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Harnessing NanoOmics and Nanozymes for Sustainable Agriculture

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Chapter 10

Nanotechnology Solutions for Sustainable Pest and Disease Control for Sustainable Agriculture and Food Security

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ABSTRACT

Each year, a significant portion of crops, ranging from 20% to 40%, succumb to plant pests and pathogens, resulting in substantial agricultural losses. Traditional methods of managing plant diseases heavily rely on the application of toxic pesticides, posing potential hazards to both human health and the environment. Nanotechnology presents a promising avenue for addressing these challenges by offering various advantages over conventional pesticides. These include mitigating toxicity, enhancing shelf-life, and improving the solubility of pesticides that are poorly water-soluble, thereby potentially yielding positive environmental outcomes. This review delves into two primary approaches for leveraging nanoparticles in plant disease management: employing nanoparticles independently as protective agents or utilizing them as carriers, often termed as 'magic bullets,' for delivering a range of substances such as herbicides, insecticides, fungicides, fertilizers, and RNA-interference molecules or genes directly to specific cellular organelles within plants. Nanoparticles encapsulate active compounds with high stability and biodegradability, shielding them from degradation by external factors or the host plant itself. Moreover, they minimize inadvertent dispersion into the soil, consequently reducing the need for multiple active compounds in plant treatments and thereby lowering environmental impacts. Additionally, nanoparticles

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can be functionalized with biomolecules like antibodies or aptamers to ensure target selectivity and specificity. Despite these benefits, there remain certain challenges associated with the use of nano devices for plant protection. Foremost among these is the insufficient research on the potential toxicity of certain nanomaterials, such as nano silver and nano gold, to plants, animals, and ecosystems. Accumulation of nanomaterials in plant and animal tissues could potentially enter the food chain, necessitating rigorous safety assessments and consumer education efforts. Nonetheless, the adoption of non-toxic materials, such as starch, chitin, or nano clays, as alternatives to metals, can mitigate such risks.

INTRODUCTION

Plant diseases and pests severely reduce food yields, resulting in losses that are estimated to be between 20% and 40% of global production each year. The present pest control method makes extensive use of pesticides, including herbicides, fungicides, and insecticides (Flood, J. 2010). Pesticides harm creatures that are not their intended targets because pest populations to resurrect, and cause resistance to develop—all despite their availability, speed of action, and dependability (Stephenson, G.R. 2003).

Additionally, about 90% of pesticides that are applied are lost during or after application, which has sparked interest in creating environmentally friendly, affordable pesticides. With the ability to completely transform civilization, nanotechnology offers exciting new opportunities in the food, medical, and agricultural sectors. Nanotechnology in crop protection allows for the controlled release of encapsulated pesticides, fertilizers, and other agrochemicals to combat pests and diseases. Nanosensors enable the early detection of pollutants and plant diseases, including pesticide residues (Ghormade et al., 2011; Lin et al., 2020).

The application of nanoparticles in crop protection encourages the creation of effective plant disease management strategies, providing fresh approaches to the problems stated above. Insect pests account for a substantial 14% crop loss worldwide, while plant infections are estimated to cause losses of up to 13%, or US $2,000 billion annually (Pimentel, 2009). By making it possible to administer pesticides, herbicides, and fertilizers safely and effectively at lower concentrations, nanomaterials lessen the negative impacts on pollinating insects and human health (Kuzma and VerHage, 2006; Mousavi and Rezaei, 2011).

Nano pesticide formulations allow for gradual release and improve the solubility of poorly soluble active chemicals, hence reducing toxicity and increasing efficacy (Kah et al., 2012). Due to their strong reactivity at the nanoscale, pesticide-loaded nanoparticles can be triggered to release slowly in response to environmental cues (Lauterwasser.C. 2005), providing enhanced crop protection (Debnath et al., 2011). Although nanotechnology has advanced significantly in pharmacology and medicine, its applications in agriculture are still largely untapped (Sinha, K. et al. 2017; Balaure, P.C. et al. 2017).

Nanozymes are materials that possess inherent enzyme-like characteristics. With comparable catalytic kinetics and mechanisms, they can selectively catalyze natural enzyme substrates under physiological conditions. When compared to natural enzymes, nanozymes have a number of distinct benefits, such as easy mass production, cheap cost, great stability, and customizable activity. Furthermore, nanozymes represent a novel class of synthetic enzymes that possess not only the catalytic activity like that of an enzyme but also the distinct physicochemical characteristics of nanomaterials, including superparamagnetism, photothermal properties, and fluorescence. Nanozymes have been extensively developed for in vivo disease monitoring and treatment, as well as for in vitro detection, thanks to their unique combination of physicochemical features and enzyme-like catalytic capabilities.

For instance, the majority of the research on using nanozymes to identify and detect fungi has, thus far, only focused on the identification of mycotoxins and other chemical substances linked to fungal infections. There is therefore room to investigate the use of nanozymes in the direct identification of fungi in food, particularly in the agricultural production of those commodities. Due to their inability to germinate, a large number of fungi that are present in seeds seriously impair their utility. Moreover, mushrooms yield mycotoxins, which, if ingested, can seriously harm people's health.

Numerous applications of agricultural nanotechnology exist, including increased seed germination, genetic transfer, plant hormone delivery, water management, nanobarcoding, controlled release of agrichemicals, and nanosensors (Hayles, J.; Johnson, L.; Worthley, C.; Losic, D. 2017). To accurately and precisely administer pesticides, material scientists use conjugation, encapsulation, or adsorption to generate customized nanoparticles (Khandelwal et al. 2016). As agricultural nanotechnology develops, there will be a huge increase in the ability to produce a new generation of insecticides and other actives for managing plant diseases.

