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Recent Developments in Synthesis of Nanomaterial for Agriculture: The Role of Supercritical Fluid Technology

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ABSTRACT

Fungal diseases, such as Ganoderma boninense, pose significant economic threats to oil palm plantations. Conventional fungicides, including synthetic and biofungicides, have been employed to manage these diseases, but they come with limitations such as environmental impact and limited efficacy. Other than that, weed infestation is another serious challenge in agricultural systems such as oil palm plantations. Synthetic herbicides and bioherbicides have been widely use to mitigate this problem but herbicides still have limitation in terms of health concerns. Recent advancements in nanotechnology have introduced nano-enabled crop protection most notably nanofungicides and nanoherbicides as promising alternatives, offering improved penetration and delivery of active ingredients. However, challenges such as non-uniform size distribution and polydispersity hinder their effectiveness. This review explores the potential of supercritical fluid technology (SFT) to overcome these limitations, providing a green and sustainable approach to nanoparticle production. SFT offers distinct advantages, including moderate operating temperatures and non-toxic solvents, aligning with the principles of green chemistry. The unique properties of SFT-produced nanomaterials, particularly their high surface area-to-volume ratio, demonstrate significant potential for membrane technology applications beyond agricultural contexts. Future perspectives highlight the need for further research to optimize SFT processes for agricultural applications, aiming to enhance the scalability and cost-effectiveness of nanofungicide and nanoherbicide production. The integration of SFT in agriculture could revolutionize plant disease and weed management, contributing to sustainable and eco-friendly practices.

Keywords: Nanofungicides, nanoherbicides, nanoparticles, active ingredients, supercritical fluid technology, nano delivery system

1.0 INTRODUCTION

The cultivation of oil palm trees (Elaeis Guineensis) plays a vital role in the global economy, providing about 40% of all traded vegetable oil for various industries. Oil palm cultivation is on the rise across the humid tropics of Southeast Asia, Africa, and South America. The majority of global

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production, approximately 85%, is concentrated in Indonesia and Malaysia, neighbouring countries in Southeast Asia (Murphy *et al*., 2021). However, these trees face significant challenges due to fungal infections, such as Basal Stem Rot (BSR) caused by the white rot fungus Ganoderma Boninense, which can lead to reduced yield by 50 to 80%, quality and safety and economic losses (Paterson, 2019). Ganoderma Boninense is a soil-borne pathogen and a major threat to global oil palm industries. In Malaysia and Indonesia, the pathogen has caused havoc in the past. For instance, BSR leads to about 43% economic loss within six months of infection. Without effective control measures, it is estimated that by 2040, G. Boninense could affect 860,610 hectares of mature, oil-yielding trees in Malaysia (Khoo & Chong, 2024). Controlling BSR is particularly challenging because the fungus persists in the soil, complicating disease management efforts.

Conventional approaches to manage BSR, including sanitation, soil mounding, and the use of biological control agents (BCA), primarily rely on fungicides (Nur-Rashyeda *et al*., 2023). However, these methods have significant limitations. For instance, soil mounding, where soil is heaped around the trunk to a height of approximately 75 cm, has proven ineffective in regulating BSR (Jazuli *et al*., 2022). Similarly, sanitation measures such as clean clearing and windrowing, which involve chipping, pulverizing, and stacking infected palms to promote natural decomposition, can be costly and fail to prevent fungal survival, leading to reinfection of healthy palms. While extensive research has been conducted on BCAs for G. boninense, their practical application remains limited due to poor field efficacy and vulnerability to adverse environmental conditions(Siddiqui *et al*., 2021). Fungicides are chemicals that prevent, destroy, or inhibit the growth of fungi diseases in crops (Koli *et al*., 2019). A study showed that hexaconazole, applied via pressure injection, reduced BSR spread in infected oil palms, with 70% of treated palms producing fruit bunches after five years. Although ergosterol (a fungal marker) persisted in diseased tissues, indicating limited efficacy, the treatment extended the productive period of infected palms. (Khoo & Chong, 2024). Conventional fungicides, including synthetic agents such as azoxystrobin, chlorothalonil, and thiophanate methyl, have long been essential for managing fungal infections like basal stem rot (BSR) in oil palm. Valued for their rapid action and broad-spectrum efficacy across diverse crops, these formulations remain primary defense tools for farmers. However, persistent use raises serious concerns regarding biodiversity loss, fungicide resistance development, and environmental and human health risks, underscoring the urgent need for sustainable alternatives that maintain efficacy while mitigating these detrimental impacts. (Abbey *et al*., 2019).

