the cost of pesticide formulation
- 5- More safety in environment
- 6- Reducing the concentrations required

Nanopesticides classified into two main classes; organic nanopesticides and inorganic pesticides [19].

6.2. Organic Nanopesticides

Any nanopesticide formulation consists of two main contents; the first content is active ingredient and the second one is nanocarrier or polymer (such as chitosan, polyethylene glycol, etc.). The nanopolymers are among the strategies most target to overcome significant modern farming challenges, especially those related to increasing production vs environmental impacts and pesticides reduced application rates [20]. Recently, there are many types of nanopesticides formulations; such as nanoinsecticides, nanoherbicides, and nanofungicides.

6.2.1. Organic Nanoinsecticides

Almost pesticides quantity used in application are losses due to many factors. Approximately more than 99% of the pesticides used are lost in the environment and do not reach the target site in treated plants. So, many conventional formulations were developed to nanoformulations to resolve this issue. These formulations such as nanoimidacloprid, nanoindoxacarb, nanochlorfenapyr, etc. Nanoimidacloprid and nanoindoxacarb were used against many insect pests such as the Egyptian cotton leafworm, *Spodoptera littoralis* [21]. Nanochlorfenapyr and nanoflonicamid were used against the adults of glossy clover snails, *Monacha cartusiana*. The main purpose of using nanoformulations are to decrease the pesticide concentrations, environmental contamination and the cost of application and also increase the efficacy of pesticides against the target pest [22]. Tian et al. [23] used both conventional and nanoformulations of fipronil against some insect pests. The obtained results showed that the nanoformulation of fipronil has the same activity of conventional formulation against the diamondback moth, *Plutella xylostella* and less toxic against the nontarget organisms such as the adult of zebra fish. This means that by nanotechnology it can be increase the insecticide toxicity against the target insect and the same time reduces the toxicity against the nontarget organism. On the other hand, imidacloprid (neonicotinoids) also developed as a nanoformulation as a nanocapsule formulation and evaluated against the adult stage of *Martianus dermestoides*. The LC_{50} of nanoimidacloprid reached at 95%. Moradi et al. [24] used mixture of imidacloprid and lambda-cyhalothrin as a nanocapsule formulation against *Myzus persicae*. The main purpose of this mixture is to improve and increase the efficacy of pesticide and reduce the environmental contamination. In *Spodoptera litura* ovarian cell lines, hydrophobic insecticides such as azadirachtin (botanical extract) with improved chitosan nanoparticles demonstrated a promising decrease in cell proliferation and the sustained release of drugs. Sabry and Hussein [22] developed nanoformulation to chlorfenapyr and used it against the adults of glossy clover snails, *Monacha cartusiana* compared with its conventional formulation. The obtained results showed that the efficacy of nanoformulation was the same of the conventional formulations. The concentration of nanoformulation was one-fifth of the conventional formulation. This means that the nanoformulation reduces the concentration used and therefore reduces the environment contamination and application cost. Assalin et al. [25] prepared thiamethoxam nanocapsule formulation and tested it against *Raphidocelis subcapitata* and *Artemia salina*. The LC_{50} of nanoformulation was less two-fold compared with the conventional formulation. Furthermore the efficacy of nanoformulations increased the plant uptake also increased. Yan et al. [26] found that the plant uptake for nanothiamethoxam was increased by 1.69–1.84 times compared with the conventional formulation. Ahmadvpour et al. [27] compared the nanoformulation and normal formulation of imidacloprid against wheat green aphid, *Schizaphis graminum*. The result found that the nanoformulation was ten –fold effective against *S. graminum* than the normal formulation. The LC_{50} of imidacloprid nanoformulation was 4.94 mg a.i./L compared with 58.56 mg a.i./L for normal formulation. This result means that low concentration of nanoformulation made more efficacy than the high concentration of normal formulation of imidacloprid. Xiong et al. [28] studied the physical properties of nanopesticides compared with the normal formulation. The results showed that the nanoscale particles increased the pesticide solubility, increased the pesticide stability, increased the pesticide dispersion, and improving bioavailability of the nanopesticide formulation. In the same time reduced the environmental contamination.