There are two ways in which nanoparticles can be used to protect plants:

(a) Crop protection can be obtained from the nanoparticles themselves.
(b) Using nanoparticles as delivery systems for already-available pesticides or other active components, such as double-stranded RNA (dsRNA), which can be absorbed in water or sprayed on seeds, foliar tissue, or roots. When used as transporters, nanoparticles can provide several benefits, including
    (i) Extended shelf life.
    (ii) Pesticides that are not very soluble in water become more soluble.
    (iii) Decreased toxicity.
    (iv) Increasing the target pest's site-specific absorption.

Insect pest management and correct chemical adsorption by plants are made possible by the delayed and effective release of agrochemicals, such as pesticides or insecticides, to a specific host plant through nano encapsulation (Scrinis and Lyons, 2007). Several research have demonstrated the dependability, affordability, and effectiveness of using various metal nanoparticles as insect pest controllers (Stadler et al., 2010; Barik et al., 2008; Goswami et al., 2010). They also allow for uniform and incredibly small droplet sizes, which makes efficient delivery systems for industrial applications possible (Forgiarini et al., 2001; Lee and Tadros, 1982). Additionally, nanoparticles are a viable and effective substitute for conventional pesticides, especially when it comes to fighting pests that are resistant to pesticides.

Using nanoparticles for direct protection as well as dsRNA carriers for RNA interference (RNAi)-mediated protection and pesticide, fungicide, and herbicide delivery are the topics of this review of recent developments in plant disease control. Notwithstanding the potential of nanotechnology, its limited commercial implementations have hindered its advancement in agricultural applications. Only a limited percentage of research on agrochemicals loaded with nanoparticles has involved field testing or addressed environmental issues. For agricultural nanotechnology to advance, it is imperative that further studies concentrate on assessing crop plants, target pests, and conduct both short- and long-term field trials.

Figure 1. Activity of nanoparticles in plant disease management

PLANT DISEASE DIAGNOSIS USING NANO PARTICLES

Traditionally, plant disease diagnosis has been based on human observers' visual evaluation of the condition followed by microscopic analysis. Microbiological diagnostics examines characteristics of pathogens, including fruiting bodies, mycelium structure, spore form, color, and arrangement. Pathogens can then be cultured on particular culture media and separated for additional examination (Fang and Ramasamy, 2015). Unfortunately, these processes—which are frequently carried out in industries and research laboratories—are time-consuming, expensive, personnel-intensive, and facility-dependent. This hinders their broad application in the diagnosis of disease, particularly in underdeveloped nations.

Diagnostic techniques include microbiology, molecular biology, and serology are also used to identify plant diseases. Many direct methods are available for monitoring plant diseases, including enzyme-linked immunosorbent assay (ELISA), immunofluorescence, flow cytometry, fluorescence in situ hybridization, polymerase chain reaction (PCR) for nucleic acid detection, and immunofluorescence. In addition, indirect methods such thermography, gas chromatography, fluorescence imaging, and hyperspectral methods are employed (Mc Cartney et al. 2003).

For example, the development of better fungicides and resistant crop types is aided by the use of molecular techniques to identify phytopathogens and study fungicide resistance in wheat. Additionally, phytopathogen populations and their interactions within plants are studied using molecular approaches. New sensors based on nanotechnology are being developed that offer fast, accurate, and affordable plant pathogen identification. Farmers can now detect infections, volatile substances, chemical residues in crops, and environmental changes with the help of these sensors. Metal, metal oxide, and carbon nanoparticles are often utilized nanomaterials in agriculture. Agriculture could undergo a transformation when cutting-edge tactics and nanosensing technologies are combined. A few different kinds of nanosensors are described here (Omanovic-Miklicanina and Maksimovic, 2016).

Diagnosis of Plant Disease Through Metal NPs

According to (Singh et al. 2017), metal nanoparticles (NPs) are remarkable due to their high melting temperatures, hardness, catalytic activity, and distinctive colors. They are able to detect infections with exceptional precision and higher sensitivity than conventional detection limits due to their raised surface area to volume ratio. A less complicated and more affordable option to enzyme tests is the electrochemical detection of metal nanoparticles (NPs). Consequently, in the diagnosis of phytopathogens, metal nanoparticles are gradually replacing enzyme labeling techniques. Nucleic acids with silver (Ag), gold (Au), zinc (ZnS), lead (PbS), and cadmium (CdS) concentrations are all highly useful for sample detection. Because of their higher surface atom fraction, greater surface area, and stronger antibacterial qualities than bulk silver, Ag NPs are the most studied and applied of these in bio-systems.

Diagnosis of Plant Disease Through Metal Oxide NPs

Plant science finds various applications for metal oxides due to their high density of edge surface sites. This benefit is especially noticeable when using metal oxide nanoparticles (NPs) as solid-state gas detectors in commercial, industrial, and residential environments (Sun et al., 2012). These instruments can distinguish volatile metabolites peculiar to a given pathogen with the right adjustments. Moreover, metal oxide nanoparticles (NPs) are useful sensors for identifying volatile organic chemicals due to their affordability, conductivity, and malleability for shape (Fang and Ramasamy, 2015). ZnONPs are utilized, for instance, in the creation of biosensors and gas sensors (Sabir et al., 2014). According to Fang et al. (2014), plants afflicted with the pathogenic fungus Phytophthora cactorum have been known to release volatile p-ethylguaiacol when they are linked to carbon electrodes. TiO2NPs and SnO2NPs have also been utilized to detect this release.

