

Eco-friendly Management of Phytopathogens through Nanopesticides: A Sustainable Approach

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Abstract

Biopesticides have frequently been the focus of attention on a global scale as a safer alternative to chemical pest control that may provide less damage to both humans and the environment. The usage of biopesticides is rising rapidly worldwide, at 10 per cent a year. With the idea of limited application for most significant impact, nanotechnology has produced novel tools for pest management in agriculture, including nanopesticides and nanosensors. In contrast to conventional chemical pesticides, nanopesticides are formulations of a pesticide's active component in nanoform that have delayed degradation, targeted distribution, and controlled release of the active ingredient over longer periods of time. In accordance with lots of studies, incorporating certain biological agents in nanoparticulate systems increases their effectiveness against pests while lowering losses resulting from physical deterioration. The development and evaluation of nanobiopesticides have been the subject of laboratory-only research to date using techniques like the creation of nanocomposites, nanoengineered biopesticides, coating nanoparticles with bio-pesticides etc. The formulation of appropriate, globally acceptable biosafety and registration requirements is necessary to enable the effective use of these formulations for pest management at the field level.

Key Words	Bioformulation, Nanopesticides, Phytopathogens, Plant protection, Sustainability
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Introduction

Nanotechnology is revolutionizing agricultural and food waste in underdeveloped countries via sustainable agriculture and circular economy application (Preethi et al. 2024). In developing countries, more than 60% of the population relies upon agriculture for their livelihood either directly or indirectly. In present days, agricultural scientists are facing challenges like climate change, stagnation in crop yields, multi-nutrient deficiencies, low

nutrient use efficiency, declining soil organic matter, shrinking arable land and reduced water levels and shortage of labour (Elizabath et al. 2019). To counter these issues many agriculturists and environmentalists have designed many practices for sustainable development and bioformulations are one of them. In all the green practices developed, there were limitations in effectively delivering the crop growth requirements (Sahai et al. 2019). These delivery models called carriers, these carriers can deliver pesticides, fertilizers, biocontrol agents and so many which are required for plants. Nanoparticles are small molecules with a size range of 1-100 nm with different physiochemical properties (El-Saadony et al. 2019). Nano-fertilizers have a high sorption capability, a large surface area and regulated release kinetics to specific sites, making them a better delivery system to provide fertilizers to the plants (Rameshaiah et al. 2015). Addition of fertilizers to soil may lead to loss of fertilizers and therefore more fertilizer should be added to compensate loss (Ombódi and Saigusa 2000), whereas foliar fertilizer application is effective but nutrients might fail to penetrate cell wall pores as their size vary from 5 to 20 micron (Benzon et al. 2015), while nanoparticles with smaller diameter can easily pass through cell wall pores (Moore 2006). The features of nano-fertilizers are delivering the appropriate nutrients for enhancing plant growth through soil and foliar applications, they are cost effective and sustainable sources for plant nutrients, they help in preventing pollution, they have a high fertilization efficiency (Guru et al. 2015).

Irrational use of pesticides possess threat to ecosystem and human health (Kuhlbusch et al. 2018). Nanoencapsulation of pesticide can help in slow and controlled release of pesticide for a prolonged time reducing loss of unwanted pesticide (Agrawal and Rathore 2014). Nanoparticles were also used against viruses and in managing maturation of fruits (Hawthorne et al. 2014). Nanotechnology is used in agriculture and food production as nano sensors for monitoring crop growth and pest control by early detection of disease-causing pests in plants (Bhagat et al. 2015). Remarkable opportunities were introduced in agriculture by using nanotechnology-based delivery systems, resulting in smart controlled slow release of fertilizers and agrochemicals required to enhance crop yield (Prasad et al. 2017). Agrochemical industries are mainly focusing on increasing crop yields regardless the risk of nano technology, while toxic effects of nanotechnology towards environment and human health received little to no attention. Therefore, it is necessary to also focus on nanoparticles reactivity, biodegradation time, levels of bioaccumulation, retention time, toxicity of waste (Chaud et al. 2021).

The integration of nanotechnology and agriculture has emerged as a ray of hope in a time when concerns about global sustainability are on the rise. This progressive approach might address some of the most urgent issues confronting the globe today, like the sustainable handling of food and agricultural waste, and encourage the adoption of circular economy principles, especially in poor nations. A substantial and frequently underutilized resource that is essential to the sustainability of the food supply chain is agricultural and food waste (Manna et al., 2023). Taking into account research findings worldwide, we found significant improvements with nanotechnology over traditional methods which underscores the practical benefits of nanotechnology, including increased crop yields, efficient resource use, and reduced environmental footprint. This comprehensive review aims to investigate the association between agricultural systems and nanotechnology, emphasizing how it might improve resilience, sustainability, and production.

Nanotechnology in Agriculture

Nanoscience is being investigated in the areas of water management, controlled applications of agrochemicals, plant hormone administration, seed germination, transfer of genes of interest and nano-biosensors (Hayles et al. 2017). Additionally, by conjugation, adsorption, or encapsulation, nanoparticles are created to have the appropriate features (size, shape, surface area, etc.) for use as a protectant, therapeutant or for the site-specific delivery of active substances like fungicides (Khandelwal et al. 2016). Plants can be treated with nanobased materials through foliar spraying, soil application, seed treatment, and root dip treatment. In plants, the metallic oxides, nonmetals, metalloids, polymeric and carbon nanomaterials show growth-promoting and disease-suppressive properties (Elmer et al. 2018). The most often studied nanoparticles are made of iron, zinc oxide, silver, gold and many more. The use of nanoparticles involves three primary mechanisms such as (a) using nanoparticles as biosensors (b) using nanoparticles as therapeutics or protectants and (c) using nanoparticles as intelligent delivery systems for active ingredients like target genes or fungicides. Against a range of soilborne pathogens, such as Fusarium oxysporum, Sclerotium rolfsii, Rhizoctonia solani and Sclerotinia sclerotiorum (Abdelrhim et al. 2021), Ralstonia solanacearum (Khairy et al. 2022), soil-borne viruses, such as Barley yellow mosaic virus (BaYMV) (Aref et al. 2012) etc., the nanoparticles may act as protective or therapeutic agents. The primary methods of combating microbes are agglutination and rupture of cell membranes, suppression of RNA, protein, toxin, and enzyme synthesis, including H⁺ATPase, as well as obstruction of nutrition flow (Dakal et al. 2016). Additionally, nanoparticles serve as carrier molecules, enabling the targeted release of active substances into the plant system and lowering the amount of chemicals released into the environment. Improved pesticide water solubility, site-specific distribution and uptake by target sites, longer shelf life, less impact on non-target organisms and residual environmental effects are just a few advantages of the nano-based formulations (Hayles et al. 2017). Furthermore, nano-based formulations exhibit higher stability and activity in comparison to conventional pesticides, especially in adverse environmental circumstances like rainfall and UV exposure. Multifunctional role of nanotechnology showed in Fig. 1.