Synthetic fungicides can negatively impact biodiversity, as their broad-spectrum activity often harms beneficial organisms, including microbes and insects that are crucial to ecological balance. This disruption can affect ecosystem services such as pollination and natural pest control, which are vital for sustainable agriculture (Wu *et al*., 2023). Furthermore, prolonged use of synthetic fungicides can lead to resistance in fungal populations, necessitating the development of more potent chemicals and fostering a cycle of dependence on these fungicides (Thind, 2021). Their persistence in the environment can also lead to long term contamination of soil, water, and plant tissues, posing risks to non-target organisms (Ul Haq *et al*., 2020). In addition to environmental concerns, synthetic fungicides pose health risks to farmers, farmworkers, and consumers. Prolonged exposure during application can cause skin irritation, respiratory issues, and other long-term health problems. Consumers may also ingest residual fungicides present on produce such as fruits, vegetables, and grains. Financially, the frequent use of synthetic fungicides is costly, creating economic challenges for farmers striving for sustainable production. While synthetic fungicides remain a crucial tool for disease prevention, their limitations underscore the importance of adopting more sustainable and eco-friendly alternatives.

Another overlooked limitation of conventional fungicides is their inability to maintain uniformity in particle size distribution, which directly impacts absorption and translocation efficiency within the plant. Studies have shown that high polydispersity index (PDI) values in traditional formulations hinder consistent bioavailability, resulting in poor coverage and reduced efficacy. Addressing this formulation weakness is essential, particularly when aiming for systemic delivery in crops like oil palm that require deep vascular penetration for effective disease suppression (Motta *et al*., 2016).

Biofungicides, derived from natural sources, offer an environmentally sustainable alternative for managing agricultural fungal diseases. These agents exhibit high selectivity against pathogens while preserving beneficial organisms, as they disrupt fungal energy production, biosynthesis, and cell structure integrity. With low toxicity to humans and animals and minimal environmental impact due to their natural composition and low active ingredient concentrations, biofungicides represent a promising approach to disease control that aligns with sustainable agricultural practices. (Khakimov *et al*., 2020). Biofungicides are also cost-effective and can be applied in areas where synthetic fungicides are prohibited, such as recreational zones and urban landscapes (Abbey *et al*., 2019). However, biofungicides have limitations that affect their practicality and applicability. Their high selectivity can restrict their use to specific pathogens, requiring precise disease identification before application, which increases time and resource demands (Kumar *et al*., 2021). Environmental factors, such as temperature fluctuations and rain, can reduce their efficacy by degrading bioactive proteins and enzymes or washing them away (J. Köhl *et al*., 2019). Some biofungicides also depend on specific inducers to release stable, fungi-inhibiting metabolites, which can be disrupted by repressor molecules produced by pathogenic microbes (L. Ons *et al*., 2020).

Another issue is the inconsistent particle morphology resulting from biofungicide production methods. Microbial and biologically derived particles often display wide size variation, reducing their potential for uniform delivery and long-term storage stability. Despite their green credentials, the inherent variability in biological synthesis processes must be overcome to make biofungicides a viable large-scale solution (Hamrouni *et al*., 2025).

In addition to fungal threats, weed infestation presents another serious challenge in agricultural systems such as oil palm plantations. Uncontrolled weed growth competes with crops for essential resources like light, water, and nutrients, thereby reducing yield potential. To manage this, chemical herbicides have traditionally served as the primary line of defense. However, much like synthetic fungicides, these formulations are associated with significant environmental, health, and efficacy concerns.