Diagnosis of Plant Disease Through Magnetic NPs

Since the size of magnetic nanoparticles (NPs) is similar to that of the magnetic domain, they have special properties. They behave in two ways: they are super paramagnets and single-domain ferromagnets. Although magnetic nanoparticles have long been used in biomedical science, little is known about their potential use in plant pathology. Using carbon-coated magnetic nanoparticles, researchers have tracked the path, deposition, and movement of NPs within plant cells (González-Melendi et al. 2008). Furthermore, a brand-new NP immunoassay has been created to measure mycotoxin levels in plants in real time. This test, according to Mak et al. (2010), employs magnetic nanotags attached to a spin valve sensor surface that has been immobilized using capture antibodies. Furthermore, superparamagnetic NPs have been used to produce a reliable and quick ELISA technique that dramatically shortens coating, enzyme blocking, and competition periods when compared to traditional ELISA (Radoi et al. 2008).

Diagnosis of Plant Disease Through Carbon NPs

One of the most common atoms on Earth, carbon is the essential component of many metabolic reactions. Because of its unique benefits over other materials, carbon nanoparticles (NPs) are the most widely used artificial nanomaterial. Carbon nanotubes (CNTs) are cylindrical carbon allotropes that have been demonstrated to improve plant development through increased water absorption. CNTs are essential parts of biosensors because of their remarkable electrochemical qualities, which are their flexibility in binding to many chemical species (Balasubramanian and Burghard, 2006), high length-to-diameter ratio, and capacity to promote rapid electron transfer kinetics (Yu et al., 2003). By taking use of these characteristics, CNTs are being used to diagnose plant diseases. They are able to identify plant metabolites that are important for evaluating phytopathological diseases, as changes in the metabolism of aromatic compounds can be an indicator of these diseases. Among volatile metabolites, phenolic chemicals are particularly important for controlling plant diseases. However, electrode corrosion brought on by phenol exposure, which results in the development of dimeric or polymeric oxidation products, makes it difficult to detect phenols with amperometric and potentiometric instruments.

NANO-DIAGNOSTIC SENSORS AND EQUIPMENT

In order to effectively manage polycyclic diseases in agriculture, early crop pathogen detection is crucial. This calls for the use of sensitive gadgets and effective identification methods. Plant illnesses are detected using a variety of techniques, such as detecting metabolites that are produced in response to stress in plants, such as methyl jasmonate, salicylic acid, and jasmononic acid; alternatively, the pathogen might be identified by genetic, serological, or volatile studies. Also employed is host-induced biomarker analysis, which looks at volatiles, proteins, and transcripts (Martinelli et al., 2015). Whether directly or by the detection of substances released by the diseases themselves, nanosensors are essential for the detection of pathogens. For example, plant pathogenic fungus Sclerotinia sclerotiorum has been detected using nanosensors that include CuNPs with a gold electrode. By measuring the rate at which salicylic acid is produced, these nanosensors enable the estimate of according to Wang et al. (2010), the severity of the infection.

Portable Diagnostic Tools

Our constant need for early detection has spurred us to develop cutting-edge diagnostic tools that can find even the tiniest signs of illness. According to (Weigl et al. 2008), these instruments need to have competitive sensors, incorporate on-chip processing for sample preparation, and reduce the number of manipulation steps. Recent technology advancements have made it possible for agriculture to use portable diagnostic tools for plant diseases. A range of portable technologies are currently on the market, such as portable genome sequencers, lateral flow devices (LFDs), nanodiagnostic kits, immunoprinting kits, portable PCR equipment, and loop-mediated isothermal amplification (LAMP-PCR). These are quick, strong, and easy to use tools. Nevertheless, they are mostly in the developmental stage, frequently costly, and not easily available (Khiyami et al., 2014).

Nano FABRICATION IMAGING

Phytopathogen detection is made easier by the viewing of plant tissues and cells made possible by advanced nano diagnostic imaging techniques. With the advent of this new tool, phytopathologists now have much greater access to diagnostic tools that can help with early disease diagnosis (Rosen et al., 2011). Through the manipulation of nanoparticles' (NPs') physical and chemical properties, these instruments have enhanced signal strength, contrast, tissue specificity, and imaging time. The properties of pathogens, their interactions with hosts, and the onset of infection processes are all revealed by means of such imaging techniques. To effectively design compounds to counteract the impacts of infections, a deeper understanding of disease pathways is necessary (Meng et al., 2005).