Fig.1 Versatile role of Nanotechnology in Agriculture (Source: made by authors)

The Multifaceted Role of Nanotechnology in Sustainable Crop Production and Disease Management

Another important aspect of plant health management is the use of fertilizers. Nanofertilizers bear the potential to increase the release and uptake efficacy of nutrients thereby boosting plant disease resistance. It has widely been explored in plant/disease systems *viz.*, Fusarium wilt in tomato, chrysanthemum, root and crown rot in asparagus, red root rot in tea, Verticillium wilt in brinjal (Elmer et al. 2018).

Nanoparticles

Nanoparticles are characterized as particles in which at least half have dimensions ranging from 1 to 100 nm. Compared to bulk materials, nanoparticles have a substantially greater surface-to-mass ratio (Modena et al. 2019). Various types of nanoparticles tabulated in Table 1. Nanoparticle characteristics, such as their optical, magnetic and electrical qualities, differ greatly from those of traditional materials (Khan et al. 2017). Nanoparticles can be found in diverse chemical compositions, spanning from micelles to metal (oxide), synthetic polymers to large biomolecules. Each of these materials exhibits distinct chemistry, analysable through various methods such as optical spectroscopy, X-ray fluorescence and absorbance, Raman spectroscopy, and solid-state NMR (Ma 2016). While they are commonly assumed to be spherical, nanoparticles actually exhibit a wide range of geometric and irregular shapes (Li et al. 2014).

S.N.	Types of nano particles	Examples	Applications
1.	Metal based nanoparticles	Copper,	Zinc based nanoparticles inhibit fungal
		silver, silicon,	growth Copper nanoparticles may act asbio-
		Titanium oxide, zinc	pesticides and silicon- germanium isused as
			soil supplementation.
2.	Nanoscale polymers	Nylon-	Mainly used as in catalytic processes and
		6/montmorillonite	moisture removal
		montmorillonite-	
		Alginate	
3.	Carbon based nano	Carbon nanotubes	Improving plant health and environmental
	materials	[CNT], fullerenes	cleanup
4.	Nano emulsions	Beta-cypermethrin	Nano emulsions are finding application in
		methyl laurate, alkyl	diverse areas such as drug delivery, food,
		polyglycolides	cosmetics, pharmaceuticals, and material
			synthesis
5.	Clay encapsulations	Organic layered	clay tubes are an excellent miniature
		double hydroxides,	container for encasing chemical agentsand
		anionic inorganic	attractive for applications in drug delivery,
			antimicrobial materials, self- healing
			polymeric composites and regenerative
			medicine

Table 1. Different types of Nano materials and their applications

6.	Nanogels	Polyethyleneimine	(N-isopropylacrylamide) (PNIPAM)-based		
		PEG -polyplex	nanogels with high deformability structure		
		nanogel	were successfully constructed for smart		
			pesticide delivery and effective pest		
			Control		
7.	Dendromers	poly(L-lysine) (PLL),	potential applications of dendrimers include		
	(Nanoparticles)	and triazene	gene transfection, a catalyst for		
			nanostructures, rheology modification		

Nanoparticles can be characterized using high-resolution microscopy technologies, such as electron and scanning probe microscopy, capable of detecting features with submanometer resolution (Park et al. 2015). The potential to synthesize nanoparticles with porous frameworks has significantly broadened the application scope of nanomaterials (Baeza et al. 2017). The surface-to-volume ratio of the nanoparticles is dramatically increased by porosity, exceeding that of solid particles with identical diameters by many orders of magnitude (Modena et al. 2019). Various types of nanoparticles exist, including zerovalent metal nanoparticles, metal oxide nanoparticles, carbon nanotubes, nanocomposites, quantum dots among others. Each of these holds distinct significance in the realm of nanotechnology (Singh et al. 2019). Various techniques are employed for synthesizing nanoparticles, including biological, chemical, and physical methods. However, chemical and physical approaches are not cost-effective and often involve the use of hazardous and toxic compounds. It is widely acknowledged that these methods pose risks to human and environmental health due to harmful radiation, synthetic reductants in concentrated forms, and stabilizing agents. In contrast, biological methods relying on plants and microbes are more efficient, cost-effective, and environmentally friendly. They entail a one-step bio reduction process, offering a safer alternative with fewer adverse impacts (Ul Haq and Ijaz et al. 2019).