Synthetic herbicides like glyphosate, 2,4-D, and atrazine are widely used for their broad-spectrum efficacy, cost-effectiveness, and rapid action through inhibition of essential plant enzymatic pathways. However, growing sustainability concerns highlight critical limitations, including herbicide-resistant weed populations, environmental persistence, and non-target toxicity. Prolonged use results in soil and water accumulation, endangering beneficial microorganisms and aquatic ecosystems while increasing food chain contamination risks. (Mohd Ghazi *et al*., 2023). Human exposure to synthetic herbicides, particularly during mixing, spraying, or residue ingestion, has also raised health concerns. Reported risks include dermal irritation, respiratory complications, and potential carcinogenicity (Curl *et al*., 2020). These challenges, combined with regulatory scrutiny and rising public awareness, have driven the search for safer alternatives.

One such alternative is the use of bioherbicides, which are derived from natural sources including plant-based compounds (e.g., orange oil, acetic acid), bacteria, and fungi. Bioherbicides typically exhibit high selectivity and biodegradability, making them environmentally benign. They function by disrupting key cellular processes in target weeds, such as energy metabolism, cell wall biosynthesis, or membrane integrity (Yadav, 2017). Additionally, due to their low toxicity, bioherbicides are particularly suited for application in environmentally sensitive areas such as urban landscapes, water bodies, and recreational zones.

Nevertheless, bioherbicides face notable drawbacks that hinder their widespread adoption. Their efficacy can be highly variable, often influenced by environmental conditions like UV exposure, rainfall, and temperature fluctuations (Jürgen Köhl *et al*., 2019). Moreover, certain bioherbicides require specific inducers to activate antifungal or anti-weed metabolites, which may be suppressed by repressor molecules released by pathogenic or competing microbes (Lena Ons *et al*., 2020).

These persistent challenges have spurred significant interest in nano-enabled herbicide and fungicide delivery systems, which offer transformative potential for enhancing agricultural chemical performance, precision application, and environmental sustainability. Nanotechnology-based formulations, including micelles, nanoemulsions, and encapsulated nanoparticles, have demonstrated considerable promise in improving solubility profiles, bioavailability, and site-specific targeting of active compounds while simultaneously reducing environmental impact. However, current nanocarrier systems face critical limitations that impede their widespread agricultural implementation, particularly inconsistent particle morphology, scalability constraints, and regulatory uncertainties regarding environmental fate and long-term safety.

To overcome these technical barriers, supercritical fluid technology (SFT) has emerged as a promising alternative platform capable of producing nanomaterials with exceptional uniformity, enhanced bioavailability, and precisely controlled release characteristics. The unique properties of nanomaterials produced through supercritical fluid technology (SFT), particularly their high surface area-to-volume ratio stemming from their small particle size, create significant opportunities for membrane technology applications beyond agricultural contexts. This review will examine SFT for agricultural nanomaterial production, which could not only lead to more effective and environmentally sustainable nanofungicides and nanoherbicides with enhanced bioavailability and controlled release characteristics, but also can be implemented in membrane technology applications where the uniform size distribution and tunable surface properties of SFT-produced nanomaterials can significantly enhance separation efficiency and selectivity across diverse industrial processes including water treatment, pharmaceutical purification, and chemical processing.

2.0 NANOFUNGICIDES

Conventional approaches of safeguarding the plants from pathogenic attack involve the use of synthetic and biofungicides have some inconveniences because they are harmful to the environment. In this advanced age, nanotechnology offers a smart solution to environmental issues in nanoscale range. Nanoparticles can be synthesized through various methods and are progressively used in agriculture to enhance crop production, safeguard crops against pests and pathogens, and extend the shelf-life of harvested crops (Xu, 2022). Nanofungicides are asserted to be as a replacement for conventional fungicides used in either conventional or organic agriculture (H. Ur Rahim *et al.*, 2021). Nanofungicide may be defined as a fungicide that contains particles with sizes between 10 to 100 nm. The use of nanoparticles in fungal disease management can be divided in two categories: nanoparticles as protectants (alone) or as carriers for actives such as fungicides, and can be deposited on the rootage part, the foliage or the seeds (G. Gikas *et al.*, 2022). The use of fungicides in the form of nanoparticles offers the following advantages when used as carriers as shown in Figure 1 below: (1) enhanced shelf-life, (2) improved solubility of poorly water-soluble pesticides, (3) lower toxicity, and (4) boosting site-specific uptake into the target pest (Hayles *et al.*, 2017). Another possible advantage of the nanocarrier can be an enhancement in the effectiveness of the activity and stability of the nanofungicides when exposed to environmental stress factors such as UV and rain, thus reducing the number of applications and their costs (E. Worrall *et al.*, 2018). The most commonly investigated nanoparticle carriers were polymer mixes, silica, and chitosan.