NANOPARTICLE TYPES FOR MANAGEMENT OF PLANT DISEASES

Nanoparticles as Protectants

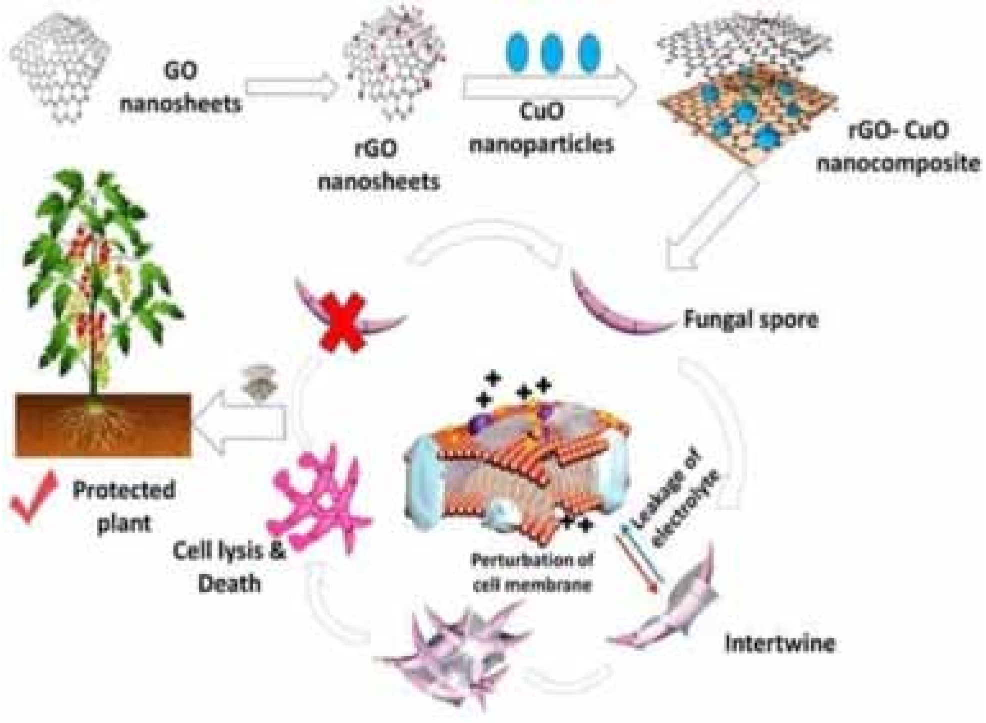
When compared to molecules and bulk materials, nanoparticles—which vary in size from 10 to 100 nanometers (nm)—have unique chemical, physical, and biological properties (Yang, W.; Peters, J.I.; Williams, R.O. 2008). These tiny compounds can be applied directly to the roots, foliage, or seeds of plants to offer protection from insects, bacteria, fungi, viruses, and other pests and diseases. Silver, copper, zinc oxide, and titanium dioxide have received special attention due to their antibacterial, antifungal, and antiviral properties (Kah, M.; Hofmann, T. 2014; Gogos, A.; Knauer, K.; Bucheli, T.D. 2012). A brief synopsis and updates from recent literature reviews on the types of nanoparticles now in use are given in this section (Mishra, S.; Singh, H. 2014; Sadeghi, R., Yao, Y.; Kokini, J.L.; Rodriguez, R.J. (2017).

A recent spike in the popularity of silver nanoparticles has been attributed to the utilization of using "green synthesis" techniques, one can use plants, bacteria, fungi, or yeast (Rafique, M.; Sadaf, I.; Rafique, M.S.; Tahir, M.B. 2017). Surprisingly, studies have shown that silver nanoparticles exhibit strong antifungal properties against a range of pathogens, including Botrytis cinerea, Rhizoctonia solani, Macrophomina phaseolina, Alternaria alternata, and Sclerotinia sclerotiorum (Krishnaraj, C. et al. 2012). According to Jain and Kothari (2014), the sun-hemp rosette virus was completely suppressed when silver nanoparticles were sprayed on bean leaves. Furthermore, silver nanoparticles were found to improve resistance against the bean yellow mosaic virus in fava bean plants when administered after infection, outperforming pre-infection or simultaneous application (Elbeshehy et al.). Production, toxicity, and soil interaction are still major obstacles in the way of their great potential for managing plant diseases.

Nanoparticles of gold, copper, titanium dioxide, and silver are also frequently employed. Although the main use of copper and titanium dioxide nanoparticles is in fertilizers, more research should be done to determine how well they may be used to control plant diseases. Fertilizers containing titanium dioxide nanoparticles have demonstrated potential in preventing viral infections and shielding plants from bacterial infections (Sadeghi et al.). Moreover, it has been shown that the introduction of gold nanoparticles via mechanical abrasion can damage Barley yellow mosaic virus particles, giving plants resilience.

Another extensively studied nanoparticle is chitosan, which has negligible toxicity to humans and animals and advantageous biological qualities such biodegradability, biocompatibility, and antibacterial activity (Cota-Arriola, et al. 2013). It has been discovered that chitosan nanoparticles can create viral resistance in a variety of plant tissues, shielding alfalfa, hemp, peanut, potato, and cucumber from

Figure 2. Nanoparticles as protectants



mosaic viruses (Kochkina, Z. et al. 1994). Additionally, they have antibacterial qualities that work well against fungi, such as Fusarium bunch rot in grapes and Fusarium crown root rot in tomatoes, but less well against bacteria (Malerba and Cerana 2016).

Agglutination, breakdown of cell membranes, reduction of H+ ATPase activity, and creation of toxins, microbial growth, mRNA and protein synthesis, and obstruction of nutrition flow are some of the mechanisms that underlie chitosan's antimicrobial activities. Additionally, chitosan has demonstrated effectiveness against a variety of pests, including as cotton leafworms, oleander aphids, root-knot nematodes, and spear psylla nymphs. Chitosan is a highly promising substance for use in agriculture, both on its own and as a carrier.

Nanoparticles That Act as Carrier

In order to facilitate the creation of effective agricultural formulations, nanoparticles operate as carriers for the entrapment, encapsulation, absorption, or attachment of active compounds. Below is a list of common nanoparticles that are employed as carriers for fungicides, herbicides, insecticides, and chemicals that induce RNAi.

Silica nanoparticles- One unique feature of silica nanoparticles is their ease of synthesis, which allows for exact control over their size, shape, and structure. Mody et al. (2014) claim that this makes them superior delivery vehicles. Mesoporous and porous hollow silica nanoparticles (PHSNs) are two examples; both have a spherical structure with porous characteristics. In order to protect the active components and provide prolonged release, insecticides are often encapsulated within PHSNs and MSNs. PHSNs' shell structure provides extra defense against UV deterioration. According to literature, silica nanoparticles are a sensible option for creating pest management solutions because silicon has been used to improve plant resilience against a variety of environmental conditions (Barik, T.; Sahu, B.; Swain, V., 2008).