6.2.2. Organic Nanoherbicides

Nanoherbicide formulations were developed in the current decade and become a new strategy to resolve all the problems caused by the conventional formulations of herbicides. The nanostructured herbicide could substantially reduce the herbicide concentrations rate and promise increased crop yield

[29]. Although the nanoparticle formulations reduce the movement and mobility of the herbicide in soil but its increasing of herbicidal efficacy in comparison with conventional formulation of atrazine [30]. The main advantage of nanoherbicides are increasing of pesticide solubility, easily dissolved in soil particles, inhibit the weeds growth and could be designed in a form that is less hard on crops. Nano-enabled herbicides are shown to have the remarkable potential to kill weeds and increasing of crop yield [15]. Recently, many conventional formulations of herbicides were developed to nanoformulations such as atrazine, ametrine, triazine. By this strategy the effectiveness of these nano-enabled herbicides increased by 84% [31]. Sousa et al. [32] used two types of atrazine formulations against *Amaranthus viridis* (slender amaranth) and *Bidens pilosa* (hairy beggar ticks). The first formulation was atrazine nanocapsule and the second was conventional formulation of atrazine. The obtained results showed that greater decrease in the photosystem II activity (above 50% inhibition) in compared with 40% with conventional formulation. The growth of *A. viridis* plants was sharply reduced by nanoatrazine (above 64% for root and 75% for shoot). Munhoz-Garcia et al. [33] evaluated many carrier agents (polymer) such as lignin (LG), zein (ZN) and chitosan (CS) to glyphosate nanoformulation. The toxicity of nanoformulation was evaluated against target and nontarget organisms. The results found that zein was the most effective polymer against some weeds such as *Eleusine indica*, *Ipomoea grandifolia* and *Amaranthus hybridus*. The efficacy of nanoformulation was 96% against *A. hybridus* compared with 40% for normal formulation. Iyarin et al. [34] used atrazine nanocapsule to control of *Striga asiatica* control. The rate slow release of nanoatrazine was 64.5% compared with 81.1% of conventional formulation of atrazine. On the other hand, the percentage of cumulative release was 4.4 and 16.2% for nano and conventional formulations of atrazine, respectively. Furthermore, the efficacy of atrazine nanoformulation was more effective than conventional formulation.

6.2.3. Organic Nanofungicides

Agricultural fungal pathogens cause approximately 70–80% losses in yield [35]. There are 1.5 million species that are classified under the kingdom ‘fungi’ and these fungal pathogens are mostly parasitic and saprophytic in nature, causing different diseases in agricultural crops. Fungal pathogens may cause great lose in the yield of different crops around the world every year [36]. The gray mold fungi, *Botrytis cinerea* is able to infect green and fruit tissues in over 200 plant varieties, and is also responsible for great damage caused to fruit during marketing and storage [37]. *B. cinerea* alone is responsible for 10% of the worldwide fungicide market, representing more than €500 million. Nanofungicides are expected to play a vital role in future to compete the plant disease as eco-friendly alternatives of conventional synthetic fungicides [38]. Cota-Arriola et al. [39] stated that chitosan is a well-known nanoparticle with suitable biological features, for example, antimicrobial action, non-allergenicity, biocompatibility and biodegradability having low-toxic effects on nontarget organisms (animals and human). On the other hand, Kashyap et al. [40] showed that the nanoparticles of chitosan have caused a significant antifungal effect, for example, management tomato root rot, *Botrytis bunch* rot (grapes), *Pyricularia grisea* (rice plant), and *Fusarium* crown. The high molecular weight characterization of chitosan helps to fast penetrate through the cell membrane and cell wall of plant cell. This molecular weight increases the efficacy of antimicrobial activities or effects include preventing nutrients from being absorbed from cells extracellularly, altering cell permeability, and acting as a chelator of essential metals [41]. Liu et al. [42] used nanoformulation of tebuconazole and chlorothalonil as nanocapsule formulations. These fungicides were encapsulated using the surfactant-free method, which had given rise to a more stable aqueous solution with smaller particle size diameters, and an increased uptake in the wood. Kaempferol fungicide was loaded on lecithin/chitosan (polymer). This nanoformulation has shown a great inhibition of about 67% efficacy after 2 months of storage on the petri dish containing *F. oxysporum* [43]. Tippannanavar et al. [44] used nanoformulations of some synthetic fungicide with compared the conventional formulations. The results found that the nanoformulations were very effective against *Macrophomina phaseolina*, *Rhizoctonia solani*, *Fusarium oxysporum*, and *Sclerotium rolfsii*. The efficacy of clotrimazole nanoformulation was increased compared with the normal formulation against against *R. solani* (ED₅₀ was 1.18 µg/mL).