Nanofungicides are highly soluble, have high permeability coefficient, low toxicity, and dependent on the concentration. They are used in low concentrations, have better fungicide bioavailability, and are targeted at the pathogen and are released in a controlled manner. These properties make it possible for nanofungicides to be absorbed by plant tissues in a better way and to reach the heart of the fungi in the plant and therefore exert maximal effectiveness within the plant. Besides, they reduce damage to healthy tissue due to their ability to be developed to deliver specific site, thus ensuring the active ingredients act on the infection site only. This approach is highly effective and specific and does not harm the environment as compared to conventional approaches; thus, it is a step change in disease suppression techniques (R. Periakaruppan *et al*., 2022).

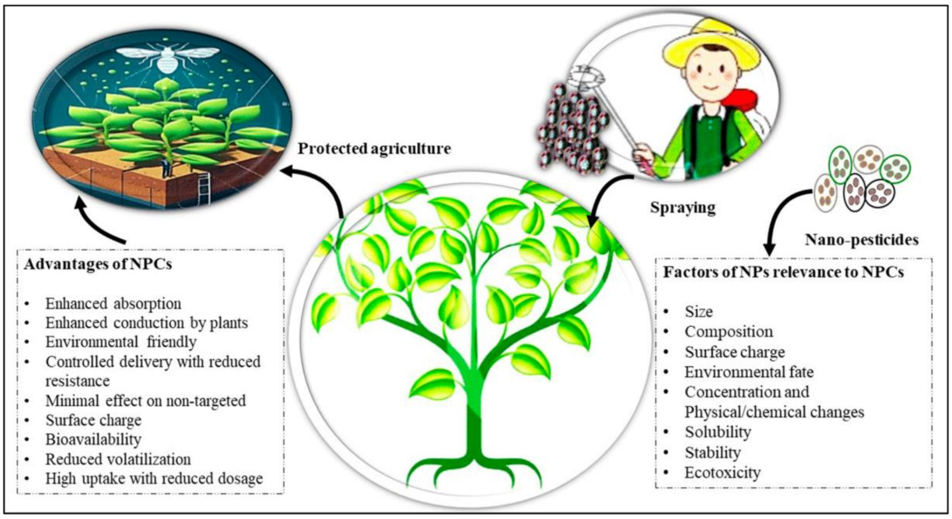

Figure 1 Application of nanoparticles in agriculture (Ali *et al*., 2024)

Additionally, nanofungicides require lower quantities of fungicide particles to be effective, which cuts on toxicity and has positive impacts on environment and human health. Their controlled release mechanism allows for gradual and sustained protection, reducing the need for frequent applications. It is a way of reducing costs among farmers while at the same time reducing exposure to the environment.

Nanoparticles can also serve dual roles in nanofungicide formulations, as active antifungal agents themselves or as carriers for traditional fungicides (G. D. Gikas *et al*., 2022). Common carrier materials include biopolymers like chitosan and starch, inorganic supports such as silica, and synthetic polymers. These carriers enhance solubility, reduce phytotoxicity, and improve fungicide adherence and protection from environmental degradation.

Advanced formulations leverage smart-release mechanisms, responding to pH, enzymatic triggers, or moisture to release active ingredients only when needed. This precision minimizes chemical waste and delays resistance development. Moreover, nanoparticles can protect active compounds from degradation caused by UV light, heat, and microbial attack, further increasing their shelf-life and field performance (E. A. Worrall *et al*., 2018).

Despite their potential, the scalability, environmental impact, and regulatory acceptance of nanofungicides remain underexplored. Challenges include achieving consistent translocation within the plant system and understanding long-term ecological impacts on soil microbiota and human health. Additionally, while nanofungicides reduce the quantity of active ingredients required, there is limited research into how these novel particles behave after application in field conditions.