Chitosan nanoparticles- Because chitosan nanoparticles are hydrophobic, they are only partially soluble in water. As a result, to increase their solubility, they are often mixed with copolymers, both inorganic and organic. Due of its hydroxyl groups and reactive amines, chitosan can undergo graft reactions, modifications, and ionic interactions, all of which improve its characteristics (Li, M.; Huang, Q.; Wu, Y. 2011). Moreover, chitosan adheres strongly to the leaf and stem epidermis, prolonging contact periods and promoting the absorption of advantageous substances.

Solid lipid nanoparticles (SLNs) - At room temperature, lipids that stay solid are used to make emulsions and solid lipid nanoparticles (SLNs). One advantage of employing SLNs is their ability to form a matrix that, in the absence of organic solvents, can capture lipophilic active molecules (Ekambaram et al., 2012). Additionally, SLNs enable the controlled release of different lipophilic components by decreasing the mobility of the active inside the solid matrix. When SLNs are dissolved in water, surfactants are added to stabilize the compound. However, their primary drawbacks are restricted loading efficiency and the potential for the active to escape the structure while it is being stored (Tamjidi et al., 2013).

Layered double hydroxides (LDHs) - Layered double hydroxides (LDHs) are clay-like materials that self-organize into hexagonal sheets (Xu et al., 2006). Active molecules that are confined in the interlayer space comprise the layers of LDHs. LDH nanoparticles can decompose when they come into contact with acidic conditions like dampness and atmospheric carbon dioxide. Plant cell walls can be more easily penetrated by physiologically active substances when using positively charged LDH lactate delaminated nanoparticles (Bao et al., 2016).

Plant disease management typically uses silica, chitosan, solid lipid nanoparticles (SLN), and LDH nanoparticles as carriers. Parts devoted to insecticide, fungicide, herbicide, or RNAi contain in-depth talks on applying these and other less common forms of nanoparticles.

A BRIEF GUIDE TO FUNGICIDES AND INSECTICIDES

This section provides a brief overview of the various pesticide kinds and their classification system in an effort to encourage appropriate use and lower pesticide resistance. There are two types of insecticides: contact (which need direct touch) and systemic (absorbed by the plant). According to their effects on physiological processes such nerve/muscle, development, respiration, midgut, or unknown/non-specific, they can be further divided into at least 55 chemical classes (Sparks, T.C.; Nauen, R. 2015). Pesticide resistance can be avoided by rotating the use of thirty notable mechanisms of action (MoA). These consist of various locations and unidentified groups.

Fungicides work by either penetrating the plant at different systemic levels or by establishing a barrier on it without being absorbed. For fungicides, it is important to have enough spray coverage because there is rarely systemic movement throughout the entire plant. Fungicides are classified into fourteen different MoA categories, which are reflected by the 49 codes issued by the Fungicide Resistance Action Committee (FRAC) (Leadbeater, A.; Gisi, U.; Klein, K.-H. 2012).

Herbicides can be non-selective, affecting all plants, or selective, focusing solely on a limited set of weeds. There are three distinct ways to administer herbicides: sprinkling them on the soil prior to planting, applying them pre-emergence (before weed seedlings emerge from the soil), or applying them post-emergence (after weed seedlings have emerged). There are 23 Herbicide Resistant Action Committee (HRAC) groups for herbicides in an effort to avoid pesticide resistance. It is important to note that rotation within these groups is crucial.

Nanoparticles as Carriers of Insecticides

Numerous research with a variety of nanoparticles and conventional pesticides (27 studies) as well as bioactive compounds with insecticidal properties (13 studies) have been conducted since the early 2000s. The loading of pesticides into nanoparticles was first introduced. These studies have examined a wide variety of essential oils and eight distinct modes of action (MoA) that are not categorized by the Insecticide Resistance Action Committee (IRAC). Lipids (4 studies), chitosan (11 study), and silica (8 studies) were determined to be the most often studied nanoparticle carriers. Spodoptera litura (5 study), Helicoverpa armigera (4 studies), and Tetranychus urticae (4 studies) were the most often targeted pests.

Improving stability, decreasing volatilization, increasing water solubility, and facilitating a gradual release of active molecules were the main goals of these investigations. In the context of low water-soluble insecticides, the conventional practice involves using organic solvents to enhance solubility, thereby increasing the cost and toxicity of the insecticide. However, nanoparticles offer an alternative approach by increasing solubility and subsequently reducing toxicity. Notably, research has successfully loaded low-water-soluble insecticides into modified chitosan and porous silica Cui, H.; Zhao, X.; Cui, B.; Wang, Y.; Sun, C. 2014). None of these research has specifically assessed for decreased environmental toxicity, despite these developments.

A prominent instance is the application of modified chitosan nanoparticles for the purpose of loading the hydrophobic insecticide azadirachtin; research by Lu et al. shows that this compound has sustained drug release in addition to favorably reducing cell proliferation in S. litura ovarian cell lines. Another study carried out in 2015 by Liu et al. discovered that H. armigera larvae treated to dendrimers containing hydrophobic thiamethoxam showed increased absorption and mortality. Surprisingly, Dendrimer nanoparticles containing H. armigera were loaded it showed a marked increase in toxicity, despite the fact that it is normally resistant to thiamethoxam. Similarly, anacardic acid, when intercalated into LDH nanoparticles (Nguyen et al. 2015), shown that the application of direct mustard leaf or S. litura skin treatment resulted in higher mortality rates than the use of anacardic acid alone. These results highlight the possible advantages of using nanoparticles to improve the solubility of active components.