6.3. Inorganic Pesticides

The first generation of pesticides was called the nonorganic pesticides. The inorganic nanoparticles are further categorized into metal oxide and metal nanoparticles.

6.3.1. Inorganic Nanoinsecticides

1) Silver Nanoparticles (AgNPs)

Due to the intensive use of synthetic pesticides which increase the insect resistance and environment pollution, it is dire need to give an extra solution to find alternative options to control insect pests. Silver nanoparticle (AgNPs) can provide an accurate solution. Silver nanoparticles (AgNPs) are increasingly used in various fields, including medical, food, health care, industrial purposes, and the agricultural fields. The main advantages of silver nanoparticles (AgNPs) are non-toxic, safe and improved management to control pests, and would have significant effect on the economic costs. The nanoparticles of the silver size are ranged between 1 nm and 100 nm. The silver nanoparticle has many applications due to the large degree of commercialization. Afrasiabi et al. [45] used silver nanoparticle as a nanoinsecticide against *Heliothis virescens* (tobacco budworm) and *Trichoplusia ni* (cabbage looper). Silver nanoparticle also used against red flour beetle, *Tribolium castaneum* [46].

On the other hand, the silver nanoparticles not only effective against the agriculture pests but also the public health pests such as mosquitoes and house fly. The silver nanoparticles were used against the fourth instar larvae of *Aedes aegypti* larvae. The larvicidal activity of AgNPs at their lethal threshold concentration (4.5 µg/ml) were observed for 12 and 24 h and longed time dependent mortality rate were 23.3 ± 0.57 and $46.6 \pm 0.57\%$ respectively [47].

2) Silica Nanoparticles (SiO₂)

Silica nanoparticles are considered one of the most effective nonorganic insecticides against insect pests. The main advantages of silica nanoparticles are safety to the human, natural enemies and a plant; and toxic against insect pests. Silica dioxide (SiO₂) nanoparticles (NPs) have received considerable attention as a possible alternative to conventional insecticides. The insecticidal properties of silica NPs are thought the ability to make direct scratching of the insect cuticle (Rastogi et al. [48] or penetrate through the insect cuticular layers [49]. Silica NPs may also have an indirect insecticidal effect on pests feeding on treated plants or food by blocking the digestive tract. Silica may also destroy the digestive tract in insect herbivores that feed on silica-treated plants [50]. Silica dioxide nanoparticles were treated with different concentrations (75–425 mg/L) on field-cultivated faba bean and soybean for two growing seasons. The faba bean pests such as the cowpea aphid, *Aphis craccivora* and the American serpentine leafminer, *Liriomyza trifolii*, and the soybean pest, the cotton leafworm, *Spodoptera littoralis*, were observed along with their predators [51]. These nanoformulations were less toxic against the insect predators. Ziaee and Ganji [52] used silica nanoparticles against the adults of *Rhyzopertha dominica* and *Tribolium confusum*. The obtained results showed that silica nanoparticles have high efficacy on *R. dominica* and *T. confusum* adults. *R. dominica* was more susceptible than *T. confusum*.

3) Nanostructured Alumina

Nanoscale alumina is a nano-engineered material synthesized by oxidation of metals. This oxidation produce particles show fixed electric charges. Nanoparticles represent a promising technology to increase the efficacy of bioactive materials, surface area and many researches showed the effectiveness of nanostructured materials against many arthropod species of economic importance [53]. Nanoparticles alumina as a nonorganic insecticide was used as effective insecticide against stored product insect pests in laboratory bioassays [54]. The mechanism of action of nanostructured alumina against the target pests is by two mechanisms occurring in sequential order. First, a strong electrical binding between negatively charged NSA particles and positively charged insect. Second, dehydration of the insect body due to the strong sorbtive action of the NSA particles that remove the insect cuticular, leading to death by dehydration. The stored product insects are considered the main target of nanostructured alumina. Stadler et al. [55] used nanostructured alumina against *Sitophilus oryzae* L. and *Rhyzopertha dominica* (F.), which are major insect pests in stored food supplies throughout the

world. The obtained results showed that the nanostructured alumina was very effective against the tested insects compared with the conventional insecticides. The nanostructured alumina was a cheap and available alternative agent for insect pest's control.