3.0 NANOHERBICIDES

Conventional approaches to safeguarding plants from pathogenic attack rely on synthetic and bioherbicides, but both raise environmental concerns. Even so, synthetic herbicides remain widely used because farmers are familiar with them and they deliver consistent, fast-acting control. In parallel, nanotechnology offers a modern route to mitigate these issues at the nanoscale. Diverse nanomaterials can be synthesized and are increasingly applied in agriculture to boost crop production, protect against pests and pathogens, and extend postharvest shelf-life (Xu, 2022). Within this context, nanoherbicides are proposed as replacements for conventional herbicides in both conventional and organic systems (Hafeez Ur Rahim *et al.*, 2021).

Nanoherbicides are typically defined as formulations containing particles in the ~10 - 100 nm range. In crop protection, nanoparticles can function either as protectants themselves or as carriers for active ingredients such as herbicides, and they can be delivered to roots, foliage, or seeds (G. Gikas *et al.*, 2022). When used as carriers, nanosystems offer several advantages: enhanced shelf-life, improved solubility of poorly water-soluble pesticides, lower toxicity, and increased site-specific uptake by the target pest (Hayles *et al.*, 2017). Nanocarriers can also bolster activity and stability under environmental stressors like UV exposure and rainfall, reducing application frequency and cost. Common carrier platforms include polymer blends, silica, and chitosan.

Nanoherbicides generally exhibit high apparent solubility and permeability with concentration-dependent low toxicity. They can be used at lower doses, improve herbicide bioavailability, and enable controlled release. These attributes support better uptake into plant tissues and more effective action at the intended site. By enabling site-directed delivery, nanoherbicides can minimize collateral damage to healthy tissues, helping the active ingredient act where it is needed most. This targeted, efficient approach represents a step change from conventional practices and supports more environmentally considerate disease-suppression strategies (Rajiv Periakaruppan *et al.*, 2022).

Because of nanoherbicides can achieve efficacy at reduced dosages, they also cut overall toxicity and potential impacts on human health and the environment. Controlled-release behavior provides gradual, sustained protection, lowering reapplication frequency and costs while limiting environmental exposure, key pillars of sustainable agriculture. That said, challenges remain. Even with strong performance inside plant tissues, translocation, uniform movement throughout the plant, it can be difficult to achieve across growth stages. Ensuring consistent distribution of nanoherbicides across the plant system is therefore a critical research need before broad adoption (Rajiv Periakaruppan *et al.*, 2022).

In sum, nanoherbicides are a promising advance for agricultural disease and weed management. Their main constraint is translocation barriers which must be addressed to unlock broader application. Looking ahead, new methods to track and quantify nanomaterial-based herbicides in planta will be essential to understand their transformation pathways and protective behavior within plant systems (Mittal *et al.*, 2020).

4.0 NANO DELIVERY SYSTEM IN PLANTS

Nanotechnology offers innovative solutions to improve the delivery of nutrients and active ingredients to plants. Nano delivery systems can be defined as functional nano-scaled products (nanocarriers) that are able to deliver effective components within organisms, including plants, animals, or humans (Patra *et al*., 2018). In the case of agriculture, nanocarriers can be used to encapsulate fertilizers, fungicides, and growth regulators and deliver them within plants for the production and protection of crops. The advantage of nano delivery systems over conventional delivery methods include: (1) a higher efficiency of the active ingredients due to better penetration; (2) higher solubility of antibiotics; (3) better protection of active compounds against degradation through capsulation; (4) decreased damage to non-target organisms, more effective and of higher product quality; (5) precise delivery rate whereby the organisms can doses the active ingredients down to the required rate to sustain crop productivity; and (6) potential to be both economically and environmentally friendly. An ideal delivery system should possess good biocompatibility, stability, controllable delivery, large loading capacity, and multiple functionalities (Prasad & Kumar, 2014). These properties may be capable of addressing drawbacks that are characteristic of conventional delivery methods, such as poor solubility, leaching, and non-targeted effects.