History and Timeline

In response to the growing difficulties associated with sustainable production and ensuring food security, substantial technological progress and creative innovations have emerged in the agricultural sector in recent years (Dwivedi et al. 2016; Kou et al. 2018; Xiao et al. 2013). Nanotechnology is one such technological advancement which stands out as one of the most promising advancements in the 21st century. The concept of nanotechnology was first time introduced by an American physicist and Nobel Prize recipient, Richard Feynman in 1959. He delivered a lecture titled "There's Plenty of Room at the Bottom" at the annual meeting of the American Physical Society, which took place at the California Institute of Technology (Caltech) (Bayda et al. 2019). The term 'nanotechnology' was first time used and defined by the Japanese scientist Norio Taniguchi, who served as a professor at the Tokyo University of Science, in 1974 (Khan and Rizvi 2014). According to him, "nanotechnology primarily involves the manipulation, assembly, and alteration of materials at the scale of individual atoms or molecules" (Taniguchi et al. 1974). After Feynman's discovery of this new field of research, it piqued the interest of many scientists. Invention of scanning tunnelling microscope in 1981 and discovery of fullerene/carbon "buckyballs" (C60) in 1985 leads to emergence of nanotechnology (Kroto et al. 1985). In 1986, K. Eric Drexler published the first book on nanotechnology, titled "Engines of Creation: The Coming Era of Nanotechnology." This publication contributed to the increasing popularity of the concept of "molecular engineering" (Drexler 1986). Later on, in 1991, Drexler, Peterson, and Pergamit released another book titled "Unbounding the Future: The Nanotechnology Revolution." In this book, they introduced the terms "nanobots" and "assemblers" to describe nano processes in the field of medicine. It was after this publication that the well-known term "nanomedicine" was first coined and used (Drexler et al. 1991).

Synthesis of Nano-bioformulations Biological Synthesis of Nanoparticles by Microorganisms

Since the beginning of life on earth, biological beings and inorganic materials have been in constant contact with one another. With a well-organized mineral deposit, life may exist on this planet because of this regular contact. The relationship between inorganic molecules and living species has attracted the curiosity of scientists more and more recently. Numerous bacteria can create inorganic nanoparticles through extracellular or intracellular pathways, according to investigations. The synthesis of different nanoparticles using biological methods is covered in this section. The mechanism involved in synthesis of microbial nanoparticles showed in Fig. 2. The categories of nanoparticles covered are metallic (such as gold, silver and other metal nanoparticles), oxide (which includes both magnetic and nonmagnetic oxide nanoparticles), sulphide and other miscellaneous.

Gold Nanoparticles

The use of gold nanoparticles or AuNPs for elegant glass staining dates back to the Roman era and their history in chemistry is extensive. AuNPs have been utilized for ages to treat a variety of diseases. Michael Faraday, who may have been the first to notice that the properties of colloidal gold solutions differ from those of bulk gold is credited with starting the present age of AuNP synthesis more than 150 years ago (Hayat 1989).



Fig. 2. Depicting various steps involved in synthesis of microbial nanoparticles (Source: made by authors)

The growing need to develop environmentally benign technologies in materials synthesis has brought biosynthesis of nanoparticles—the nexus of nanotechnology and biotechnology—to significant attention (Subbarayudu and Kubendiran 2024). The extracellular production of gold nanoparticles by the actinomycete *Thermomonospora* sp. and the fungus *Fusarium oxysporum* has been reported by Ahmad et al. (2003). Additionally, they found that the fungus *Verticillium* sp. was able to synthesise gold nanoparticles inside of cells (Mukherjee et al. 2001). Bacterial cells can easily precipitate gold particles with nanoscale dimensions when they are incubated with Au³⁺ ions (Southam and Beveridge 1996).

Silver Nanoparticles

Similar to its bulk counterpart, silver nanoparticles have potent antibacterial activity against both Gram-positive and Gram-negative bacteria including strains of the latter that are extremely multi-resistant, like methicillin-resistant *Staphylococcus aureus* (Panáček et al. 2006). The creation of biomimetic methods for the formation of sophisticated nanomaterials is a result of the secrets found in nature (Gareev et al. 2022). Scientists have recently been working to employ microbes as potentially environmentally benign nanofactories for the manufacture of silver nanoparticles. It is known that a variety of bacteria can decrease the Ag⁺ ions to produce silver nanoparticles, the majority of which are spherical in shape (Fayaz et al. 2010). The bacterium *Pseudomonas stutzeri* AG259, isolated from a silver mine was shown by Klaus and colleagues to play a significant role in the reduction of Ag⁺ ions and the development of distinct sized and topographically defined AgNPs within the periplasmic space of the bacteria when it was placed in a concentrated aqueous solution of silver nitrate (Klaus et al. 1999). When

fungus, *Verticillium, Fusarium oxysporum* or *Aspergillus flavus* were used, AgNPs were created as a film in solution or deposited on the cell's surface (Jain et al. 2011).

Oxide Nanoparticles

Over the past ten years, there has been a sharp increase in the industrial use of metallic oxide nanoparticles in a wide range of applications. These applications involve the utilisation of metallic oxide nanoparticles such as silicon, titanium, iron and others, increasing the sensitivity of humans and other animals to these nanoparticles through occupational and environmental exposure (Lai et al. 2007). However, because regulatory oversight has not focused on the environmental impact of metallic oxide nanoparticles, the health implications of exposure to these particles in humans and other species have not been thoroughly studied (Lai et al. 2007). One significant class of microbial nanoparticles produced by microorganisms is the oxide nanoparticle. The process of biogenesis of oxide nanoparticles in this section. The majority of the biological systems and magnetotactic bacteria utilized to produce magnetic oxide nanoparticles and nonmagnetic oxide nanoparticles (Li et al. 2011).

Copper Oxide (CuO) Nanoparticles

Copper has been shown in multiple investigations conducted over the past two years to have exceptional antibacterial activity at the nanoscale (Cuevas et al. 2015). Copper as a metal or copper oxides exhibit broad-spectrum biocidal activity. Since copper is a necessary metal for all living things, it may find use in biomedical applications unlike silver nanoparticles which have been the subject of substantial research for their antibacterial properties (Rubilar et al. 2013). It's vital to remember that copper is currently around ten times less expensive on the market than silver so a process that makes use of copper would end up being quite economical. However, it has been noted that compared to silver nanoparticles, copper nanoparticles are less hazardous (Bondarenko et al. 2013). Under ambient conditions, microorganisms like Fusarium oxysporum can extract copper from integrated circuits found on electronic boards (Cuevas et al. 2015). No significant polydispersity was found in the pH range of 5-9 in the investigation of the biogenic synthesis of copper oxides from CuSO4 by Penicillium aurantiogriseum, P. citrinum, P. waksmanii, and F. oxysporum (Honary 2012; Hosseini et al. 2012). Only a few numbers of research evaluating various fungal strains for copper nanoparticle production have been published. It has been observed that certain strains of F. oxysporum and Penicillium sp. are capable of biosynthesizing Cu₂S and copper oxide nanoparticles (Honary et al. 2012; Hosseini et al. 2012). In the presence of three different copper salts. Ability to synthesise copper and copper oxide nanoparticles using a mycelium-free extract made by the white-rot fungus Stereum hirsutum (Cuevas et al. 2015). They also assessed the ability to characterise and evaluate the role of proteins in the formation of the nanoparticles. **Bioformulations**