The evaporation or volatilization of the active components is a common cause of pesticide loss after application. Essential oils have insecticidal effects, but they evaporate quickly because they are unstable chemically when exposed to air, light, heat, and moisture content (Lai et al. 2006). In a particular study,

Table 1. Using nanoparticles to deliver insecticides and the intended target

Insecticides	Nanoparticles	Crops	Targeted Pest
Avermectin	Polydopamine	Cucumber	Aphids
Chlorfenapyr	Silica	Brassica chinese	Cotton bollworm
Imidacloprid	Sodium alginate	unspecified	Leafhopper
Azadirachtin	Zinc oxide and chitosan	Groundnut	Groundnut bruchid
Garlic essential oil	PEG	Rice	Red flour beetle

SLN nanoparticle-encapsulated glass vials were sprayed with essential oil of Artemisia arborescens L. The evaporation rate was 45.5%, compared to 80% for the essential oil alone, with an initial burst release that happened after 48 hours. Comparably, red flour beetles (Tribolium castaneum) exposed to garlic essential oil encapsulated in polyethylene glycol (PEG) after 5 months revealed 80% mortality, while essential oil alone produced just 11% mortality.

Another approach to address evaporation issues is the use of nanoparticles to enhance the stability of active molecules, allowing for sustained release and reduced insecticide usage. According to Kumar et al. (2016), imidacloprid sprayed on okra plants that was encapsulated in sodium alginate was equally effective in field tests as imidacloprid applied alone.In a field study conducted by (Song et al. 2012), Brassica chinese was treated with silica-encapsulated chlorfenapyr, and over the course of three days, in comparison to the diamondback moth (Plutella xylostella), the study's control was comparable to or superior.

Furthermore, research has shown that nano-insecticides have the ability to offer prolonged release, which would increase both safety and efficacy. When termites were fed fipronil put into silica-shelled nanoparticles, for example, there was no first burst release, which would have allowed worker termites to return the bait to the nest (Wibowo et al. 2014). Compared to commercial insecticides, this increased the 100% mortality window by 3 days, which allowed for a more thorough colony removal. To evaluate azadirachtin's efficacy over 180 days in groundnut bruchid storage conditions, the medication was affixed onto zinc oxide or chitosan nanoparticles by (Jenne et al. 2018). Against the backdrop of other assessed formulations, neem seed kernel extract loaded into zinc oxide nanoparticles demonstrated a weight reduction of 54.61% in groundnut bruchid. These studies collectively demonstrate the effectiveness of nanoparticle formulations in addressing volatility issues and improving the overall performance of insecticides.

Nanoparticles as Carrier of Fungicides

Commencing in 1997, the initial exploration of nanofungicides involved integrating fungicides into solid wood, as demonstrated by (Laks, P.; Heiden, P.; Liu, Y., 2002). The study examined essential oils that were not included in the fungicide groups and covered nine FRAC groups. Polymer mixes, silica, and chitosan emerged as the predominant nanoparticle carriers investigated. Numerous fungi were employed to assess nanofungicide efficiency, although limited attention was given to plant testing, and toxicity studies were scarce. Nanoparticles were used to solve issues like low water solubility, reduced volatilization, and improved stability for a slow continuous release, much like pesticides.

In order to enhance the poor water-solubility of tebuconazole and boost its adherence to leaf surfaces, Hatfaludi et al. (2004) employed bacterial ghosts that were nanosized and derived from non-denatured empty cell envelopes of Gram-negative bacteria, namely Pectobacterium cypripedii. Among the plants evaluated, fluorescently tagged ghosts without loaded fungicide exhibited the highest adherence to rice leaves (with 55% surviving) when subjected to strong simulated rain in a glasshouse setting (rice, soya, cabbage, cotton, barley, and corn). On the other hand, soy leaves had the lowest adherence rate (10% remaining). Distinct plant performances were seen in connection to rainfall when six plants were treated with either ghost-loaded tebuconazole or two commercial tebuconazole treatments (WP 25 and EW 250) against various fungus. Remarkably, after being cleaned up 24 hours after treatment, ghost-loaded tebuconazole exhibited an efficacy comparable to or higher than WP 25 treatments, although the controls treated with EW 250 were often more effective.

Chitosan–lactide copolymer nanoparticles were treated with an extra low-water-soluble fungicide, pyraclostrobin, at different dosages. After three to five days, the nanofungicide's effectiveness in preventing C. gossypii inhibition was either lower than or equal to that of commercial pyraclostrobin. Seven days after therapy, an increase in inhibition was noticed. In another experiment, lecithin/chitosan was coated with the low-soluble fungicide kaempferol, and the mixture was stored for 60 days on a Petri plate with Fusarium oxysporum showed 67% inhibitory efficiency (Ilk, S.; Saglam, N.; Özgen, 2017).

Chlorothalonil and tebuconazole were loaded into different nanoparticles in a series of research to address the fungicides' limited solubility for use in solid woods. Four investigations looked at the mass loss in southern yellow pine wood over a period of 50–55 days as a result of Gloeophyllum trabeum decay. Because of its size and stability, hydrophobic chlorothalonil enclosed in nanoparticles showed inefficiency. However, minimal fungal-induced degradation of the wood was obtained with an increase in concentration. Tebuconazole coated with nanoparticles dramatically decreased the amount of fungicide administered (from about 2 kg active/m3 to 0.2 kg/m3) while barely affecting degradation. Because of its tiny pit pores, birch wood presented treatment-related issues. When encapsulated using a surfactant-free technique, chlorothalonil plus tebuconazole resulted in a more stable aqueous suspension and smaller median particle sizes, which led to higher uptake into the wood. Using southern pine exposed to G. trabeum and birch wood subjected to T. versicolor, this technique showed the effectiveness of smaller, more stable, surfactant-free nanoparticles against fungal deterioration. Additionally, it exhibited minimal degradation (five percent or less mass loss) at far lower doses for both fungicides than industry norms.