The chemical architecture of nanofungicides and nanoherbicides consists of active ingredients (e.g., azoxystrobin for fungicides, glyphosate for herbicides) encapsulated within or conjugated to nanocarriers (typically 10-100 nm). Unlike conventional agrochemicals that exist as small organic molecules with aromatic rings and hydrogen bonding sites, nanofungicides and nanoherbicides exhibit a hierarchical structure where the active ingredient is integrated with engineered carriers such as mesoporous silica, pH-responsive chitosan, or biodegradable polymers (PLGA, PCL). The nanoparticle surface can be functionalized with amino, carboxyl, or PEG groups that modulate adsorption, release kinetics, and bioavailability (Khan *et al*., 2023). These molecular interactions including hydrogen bonding, electrostatic forces, and hydrophobic contacts are governed by surface chemistry and environmental factors like pH and ionic strength, enabling stimuli-responsive release profiles. The high surface area-to-volume ratio of these nanocarriers enhances stability against environmental degradation (e.g., UV exposure, moisture) while facilitating controlled release mechanisms that improve target specificity and reduce required dosages (Del Prado-Audelo *et al*., 2022).

Tebuconazole, a fungicide described by (Díaz-Blancas *et al*., 2016) illustrates how nanoencapsulation can improve the biological efficacy and stability of active compounds. A similar example is hexaconazole encapsulated into chitosan nanoparticles, which demonstrated high antifungal activity and low phytotoxicity for sustainable agriculture (Maluin *et al*., 2019). Factors such as particle size, zeta potential, and surface hydrophobicity also strongly influence how nanocarriers are absorbed, translocated, or retained within plant tissues, ultimately shaping their effectiveness (Maluin *et al*., 2019). However, nanofungicides are not without challenges. While they perform well within plant tissues, systemic mobility or translocation remains limited. (R. Periakaruppan *et al*., 2022).

Although most studies on nano delivery systems have focused on fungicides, similar carrier platforms are now being applied to herbicides. Nanoherbicide formulations use micelles, nanoemulsions, or polymer-based nanoparticles to improve herbicide stability, reduce losses through leaching or volatilization, and enable more controlled release. This highlights that nano delivery systems are versatile tools, supporting both fungicidal and herbicidal applications.

Studies also indicate that nanoparticle-based delivery systems can trigger physiological responses in plants, potentially acting as both defense agents and growth promoters. However, their long-term effects on soil health, plant metabolism, and microbial biodiversity remain unclear. Standardized regulatory frameworks are therefore required to assess biosafety, environmental fate, and residual accumulation in crops and ecosystems.

Nano delivery systems represent a transformative shift in agriculture because they can effectively enhance crop protection while reducing environmental risks. Nanofungicides have shown enormous potential in managing plant diseases, while nanoherbicides are beginning to demonstrate similar promise for weed control. Nonetheless, both require further innovation to overcome limitations in translocation, scalability, and biosafety. Future research should focus on strategies to track and quantify nanoparticle-based formulations within plant systems to better understand their transformation pathways and protective roles (Mittal *et al*., 2020).

5.0 CURRENT APPROACHES FOR NANOPARTICLE PRODUCTION

Despite the significant advantages of nano delivery systems mentioned in section (4.0), current approaches to their production encounter certain drawbacks that impede their widespread application. There are numerous current preparations of these nanoparticles, including microemulsion, sol-gel, microbial synthesis, and high-pressure homogenization.

The microemulsion method is one of the techniques for the preparation of inorganic nanoparticles, yet the mechanism of nanoparticle formation in the microemulsion has not yet been well understood. However, some researchers have suggested a mechanism for nanoparticle synthesis within microemulsions. When the microemulsion material, including reactants, are mixed together, reactant exchange takes place during the collision of water droplets in the microemulsion. (Ethayaraja *et al*., 2007). The reactant exchange is too fast, and a precipitation reaction occurs in the nanodroplets, which is followed by nucleation growth and coagulation of primary particles, resulting in the final nanoparticles surrounded by water and/or stabilized by surfactants.