Bioformulation is a green practice developed by environmentalists and agriculturists to address issues related to biomagnification and chemical toxicity in the environment (Sahai et al. 2019). Any biologically active chemicals generated from microbial biomass or products containing microorganisms and their metabolites that might be utilized to promote plant development, acquire nutrients, and manage disease in an environmentally acceptable way are referred to as bioformulations. Essentially, a bioformulation is a blend of an active ingredient within a formulated product composed of inert (inactive) substances (Aamir et al. 2020). Bioformulation is a ready-to-use formulation that contains living cells or their metabolites (of one or more strains), supported by nontoxic and inert compounds called carriers to sustain the viability and efficiency of cells or metabolites and to lengthen their shelf life (Usta 2013). For promoting plant development, controlling phytopathogens, preserving soil fertility, and preventing disease, bio formulated solutions provide environmentally friendly substitutes to commonly used chemical fertilizers and pesticides (Arora and Mishra 2016; Khatri and Bhateria 2023). A bioformulation is a preparation of microorganisms or their active gradient that can be used in place of chemical fertilizers/pesticides. However, for the formulation to be successful, a true bio-formulated product needs to have an active component and be made of living microbes, spores, or their derivatives. Talc, Peat, carboxymethylcellulose, vermiculite, and polymers, particularly xanthan gum and diatomaceous earth are some of the most popular inert active materials. The antagonistic microbial cells have been discovered to be more effectively incorporated into the plant system and rhizosphere by using inert carrier-based bioformulations, which could be applied both foliarly and topically (Aamir et al. 2020). Starch, methyl cellulose, silica gel and gum are a few additives that help bioformulated products withstand the extreme weather conditions while also enhancing their physical, chemical, and nutritional qualities (Schisler et al. 2004). Some of the microorganism that are used in bioformulation are the strains of Trichoderma spp., Rhizobium, Bacillus, Glomus, Lactobacillus, Azospirillum, Burkholderia, Rhodococcus, Pseudomonas fluorescens, Bacillus subtilis, Azotobacter, Pseudomonas spp., Actinobacteria, Bradyrhizobium, Acetobacter, Paenibacillus, Serratia, Herbaspirillum, Blue green algae, Paenibacillus elgii, Pseudomonas putida, mycorrhizal fungi etc (Bidyarani et al. 2022).

Various nano-bioformulations Nano-bioformulation as a nano-biofertilizer

Nano-biofertilizer refers to a product comprising nano-scale materials paired with a particular microbial inoculant. Its nanoscale properties influence its application method, allowing for precise and timely nutrient delivery to field crops. Simultaneously, it enhances the functional advantages of the bio-fertilizer component within the formulation. Bio-fertilizers encompass crucial root-associated microorganisms, such as fungal mycorrhizae, Azospirillum, blue-green algae (BGA) and Bacillus species (Shanware and Taiwade 2022). The utilization of nano-biofertilizers has reduced the indiscriminate use of agrochemicals and contributed to substantiating integrated nutrient management practices for the consistent productivity of crops (Mir et al. 2015). The surface area of nutrients is increased through the process of making nanobiofertilizers, which involves coating the surface of bio-fertilizers with nanoparticles. This improves both their stability and the efficiency with which soil nutrients are taken up (Mala et al. 2017). This approach entails the live formulation of microorganisms that stimulate bacterial activity for improved plant growth. This formulation is then coated with a nanoscale polymer, a method commonly known as nanoencapsulation (Shebl et al. 2019). One of the notable advantages of nanoencapsulation technology lies in its flexibility, particularly in protecting the components of bio-fertilizers containing PGPR (plant growth-promoting rhizobacteria). This innovation has resulted in an extended shelf life and has also enabled precise control over the release of PGPR mechanisms (Gouda et al. 2018). Silicon, zinc, copper, iron, and silver are

among the most frequently employed nanoparticles in the formulation of nanobiofertilizers (Akhtar et al. 2022). Three crucial steps are involved in the creation of nanobiofertilizers: (1) the growth of the biofertilizer culture; (2) its encapsulation with nanoparticles; and (3) the assessment of its efficacy, quality, purity and shelf life (Panichikkal et al. 2021). Various formulations have been developed to improve crop production, such as the combination of nano-Zn and biofertilizer, which has been shown to enhance the physiochemical properties of sugarbeet plants. Additionally, the application of a combination of nanopharmax and humic acid in black cumin may boost the nutritional content of cumin (Shanware and Taiwade 2022). The application of Nano-biofertilizer containing specific bio-inoculants, such as *Azotobacter* strain, *Pseudomonas putida*, and *Pantoea agglomerans* strain P5, has been studied. This application has been found to raise nutrient concentrations and increase pigment content. Moreover, it enhances various plant parameters including photosynthetic productivity, leaf area, sucrose content, and other factors on different parts of the plants.

Nanobioformulation as a nanobiopesticide

Despite their pesticidal effectiveness, biopesticides have some drawbacks. Innovative formulations have been created to increase their efficacy and fix current problems (Ayilara et al. 2023). This includes nanoformulations with a smaller amount of the active ingredient that are appropriate for diverse crop protection applications. Management of plant pathogens by use of various nanoparticles depicted in Fig. 3.



Fig. 3 Management of plant pathogens by use of various nanoparticles (Source: made by authors)

The resulting biopesticidal nanoformulations can be used directly as pesticides when nanomaterials are stabilized with biopesticides and nanobiopesticides are incorporated. By gaining efficiency at lower dosages of active components, these nanobiopesticides aid in successful pest management (Vimala Devi et al. 2019).