Despite their well-known fungicidal qualities, essential oils evaporate quickly, which prevents their widespread commercial application. In comparison to bulk essential oil components, (Janatova et al. 2015) demonstrated increased antifungal activity 14 days after infection with Aspergillus niger following the effective encapsulation of five different essential oil components into MSN.In a similar vein, Nasseri et al. (2016) employed SLNs to stabilize Zataria multiflora essential oil, providing protection against six types of fungus.

Although little study has been done in this area, leaching—the transfer of chemicals and water through soil—is a significant pesticide control concern. The fungicide metalaxyl was loaded onto mesoporous silica nanoparticles (MSNs) in a study by (Wanyama 2013). Over the course of a 30-day period in soil, the leaching of encapsulated metalaxyl (11.5%) and free metalaxyl (76% release) showed noteworthy variations. Interestingly, encapsulated metalaxyl released at a rate of 47% when exposed to water, highlighting the importance of assessing pesticide behavior in agricultural settings. Using solid lipid or polymeric nanoparticles loaded with tebuconazole and/or carbendazim, (Campos et al. 2015)

Table 2. Using nanoparticles to deliver fungicides and the intended target fungus

Fungicides	Nanoparticles	Crops	Targeted Fungi
Tebuconazole	PVP and PVP copolymer	Southern pine sapwood	G. trabeum
Metalaxyl	MSN	wheat	E. graminis, L. nodorum,
Carbendazim	Polymeric and SLN	Bean seeds	C. gossypii
Ferbam	Gold	Tea	R. stolonifera
Pyrimethanil	MSN	Cucumber	A. parasiticus
Flusilazole	Chitosan–PLA graft copolymer	Wheat and barley	-
essential oil	Chitosan	cucumber	A. niger

investigated the cytotoxicity and observed a reduction in toxicity towards preosteoblast and fibroblast mice cell lines. Moreover, nanoparticles reduced release rates in soil leaching trials in comparison to commercial formulation. The effects of poly (butylene succinate) and poly (lactic acid) shells loaded with azoxystrobin and difenoconazole on zebrafish were studied by (Wang et al. 2018). They found that the shells were less hazardous than other formulations.The noteworthy finding is that validamycin-containing nanosized calcium carbonate produced a delayed release of active molecules. This was initially less effective than validamycin alone, but with time, the efficacy improved. Additionally, using carbendazim-loaded polymeric nanoparticles to inhibit fungal growth against Fusarium oxysporum and Aspergillus parasiticus, (Kumar et al. 2016) demonstrated enhanced fungal suppression on Cucumis sativa, Zea mays, and Lycopersicum esculentum seeds. Using MSNs to administer pyrimethanil, (Zhao et al. 2017) looked at how well cucumber plants absorbed it and calculated the lowest danger of buildup in edible plant portions. Their research greatly advances our knowledge of the dispersion and transfer of insecticides loaded with MSN when applied topically.

Nanoparticles and RNAi for Plant Protection

The identification of the RNAi pathway has enabled the development of innovative and inventive methods for the control of illnesses and pests. A system that has evolved to be conserved in eukaryotes, RNA interference (RNAi) is essential for controlling development, growth, and host protection against transposons and viruses. It’s interesting to note that weeds, fungi, viruses, and insects can all be targeted with this technique (Baulcombe, D. 2004).

In plants, RNA interference (RNAi) is started by double-stranded RNA (dsRNA). Subsequently, dsRNA is transformed into small-interfering RNA (siRNA) by DCL-like enzymes. The RNA of pathogens is degraded by these siRNAs when they are integrated into a RISCs (RNA-induced silencing complexes) and control them by base pairing. The pathogenic RNA cannot be used as a translation template as a result of its degradation. Since its discovery, the RNAi pathway has shown to be a potent tool for employing genetic modification to address pests and plant diseases (Robinson et al. 2014).

On the other hand, the usage of genetically modified organisms (GMOs) is controversial and governed by strict laws in many nations. Consequently, there is ongoing research focused on developing new delivery methods for dsRNA.

Nanotechnology in Crop and Crop Protection Industry

In many developing nations, agriculture serves as the cornerstone of their economies. The potential for progress in these countries hinges on their embrace of innovative agricultural technologies geared towards sustainability and efficiency. Consider the field of phytopathology, where it’s estimated that plant diseases can slash crop yields by 10–20%, dealing significant blows to the global economy. In order to overcome this obstacle, there’s a growing urgency to explore new avenues of disease management. Enter nanotechnology, offering precise delivery mechanisms for pesticides and fertilizers, thereby laying the groundwork for what’s now known as “precision farming.” This cutting-edge concept revolves around maximizing crop yields while minimizing resource input. By leveraging nanotechnology, precision farming can monitor real-time environmental conditions and tailor interventions accordingly, utilizing a network of wireless sensors and advanced computing systems. This approach, epitomized by the use of “smart dust” composed of sensors and robots, promises targeted and efficient pest control and irrigation management. The integration of nanosensors not only enhances agricultural productivity but also mitigates environmental pollution stemming from traditional farming practices. It's clear that such advancements will empower farmers with better decision-making tools. Case in point, LOFAR_Agro's application of nanosensors to monitor the microclimate of potato crops, offering insights into controlling Phytophthora infection.

Nanotechnology for Controlling Plant Pathogens

More than 70% of the main crop diseases are caused by fungi, which are important plant pathogens (Agrios, 2012). Farmers face ongoing challenges in safeguarding their crops from microbial diseases, often resorting to costly and environmentally harmful agrochemicals. Unfortunately, these practices exacerbate rather than alleviate the situation, contributing to issues like pest resistance on a global scale. It is imperative to reassess traditional agricultural methods and explore innovative substitutes (Ismail et al., 2017; Bhattacharyya et al., 2016).