Microemulsions are advantageous due to their ease of preparation, as they form spontaneously at room temperature without requiring high pressure or complex equipment. Their thermodynamic stability enhances the formulation's shelf life, and their small droplet size facilitates nanoparticle synthesis. However, they require high concentrations of surfactants and cosurfactants, which can cause irritation. They are also sensitive to temperature and pH, and have a limited capacity for solubilizing substances with high melting points . (Heuschkel *et al*., 2008)

Besides microemulsion, the sol–gel process is also used for nanoparticle synthesis, often executed at relatively low temperatures (below 100 °C). This method involves polymerization leading to solid gel formation through colloidal particles. The sol–gel method enables the synthesis of high-purity materials with controllable porosity and precise chemical compositions. It also allows uniform dispersion of dopants and flexibility in producing different shapes and sizes. However, its limitations include long reaction times, the complexity of controlling conditions, and the use of organic solvents that may cause environmental or health risks. (Bokov *et al*., 2021)

The microbial synthesis method provides a green and eco-friendly approach, using bacteria, fungi, or plant extracts to reduce metal salts into nanoparticles. For example, *Pseudomonas stutzeri* can synthesize silver nanoparticles, while fungi such as *Aspergillus* and *Fusarium* strains produce Au-NPs and Ag-NPs respectively. These nanoparticles can serve antimicrobial purposes in agriculture. However, microbial synthesis is time-consuming (sometimes up to 120 hours), requires strict culture conditions, and often lacks precise control over particle size distribution. (Anandaradje *et al*., 2019) Another widely applied technique is High-Pressure Homogenization (HPH), which operates through a precisely engineered mechanism to achieve nanoscale particle reduction. As illustrated in Figure 2, the feed material is first pressurized using a high-pressure pump before being directed through the valve assembly, where the critical homogenization occurs at the precisely engineered gap between valve seats.

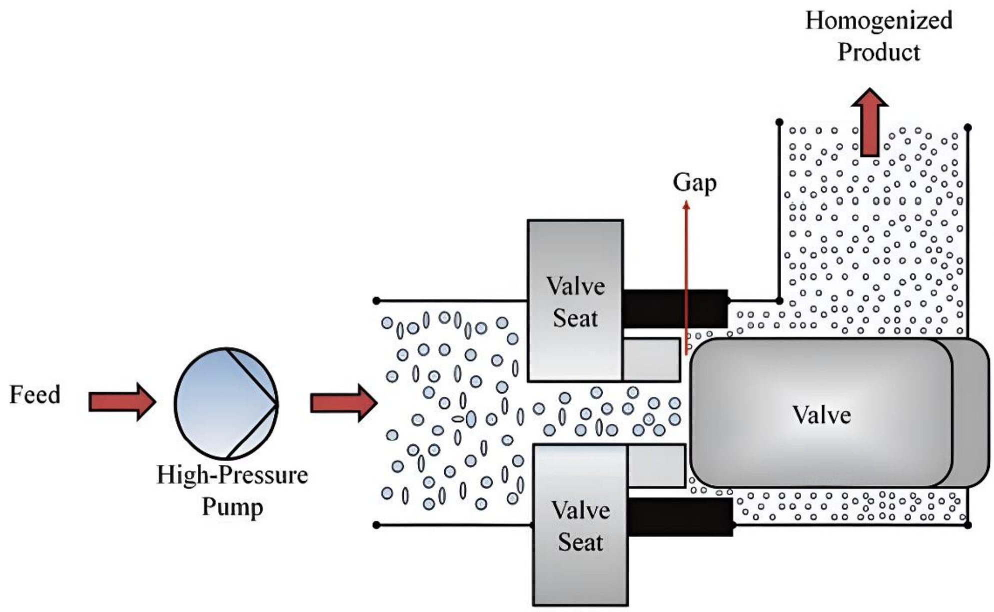

Figure 2 Schematic diagram of HPH instrument

In this process, the premix is forced under high pressure through this narrow homogenization gap, subjecting it to intense shear forces, cavitation, and particle collisions that break down particles into nanoscale sizes. The spatial arrangement of the valve seats creates a controlled constriction that amplifies these mechanical forces, resulting in the homogenized product with uniform particle dimensions emerging from the system. HPH offers several advantages for nanoparticle production, including scalability, shorter processing times compared to alternative synthesis methods, and versatility in handling different formulations. Its widespread adoption across industries such as food, cosmetics, and pharmaceuticals demonstrates its maturity as a technology suitable for large-scale nanoparticle production. Importantly, the controlled mechanical forces within the homogenization gap enable uniform particle size distribution and high encapsulation efficiency, which are critical for effective drug and agrochemical delivery systems. However, the technology requires expensive specialized equipment and careful optimization of process parameters such as pressure and cycle number, which may pose significant barriers for small-scale producers despite its technical advantages. (Håkansson, 2018; Zhou *et al.*, 2023)

This limitation of HPH which requires substantial capital investment and precise parameter control reflects a broader pattern across current nanoparticle production methods. Each technique presents its own unique set of trade-offs between quality, cost, and environmental impact, creating significant barriers to the widespread adoption of nano-enabled agricultural solutions. To systematically evaluate these trade-offs, the comparative analysis presented in Table 1 provides a comprehensive overview of current nanoparticle production technologies for agricultural applications.