Examples of various nano bioformulations as nanobiopesticides

Silver nanoparticles were developed and capped with the leaf extract of Aristolochia indica (Siva and Santhosh Kumar 2015). Management of various plant diseases by using different nanoparticles tabulated in Table 2. The resulting nanoparticles exhibited toxicity against the larva of Helicoverpa armigera. In field conditions within a cotton crop, it was observed that the combination of silver nanoparticles with the pyrethroid compound bifenthrin, extracted from Chrysanthemum, demonstrated greater toxicity to Lygus hesperus compared to Acheta domesticus. Essential oils were extracted from Zanthoxylum rhoifolium leaves (Christofoli et al. 2015). Subsequently, nanospheres were developed with these oils using nanoprecipitation, resulting in a notably high encapsulation efficiency of 96 per cent. The effectiveness against adult Tribolium castaneum (Herbst) was examined by utilizing polyethylene glycol nanoparticles as carriers for garlic essential oil. The eco-friendly production of silver nanoparticles and lead nanoparticles, utilizing extracts from Euphorbia prostrate and Avicennia marina (a mangrove plant), demonstrated pesticidal activity against Sitophilus oryzae. The outcomes revealed a 100% mortality rate after a 4-day treatment period (Vimala et al. 2019). Coating derived from cashew gum was applied to an insecticide extract obtained from Moringa seeds. This coating led to a notable enhancement in entrapment efficiency, rising from 39% to 60%. Remarkably, the released insecticide remained effective for up to 55 days following application (Paula et al. 2012). Chitosan nanoparticles (ChNPs) loaded with silver metal ions exhibit heightened antibacterial efficacy, demonstrating a low minimum inhibiting concentration (MIC) of 3 µg/ml against Escherichia coli and 6 µg/ml against Staphylococcus aureus (Du et al. 2008). Titanium dioxide nanoparticles (TDNPs), synthesized through T. viride, were evaluated for their bioefficacy against larvae and pupae of Helicoverpa armigera. The TDNPs exhibited remarkable effectiveness, causing 100 per cent mortality in first, second and third instar larvae of *H. armigera* at a concentration of 100 ppm (Kamaraj et al. 2018). Extracellular synthesis of silver nanoparticles (AgNPs) utilizing the bacterium Serratia sp. BHU-S4 revealed an inhibitory impact on the fungus Bipolaris sorokiniana. The AgNPs produced through biogenic means displayed complete inhibition of conidial germination, both on the growth medium and on wheat leaves artificially inoculated with fungal conidia (Mishra et al. 2014). Nanoemulsions formulated with neem and citronella essential oils demonstrated potent antifungal activity against Rhizoctonia solani and Sclerotium rolfsii (Ali et al. 2017). Conyza dioscoridis, Melia azedarach, and Moringa oleifera extracts were used to make silver nanoparticles (Ag-NPs), which showed increased nematocidal action against eggs and young of the root-knot nematode M. incognita (Abbassy et al. 2017). The prospective use of mycogenic zinc oxide nanoparticles (ZnONPs) as a preventative measure against potato late blight looks promising (Singh et al. 2022). Silver and gold nanoparticles were biosynthesized using Trichoderma atroviride, demonstrating potential for biological control of Phomopsis canker disease in tea plants. The nanoparticles exhibited antagonistic activity against the pathogen (Ponmurugan 2017).

Bacillus based nanobiopesticide for disease and pest reduction

Due to its great entomopathogenic potential, the genus *Bacillus* is frequently used as a biocontrol agent for managing both diseases and insects (Mampallil et al. 2017). The *Bacillus* group of bacteria is found in a diverse range of environments and is renowned for its ability to produce numerous antimicrobial compounds with diverse structures. Approximately 5–8% of

its genome is dedicated to the synthesis of secondary metabolites (Fira et al. 2018). The creation of a nano-formulation using Bt relies on top-down methods of micronization, including ball and jet milling, as well as high-pressure homogenization. These processes are employed to convert coarse powder into fine particles within the size range of $2-5 \mu m$ (Vimala Devi et al. 2019). A nanobioformulation, functioning as a nanobiopesticide is a composite of nanoparticles and microbial biocontrol agents (such as *Bacillus* sp.) (Padmakumar et al. 2023). This combination capitalizes on the higher surface area/volume ratio of nanoparticles, leading to enhanced effectiveness, reduced toxicity, increased solubility, durability and versatility. Various types of nanoparticles, including Ag, Al, Au, MnO, ZnO etc., can be integrated with different Bacillus species like B. thuringiensis, B. subtilis, B. licheniformis, etc. This integration aims to create an effective, efficient and environmentally friendly nanobiopesticide capable of suppressing the growth of diseases and pests (Kumar et al. 2021). Strains of B. subtilis have been identified for their ability to inhibit the growth of various plant pathogens, including Phomopsis, Colletotrichum truncatum, Rhizoctonia solani, Macrophomina phaseolina, Sclerotinia sclerotiorum, Colletotrichum gloeosporioides, Phytophthora infestans and others (Widnyana and Javandira 2016).

Nanomaterial	Type of pathogen	Target pathogen	Сгор	Effect	Reference
AgNPs	Fungi	Macrophomina phseolina, Fusarium fujikuroi and Rhizoctonia solani	Cotton (Gossypium herbaceum)	Reduction in mycelial growth and disease of cotton seedlings	(Zaki et al 2022)
MgONPs	Fungi	Phytophthora infestans	Potato (Solanum tuberosum)	InhibitionofPhytophthorainfestansbycellmembranedistortion,distortion,oxidativestress,disruptionofmetabolicpathwaysandmembranetransportactivitywithnoharmfuleffectonpotato	(Wang et al. 2022)
Copper oxide nanoparticles CuONPs)	Fungi	Phytophthora nicotianae	Tobacco (<i>Nicotiana</i> <i>tabacum</i>)	33.69% increase in control efficacy and tobacco black shank disease suppression without inducing phytotoxicity at 100 mg L-1 of CuO NPs treatment	(Juan et al. 2022)