Agro nanotechnology presents itself as a promising solution to agronomic problems (Sangeetha et al., 2017a). Nanoparticles (NPs) and nanotechnology-based tools offer targeted approaches to controlling plant diseases and combating pathogens. Studies have shown that NPs are effective against a range of bacterial and fungal diseases, including Aspergillus flavus, Bacillus subtilis, and Alternaria alternata (He et al., 2011; Lamsal et al., 2011; Park et al., 2006; Ocsoy et al., 2013; Jo et al., 2009; Kim et al., 2012; Rajiv et al., 2013). Because of their diverse inhibitory effects on phytopathogens, silver nanoparticles (AgNPs) have attracted a lot of attention (Bhaskar et al., 2016; Park et al., 2006; Rabab and EL-Shafey, 2013).

According to Dar and Soytong (2014) and Xue et al. (2014), NPs can be combined in a way that enhances their antimicrobial activity in a synergistic way with biocontrol agents, essential oils, or biopolymer-based substances like cupric and sulfur NPs. This can potentially reduce the total amount of pesticides required and delay the appearance of pest resistance. Furthermore, the incorporation of active components that have the potential to self-inactivate when exposed to sunlight promotes the creation of ecologically benign "nanocides" that have increased pesticide activity as well as residue degradation capabilities. Smart delivery systems, such as nano-dispersed formulations, offer cost-effective and less toxic alternatives to conventional agrochemicals, facilitating mass-scale production of fungicides while promoting targeted crop protection.

LIMITATION OF AGRONANOTECHNOLOGY

When addressing Integrated Pest Management (IPM), it's crucial to explore superior alternatives, especially considering potential future limitations on existing agrochemicals by national regulatory bodies (Srinivasan and Tung, 2015). Nanotechnology presents promising avenues, yet its full integration into agriculture remains pending commercialization. The agricultural community exhibits limited interest in biochemical based on nanotechnology since there aren't enough financial incentives. Various factors contribute to the slow adoption of nanotechnology, including governmental disengagement, a predominant focus on conventional farming methods, minimal competition within the agricultural sector, waning youth enthusiasm, heightened input costs, insufficient farming expertise, and public indifference (Mukhopadhyay, 2014). Agro nanotechnology holds vast potential to enhance farmer livelihoods by revolutionizing agricultural practices. Raising awareness about this science is crucial for bolstering its acceptance and expediting the discovery of new applications in the field.

FUTURE PROSPECTIVES

The potential uses of nanomaterials in agriculture are being investigated more and more, with a focus on reducing the need for plant protection products, minimizing nutrient loss during fertilization, and optimizing nutrient management to enhance yields. Despite the promising benefits, the integration of nanotechnology into agriculture remains relatively limited compared to other sectors. Numerous nanoparticles, nanocapsules, and viral capsids are examples of nanotools and devices that show promise for water treatment, targeted delivery of active chemicals, enhanced plant nutrient absorption, and disease detection and treatment. Recently, powerful substitutes for natural enzymes known as nanozymes have been discovered. As was previously said, despite being in the early phases of research, their application has grown significantly in a variety of biomolecule detection and treatment techniques. Although nanozymes have several benefits, including low cost, high stability, durability, ease of mass production, and long-term storage capacity, there are a number of issues that need to be resolved before they can be used in real-world applications. For instance, ongoing research investigates the application of starch-based nanoparticles as environmentally friendly pesticide and biostimulant delivery methods. For extremely sensitive bio-chemical sensors, novel nanomaterials with distinctive chemical, physical, and mechanical properties—such as fullerenes, nanofibers, and electrochemically active carbon nanotubes—have been produced. While some nano-products tailored for agriculture have entered the market, such as soil-enhancers promoting efficient water distribution and storage, their commercial adoption remains limited due to high development costs. Usually, greater profits in the pharmaceutical or medical industries outweigh these expenditures, which are not yet realized in agriculture. Nonetheless, research persists within the agro-chemical industry to explore potential future advantages and widen the scope of nano-based solutions for agricultural challenges.

CONCLUSION

Over the past few decades, the global human population has surged at an unprecedented rate, leading to rapid industrialization, the loss of arable land, and widespread urbanization. Current agricultural methods such as plant breeding and IPM (Integrated Pest Management) are struggling to keep pace with the demands of feeding billions of people. Thus, there is a pressing need for innovative solutions that can address both current and future food requirements. One promising avenue is agro-nanotechnology, a field that has emerged relatively recently, offering potential solutions to these challenges. By harnessing the power of nanoparticles (NPs), we can potentially reduce reliance on chemical inputs, minimize nutrient loss, and boost crop yields. With regard to the application of nanozyme-based systems for pathogen detection and control, this study provides a thorough summary of current developments. When it comes to improved catalytic activity, high stability, easy preparation, customizable size, and cost-effectiveness, nanozymes are clearly better to their natural enzyme counterparts. Nanozymes are positioned as very promising agents for antibacterial applications and flexible detection medium due to their properties. Although modern nanozymes have impressive antibacterial and detecting capabilities, most of their applications are still in the early stages. This technique is very promising for addressing problems including rising chemical input costs, overuse of pesticides, and groundwater and soil contamination. For instance, zero-valent iron nanoparticles show promise in remediating soil contaminated with pesticides due to their strong affinity for heavy metals and organic compounds. Additionally, iron nanoparticles exhibit excellent soil-binding properties akin to calcium carbonate (CaCO3). Furthermore, to address concerns about environmental sustainability, there should be a greater emphasis on utilizing agricultural waste materials as raw materials for nanoparticle manufacturing.

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