6.3.2. Inorganic Nanoherbicides

Nanoparticles can be used as good carrier and also can be added as a nanoformulation when mixed with herbicides. Silica dioxide nanoparticles (SiNP) were used as inorganic herbicide nanoformulation in the recent past for active substances which are susceptible to pH. These silica nanoparticles formulations reduce the concentrations of herbicides used compared with the normal formulations. These strategies improve and stabilize the herbicide formulations and reduce their residues of herbicides in the plant leaves [56]. Magnesium-aluminum associated with sepiolite clay was used as synergism agent to herbicides to reduce the herbicide leaching in the soil [57]. Zinc oxide nanoparticles were used as removal residues of the glyphosate (worldwide herbicides). The obtained results showed that zinc oxide nanoparticles were very effective in the removal of glyphosate [58]. Jiang et al. [59] used green silver nanoparticles, extracted from the root of *Zanthoxylum nitidum* and evaluated as a nanoherbicide. The nano size particles were 445 nm. The results found the green silver nanoparticles were very effective against the germination of seeds and growth of seedling of *Bidens Pilosa*.

6.3.3. Inorganic Nanofungicides

Inorganic nanoparticles (INPs) have dynamically introduced in plant protection field. The absorption of inorganic nanoparticles by plants mostly related to the particles size, chemical components, morphology, and the type of polymers (carriers) on their surface [60]. Particularly, inorganic nanoparticles which have antifungal activity are effective at low rates, while the slow release of less toxic chemicals reduces the development of resistance and create a good protection from biodegradation [61].

1) Cu-Based Nanoparticles

Copper nanoparticles (CuNPs) were used to be most effective in inhibiting mycelial growth of most fungi (EC₅₀ values ranging between 162 and 310 µg/mL) [35]. The copper-based nanoparticles have excellent properties as a fungicide. The small particles size of CuNPs allow to easy absorption and uptake by the plants [62]. On the other hand, olive crop was treated with copper fungicides to control of foliar and fruit diseases such as olive leaf spot caused by *Fusicladium oleagineum* and anthracnose caused by *Colletotrichum spp.* [63]. The obtained results showed that copper nanoparticles exhibited a good protectant activity against both *F. oleagineum* and *Colletotrichum acutatum* with control efficacy values significantly higher than those achieved by the applications of normal formulations. Copper nanoparticles antifungal efficacy against *Fusarium solani*, *Neofusicoccum sp.*, and *Fusarium oxysporum* was investigated [64]. Although the antifungal activity of nanoformulations differs for each fungal species, it was found that the copper nanoparticles make good morphological changes in the mycelium. Furthermore, the damage of the cell membranes of the pathogens was revealed by microscopic observations. Viet et al. [65] evaluated the antifungal activity of copper nanoparticles by used it against *Fusarium sp.* The copper nanoparticles were obtained with the average particles size in the range of 20–50 nm having spherical shape. The results showed that when copper nanoparticles were used at 450 ppm concentration in 9-day incubation, 93.98% of fungal growth was inhibited. Oussou-Azo et al. [66] used copper nanoparticles against *Colletotrichum gloeosporioides*. The obtained results showed that nanoformulation of copper had significant antifungal activities, with copper nanoparticles causes the most sustainable efficacy and was more effective than its oxidative formulation (CuO-NPs).

2) Zinc Oxide (ZnO) Nanoparticles

The unparalleled physicochemical and biological properties of zinc oxide nanoparticles also make them attractive to the food industry for use as a promising antifungal agent [67]. A nanoparticle of zinc oxide (ZnO NPs) was effective in controlling of the postharvest disease caused by some fungal species (*Botrytis cinerea* and *Penicillium expansum*) [68]. The obtained results showed that zinc oxide nanoparticles at concentrations greater than 3 mmol L⁻¹ can significantly inhibit the growth of *B.*