Table 2. Management of soil borne plant pathogenic organisms by using various Nanoparticles

Capped AgNPs	Fungi	Sclerotinia sclerotiorum	Vegetables	Inhibition of mycelial	(Guilger et
				growth and scierotia germination	al. 2021)
Chitosan NPs	Fungi	Fusarium oxysporum,	Cereals,	Reduction in mycelial	(Boruah
		Rhizoctonia solani, Sclerotium rolfsii	Vegetables	growth	and Dutta 2021)
Carboxymethyl	Fungi	Phytophthora capsici	Black pepper	Antifungal activity	(Hai et al.
cellulose coated core/shell		Host: <i>Black pepper</i>	(Piper nigrum)	against <i>P. capsici</i> with MIC 75 ppm	2021)
SiO2@Cu nanoparticles					
Zinc oxide	Bacteria	Ralstonia solanacearum	Tomato	Reduced incidence of	(Jiang et
(ZnO), Iron oxide (FeO) and		Host: Tomato	(Solanum lvcopersicum)	tomato bacterial wilt disease	al. 2021)
Copper oxide			ij cop ci stetilit)		
(CuO)					
nanoparticles					
AgNPs	Fungi	Sclerotinia sclerotiorum	Mustard (Brassica	Inhibition of hyphal growth, sclerotial	(Tomah et al. 2020)
			juncea)	formation and	
				myceliogenic germination of sclerotia	
Magnesium	Fungi	Phytophthora nicotianae and	Tobacco	Inhibition of fungal	(Chen et
oxide		Thielaviopsis basicola	(Nicotiana	growth, spore	al. 2020)
nanoparticles			tabacum)	germination and	
(MgONPs)				impediment of	
				sporangium development	
AgNPs	Nematodes	Meloidogyne javanica	Tomato	Nematicidal activity on	(Ghareeb
			(Solanum	egg hatchability and	et al. 2020)
			lycopersicum)	juvenile mortality.	
				Reduction in number of	
				galls, egg masses,	
				number of females per	
				root/plant and mortality	
Silver	Fungi	Sclerotium rolfsii. Rhizoctonia	Cereals.	Mycelial growth	(Kaman
Nanoparticles		solani, Sclerotinia sclerotiorum	Pulses and	inhibition at 100 ppm	and Dutta
(AgNPs)		and Fusarium oxysporum	vegetables	AgNP	2019)
Copper/Iron	Nematodes	Meloidogyne incognita	Tomato	Nematicidal activity such	
NPs		and <i>M. javanica</i>	(Solanum	as paralysis, biological	(Gkanatsio
			lycopersicum)	cycle arrest, reduction in	u et al.
				number of galls with	2019)
				lowest EC50 value as	

				compared to commercial nematicides
AgNPs	Fungi	<i>Fusarium solani</i> and	Strawberry	The nanoparticle showed (Ruiz-
		Macrophomina phaseolina	(Fragaria	broad spectrum Romero et
			ananassa)	antagonism against M al. 2018)
				phaseolina (67.05%) and
				F. solani (83.05%)
Gold	Virus	Barley yellow dwarf virus	Barley	A high yield of ruined (Alkubaisi
nanoparticles		(BaYDV)	(Hordeum	virus like particles and Arif
(AuNPs)			vulgare)	(VLPs) were also 2017)
				observed
AgNPs	Fungi	Phomopsis sp. Host: Soybean	Soybean	Absolute inhibition of (Mendes et
		seeds	(Glycine max)	the pathogen was al. 2014)
				observed 270 and 540
				ppm concentration

Mode of action of nanobioformulation:

When beneficial bacteria are introduced into the soil as biofertilizers, they colonize and multiply quickly. This microbial activity plays a crucial role in converting typically insoluble and organic nutrients into soluble forms, making it easier for plants to absorb them. Biofertilizers that include nitrogen-fixing bacteria like *Rhizobium*, *Frankia*, *Xanthomonas*, and others have the capability to produce the nitrogenase enzyme.



Fig.4. Hustrating various mode of action of bionanoformulation (Source: made by authors)

Unveiling the Mechanisms: Diverse Modes of Action of Bionanoformulations in Enhancing Agricultural Productivity and Disease Control This enzyme, in turn, facilitates the conversion of nitrogen into ammonia (Patel et al. 2023). Phosphate-solubilizing microorganisms like *Bacillus, Aspergillus*, and *Pseudomonas* produce enzymes or organic acids that play a catalytic role in converting insoluble phosphate complexes, such as aluminum and tricalcium phosphates, into soluble forms that plants can readily absorb (Tian et al. 2021). These microorganisms, known as Plant Growth-Promoting Rhizobacteria (PGPR), also release substances like iron, vitamins, and hormones that are essential for plant growth. Additionally, the relationship between PGPR and plants is strengthened through cellular communication methods, such as quorum sensing. This serves as a signalling mechanism through which microorganisms assess their environment and coordinate their activities within the rhizosphere (Sarbani and Yahaya 2022).

Advantages and disadvantages of nanobioformulations Advantages:

Nanobioformulations is the combination of biofertilizers with nanonutrient particles. These nanobioformulations may incorporate one or more beneficial microorganisms that including soil nitrogen-fixing enhance productivity, bacteria, phosphatesolubilizing/mobilizing organisms, and plant growth-promoting stimulators (Tarafdar 2022). Compared to traditional pesticides, nanopesticides offer superior performance and are better suited for widespread use in the global context of climate change and resource scarcity (Wang et al. 2022). Nanoformulations stand out as a vital component in contemporary agricultural technology (Sahu et al. 2021). Nanoformulations encompass the process of coating, encapsulating, adsorbing, or entrapping fertilizers, pesticides, and nutrient supplements within the voids, pockets, or pores of nanomaterials (Bhardwaj et al. 2022). There are various advantages of using nanobioformulation instead of conventional chemical fertilizer. The inoculation of plants with NBFs improves plant development and resistance to stress, utilizing nanobiofertilizer formulations can contribute to the advancement of sustainable agriculture development (Garg et al. 2023). The application of nanobioformulations in agriculture presents an opportunity to enhance global food production sustainability. The significant advantages of nanofertilizers over traditional chemical fertilizers revolve around their nutrient delivery systems (Yadav et al. 2023). For instance, nanofertilizers can release nutrients gradually over a period of 45 to 50 days, in contrast to the 5 to 10 days typical of conventional fertilizers. This extended release improves nutrient use efficiency up to 20 times, reducing nutrient requirements and cutting down on transportation and application costs. Nanoparticles are considered effective carriers for delivering nutrients to specific locations through methods such as encapsulation or creating nanoscale emulsions. Interestingly, the surface coating of nanomaterials on fertilizer particles offers better adhesion due to their higher surface tension compared to conventional surfaces. This improved adhesion facilitates controlled nutrient release (Brady and Weil 1999; DeRosa et al. 2010; Bhattacharyya et al. 2016). Nanobioformulations possess a great advantage over conventional fertilizers as they exhibit specificity, reduced toxicity, and gradual release of nutrients (Cui et al. 2010). Another advantage of using nano biofertilizers is it prevents soil from becoming excessively loaded with salts, a common issue associated with the over-application of conventional fertilizers (Tarafdar 2022). Moreover, the application of nanotechnology in agriculture counteracts the

problems such as crop yield, food security, climate change, and sustainability (Mishra et al., 2014).

Disadvantages:

Although the future of nanopesticides in agriculture development appears promising, the human exposure to dangerous agrochemicals able to cross biological barriers (e.g., blood-brain barrier, blood-placental barrier, and blood-retinal barrier) is a significant concern as it can cause irreversible damage to vital organs. The risks posed by the exposure to hazardous nanopesticides, which are able to induce toxic and genotoxic events, are currently receiving great attention by studying the effect not only on the chemical composition of the bulk material but also on the physicochemical properties of nanopesticides such as size, electrical charge, and surface properties (Grillo et al. 2012; Zielinska et al. 2020).

According to studies, nanoparticles may have negative impact on soil, plant and animal's health. Nanoparticles have the potential to alter the composition and structure of soil, potentially leading to reduced water retention and nutrient accessibility. Moreover, there is a possibility that plants may absorb these nanoparticles, which could impact food chains and affect plant growth (Ahmed et al. 2021). Nanomaterials may enter in aquatic habitat, potentially affects aquatic ecosystems and may become part of the aquatic food chain. Nanoparticles can easily enter into the biological systems which is not possible for the larger particles. The ability of nanoparticles to cross cell membranes depends on their size. In situations where farm workers are spraying nanoparticles, there is a potential risk of inhalation, which could allow these nanoparticles to enter the bloodstream and potentially reach various target sites within the body, including the brain, liver, or heart (Suppan 2017). These nanoparticles might affect the regulatory mechanisms of enzymes and other proteins (Saptarshi et al. 2013). There is a possibility of nanoparticles entering food chains, with potential implications for human health. Therefore, it is crucial to prioritize the development of a skilled workforce that comprehends the intricacies of agricultural production systems, enabling the successful integration of nanotechnology applications in agriculture (Siddhartha 2014). However, the exact consequences of their presence on human health and aquatic ecosystems remain uncertain at this time (Li et al. 2014). It may adversely affect biodiversity and ecosystem health as even small changes may upset sensitive balances, there are worries about how long-term usage of nano-materials will affect biodiversity and ecosystem dynamics (Ahmed et al. 2021).

Nanopesticides, which are nano-formulated pesticides, offer innovative solutions to pest and disease management. Their effectiveness, however, depends on formulation, target pests, and environmental interactions. Below are the pros and cons of different nano-pesticides with references to specific case studies:

Type of Nano- pesticide	Pros	Cons	References
Nano-Encapsulation	 Controlled release reduces application frequency and enhances efficacy. 	 High cost of nano - carrier synthesis. 	Arratia-Quijada et al. 2024; Dinh et al. 2024

	Enhanced targeting	> Potential residue	
	minimizes non-target	persistence of	
	exposure.	encapsulation materials.	
	Protects active ingredients	 Limited biodegradability. 	
	from degradation.		
	Nano-encapsulated carbendazim	n effectively controlled Fusarium	Sandhya 2024
	oxysporum with 50% lower do	oses. Phytotoxicity evaluation of	
Case Study:	nanoformulated fungicide cont	firmed that the nanoformulated	
	carbendazim is safer for germina	ation and root growth of the seeds	
	of Cucumis sativa, Zea mays, an	d Lycopersicum esculantum.	
Nano-Emulsions	Improved solubility of		Mustafa and
	hydrophobic pesticides,	Stability issues like phase	Hussein 2020
	enhancing efficacy.	separation during storage.	
	 Uniform distribution leads 	 Energy-intensive 	
	to better plant coverage.	production processes (e.g.,	
	Reduces environmental	ultrasonication).	
	impact by lowering active	,	
	ingredient runoff.		
Case Study:	Citronella-oil (1%) and biosilic	a (2%) nanoemulsion, and neem	Djiwanti et al.
	oil formulas (1%) effectively s	2022	
	(99.33% and 97.65%, and 99.6		
	sinensetin content/production in		
	could be evaluated further in the	plantation in the field.	Seath at al 2010
	- Broad-spectrum activity with	Detential physicity and	Saqib et al. 2019
Nano-Metal Oxides	inspecticidal properties	- Potential phytotoxicity and	
$(e \sigma C u O 7 n O)$	- Low chance of resistance	- Expensive and energy-	
(c.g., CuO, ZhO)	development due to multiple	intensive to produce at scale	
	action modes.	intensive to produce at scale.	
Case Study:	CuO nanoparticles inhibited P.	seudomonas syringae in tomato	Banik and Pérez-
j-	plants effectively. Another stu	idy reported that Pseudomonas	de-Luque 2017;
	syringae was inhibited after exp	posure to 200 mg L^{-1} of Cu-based	Tortella et al. 2024
	NPs without any negative effect	t on other microbes indicating its	
	selective effect.	-	
	➢ Economical and readily	> I imited commetibility with	Margal et al. 2023;
	available materials.	Elimited compatibility with contain active ingradients	Rana et al. 2024
Nano-Clays	Reduces pesticide leaching	Earmers' unfamiliarity	
L L	and improves soil	with application	
	retention.	techniques	
	 Environmentally benign. 	1	
Case Study:	Clay composite nono formulatio	one reduced herbiside leaching by	
	40% in field trials	ons reduced heroredue reaching by	