cinerea and *P. expansum*. *P. expansum* was more susceptible to the treatment with zinc oxide nanoparticles than *B. cinerea*. The results showed also, zinc oxide nanoparticles inhibited the growth of *B. cinerea* by affecting cellular functions, which caused deformation in fungal hyphae. In comparison, zinc oxide nanoparticles inhibited the development of conidiophores and conidia of *P. expansum*, which eventually led to the death of fungal hyphae. These results concluded that zinc oxide nanoparticles could be used as an effective and alternative fungicide in agricultural and food safety applications. Zinc oxide nanoparticles were also effective against *Colletotrichum sp.* fungus. Mosquera-Sanchez et al. [69] found that zinc oxide nanoparticles were very effective against *Colletotrichum sp.* The zinc oxide nanoparticles showed an appreciable percent inhibition of fungal growth, ~96% for the concentration of 15 mmol L⁻¹ at 6 days, causing loss in the continuity of some hyphae and the formation of groups of hyphal structures. Additionally, the zinc oxide nanoparticles were very effective in the formation of structures of compact appearance within the hypha, as well as decreasing the cytoplasmic space.

3) Magnesium Oxide Nanoparticles (MgO NPs)

Magnesium oxide nanoparticles (MgO NPs), have many advantages such as, non-toxic for nontarget organisms, ecofriendly, available in the environment, and biocompatibility with human cells. Magnesium oxide nanoparticles are recognized as safe disinfection agents by the U.S. Food and Drug Administration without any harmful byproducts [70]. The fungicidal activity of magnesium oxide nanoparticles were evaluated against soilborne *Phytophthora nicotianae* and *Thielaviopsis basicola* for the first time under laboratory and greenhouse conditions. The results showed that magnesium oxide nanoparticles practically inhibit the fungal growth and spore germination and impede sporangium development more efficiently than could macroscale equivalents. Magnesium oxide nanoparticles also were tested against *Candida albicans* [71]. Magnesium oxide nanoparticles was used against clubroot which caused by *Plasmodiophora brassicae* [72]. The percent of clubroot reduction by using magnesium oxide nanoparticles (500 mg/L) was 54.9%.

4) Selenium Nanoparticles (SeNPs)

Selenium is a very effective metal used against phytopathogenic fungi. So, selenium nanoparticles may be playing an important role in suppression of the phytopathogenic fungi [73]. Green selenium nanoparticles (plant extract) was extracted from *Amphipterygium glaucum* leaves and flower of *Calendula officinalis* and evaluated against both *Fusarium oxysporum* and *Colletotrichum gloeosporioides*. The results found that selenium nanoparticles were very effective against both *F. oxysporum* and *C. gloeosporioides* at concentration 0.25 mg/mL. Desouky et al. [74] evaluated the efficacy of selenium nanoparticles as a fungicide against *Sclerotinia sclerotiorum*. The results found that when 0.5 ppm concentration of selenium nanoparticles was used, the inhibitory percent reached at 100 for *S. sclerotiorum*. This result means the selenium nanoparticles was very effective as a fungicide. On the other hand, selenium nanoparticles were evaluated against *Fusarium sp.* 072, *Acremonium cucurbitacearum* 502, and *Acremonium strictum* 048 by Vasylenko and Derevianko [75]. The results showed that reduction colony of *A. cucurbitacearum* 502 were reached at 86.67%. The results recommended that selenium nanoparticles greatly inhibited all tested colonies of phytoparasitic fungi.

7. CONCLUSION

Nanotechnology plays an important role in agricultural economy by minimizes the cost of agricultural processes and increases the agricultural yield. Pesticides are the main component of the agricultural economy. The average global consumption of agricultural pesticides increased from 1.6 kilograms per area of cropland in 1990 to 2.7 kilograms in 2019. More than 75% of agriculture costs are pesticides. Using of nanopesticides could be reduced the cost to less than 20%. This means that reduction in agricultural cost and increasing in agricultural production. The main technical challenges for the future of nanopesticide formulations are safety food and environmental safety. These refer to the long-term effects of nanoformulations. In addition to, the nanopesticide residues in plant tissues (leaves and fruits), the bioaccumulation effects of nanopesticides especially in underground water. Nanopesticides not only decreased the side effects of normal formulations of pesticides but also

improve the physical properties of pesticides such as solubility and distribution in plants. These results concluded that nanopesticides mean less pesticide concentrations and high pesticides efficacy. Therefore, these results lead to reduce toxicity for nontarget organisms, reducing the cost of pesticide application and reducing the pesticide residues in crops. This concept can be defined as bioeconomy.

The results obtained recommend the use of nano-pesticides as alternative to conventional formulations, as this approach can reduce control costs and increase effectiveness against target pests.

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