	➢ Highly effective against a		Zahoor et al. 2021;
	wide range of pathogens	➢ Risk of toxicity to	More et al. 2023
	like bacteria, fungi and	beneficial microorganisms	
Nanosilver	some viruses.	and aquatic ecosystems.	
	➢ Compatible with	> Expensive production and	
	biocontrol agents.	regulatory challenges.	
	 Long-lasting efficacy. 		
Case Study:	Silver nanoparticles controlled	Alternaria solani causes early	Ansari et al. 2023
	blight on potatoes more effective		
	Lower concentrations of silver 1		
	PO, PPO, and PAL production	n. These defensive mechanisms	
	clearly demonstrate the fung	icidal potential of AgNPs and	
	recommend their utilization in d	ifferent crop protection programs.	

Future Directions

Research into nanotechnology applications for use in agriculture especially in the field of crop protection has become increasingly popular over the past decade. This analysis of the latest research trends provides a useful basis for identifying research gaps and future priorities. The development of novel plant-protection products has received greater attention than other applications, such as those related to nanosensors or fertilizers. Remarkable opportunities to renew agriculture practices have been introduced by using nanotechnology-based delivery systems, attributed to the smart controlled release profile of fertilizers and agrichemicals require to enhance crop productivity (Prasad et al. 2017). Such systems play a critical role in agriculture, improving fertilizers and agrochemicals performances (Fraceto et al. 2016). Presently, numerous research initiatives of nanopesticides prioritize performance optimization, including enhancing activity (Li et al. 2022), targeted deposition (Su et al. 2023), improved safety (Gao et al. 2018), and controlled release (Xiao et al. 2022).

However, some nanopesticides might be designed without initial consideration for specific application scenarios or are limited to traditional spraying methods. This research idea contradicts the needs of pesticide application in future diversified agriculture. Furthermore, there is a scarcity of review covering existing nanopesticides developed for diverse agricultural scenarios. It should be noted that the plant cultivation environment is diverse,125 and future application scenarios for pesticides might be more extensive, such as cities, oceans, and even deserts. This is crucial information that developers and manufacturers of nanopesticides must not overlook. As agricultural mechanization advances, pesticide application methods are also evolving. Therefore, this review focuses on 'Scenario-oriented Nanopesticides', highlighting the importance of prioritizing practical and specific application scenarios in the future development of nanopesticides to enhance sustainable development potential and resource utilization.

In addition to the application methods, experimental research targeting specific scenarios should consider environmental conditions when pests and diseases occur (such as

temperature, humidity, and pH) as well as microenvironmental changes within the plant (such as enzymes, ROS and hormones). More importantly, these products need to be validated in the field to bridge the gap between the scientific and industrial circles and provide the public with a more objective and realistic understanding. In addition, it is crucial to consider the environmental impact and biosafety of nanopesticides. Manufactured nanopesticides require a comprehensive evaluation system.126 Scenario-oriented nanopesticides can more accurately target actual production needs and accelerate the industrialization process. In the context of sustainable agriculture, this concept is expected to lead the future development of nanopesticides.

Conclusion

Plant diseases that are carried by the soil, such as fungi, bacteria, viruses, and nematodes, can damage a plant's root system and collar, resulting in significant financial loss. Because chemical pesticides are unable to penetrate the soil system and do significant harm to the environment and soil, managing such diseases with traditional methods is challenging. One possible management approach to lessen the threat of soil-borne plant diseases is nanobiotechnology. Because of their many antibacterial characteristics, such as the production of reactive oxygen species (ROS), toxicity from nanoparticles, and destabilization of cell membranes, organelles, and other macromolecules, nanomaterials can be used to control soilborne diseases. Because of their smaller size and higher surface area to volume ratio, nanoparticles have a higher potential for penetration and better interactions with bacteria that live in soil, which increases the effectiveness of their control. In order to lessen the amount of chemicals that are released into the environment, nanomaterials can also be employed as intelligent pesticide, fungicide, and fertilizer delivery systems. In addition to validating these technologies against current technologies, more study is required to ascertain the viability, sustainability, efficiency, application and releasability of goods based on nanotechnology in real-world.

Nanopesticides, as a promising technology, bring scientific and technological impetus to sustainable development and green revolution of agriculture. The excellent physicochemical properties, beneficial biological effects, and functional potential of nanopesticides have significantly contributed to improving utilization rates of pesticides, enhancing pest and disease management, and alleviating stresses. In conclusion, the development and production of nanopesticides will necessarily lead to an increased amount of nanopesticides applied in agriculture. A reliable and comprehensive risk assessment before widespread application is the first line of defense to ensure environmental safety and human health. There have been serious environmental issues, like DDT or neonicotinoids in human history, which were allowed to occur due to lack of a comprehensive assessment of environmental risk in advance. For nanopesticides, we should learn the lesson and avoid a similar outcome in the future. Unexpected risk of nanopesticides comes from their possible toxicity to nontarget organisms, transportation, and bioaccumulation, and from interactions with other pollutants in the environment. These processes should be the focus of the regulatory framework for nanopesticide risk assessment. In order to lessen the amount of chemicals that are released into the environment, nanomaterials can also be employed as intelligent pesticide, fungicide, and

fertilizer delivery systems. In addition to validating these technologies against current technologies, more study is required to ascertain the viability, sustainability, efficiency, application and releasability of goods based on nanotechnology in real-world.

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Authors contribution

All authors made substantial contributions to conception and design, acquisition of data, or analysis and interpretation of data; took part in drafting the article or revising it critically for important intellectual content; agreed to submit to the current journal; gave final approval of the version to be published; and agreed to be accountable for all aspects of the work.

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