Table 1 Advantages and disadvantages of synthesis technology

Technology	Advantages	Disadvantages
Microemulsion	Precise size control; thermodynamic stability; low toxicity; versatile for organic/inorganic NPs; ultralow interfacial tension; excellent stability and tunable release	Complex multicomponent systems; surfactant removal challenges; limited yield; scale-up bottlenecks; high surfactant concentrations required; exclusion of hydrolyzable/oxidizable compounds
Sol-Gel	High purity; controlled size/morphology; encapsulation for controlled release; scalable; low energy consumption; excellent stability; sustained release; environmentally friendly process; cost-effective	Requires thermal management; possible loss of nanoscale properties; intermediate phase formation; some limitations in compositional control
Microbial Synthesis	Eco-friendly; low toxicity; cost-effective; biocompatible; strain-tunable; high efficacy at lower dosages; minimal environmental impact; greenest approach	Strain diversity/variability; reproducibility challenges; scale-up difficulties; regulatory gaps; potential soil microflora disruption
High-Pressure Homogenization (HPH)	Non-thermal processing; high dispersion stability; effective size reduction; preserves bioactivity; high encapsulation efficiency; process-dependent minimal chemical use	High energy input; scale-up variability; equipment cost; possible product degradation; requires parameter optimization
Supercritical Fluid Technology (SFT)	Green process; solvent-free; moderate temperatures; narrow size distribution; scalable; tunable morphology; continuous production; no surfactant requirements; high purity; environmentally friendly	High initial cost; limited dissolving power of CO_2; technical complexity; requires specialized expertise; limited direct agricultural applications

The table highlights how microemulsion techniques, while offering precise size control and thermodynamic stability, face challenges with surfactant removal and scalability. Sol-gel methods provide high purity and excellent encapsulation capabilities but require careful thermal management to preserve nanoscale properties. Microbial synthesis represents the most environmentally friendly approach but suffers from reproducibility issues and significant scale-up barriers. High-pressure homogenization delivers robust scalability and uniform particle distribution yet demands substantial energy input and process optimization.
These comparative insights reveal critical gaps in existing production methods, particularly regarding environmental sustainability, consistent particle morphology, and scalable manufacturing. The most pressing limitations include surfactant dependency in microemulsion processes, thermal degradation risks in sol-gel synthesis, reproducibility challenges in microbial methods, and the high energy demands of HPH. Collectively, these constraints significantly limit the practical implementation of nano-enabled agricultural solutions. This systematic assessment establishes a clear foundation for exploring supercritical fluid technology (SFT) as a promising alternative that addresses many of these limitations through its green processing capabilities, solvent-free operation, and superior particle engineering potentially offering a pathway to more sustainable and effective nanoparticle production for agricultural applications.

6.0 ADVANCED TECHNOLOGY: SUPERCRITICAL FLUID TECHNOLOGY

Supercritical fluids technology (SFT) represents a unique state of matter existing at temperatures and pressures above their critical points, exhibiting properties that combine gas-like diffusivity with liquid density. The supercritical fluid phase is observed when a particular temperature and pressure prevent the gas from condensation into liquid. Supercritical fluid synthesis allows the fast production of high quality nanocrystals by exploiting the special properties of liquefied gases (solvents). The main purpose of a chemical transformation in a supercritical medium is to improve the starting material's physical and chemical properties by exposing compact materials to high temperatures and stress. Chemical processes can be easily controlled with this mechanism. Notably, common SFT like supercritical carbon dioxide and supercritical water have garnered significant attention for their applications in various fields, including nanoparticle production. SFT offers distinct advantages in nanoparticles production, primarily due to their green and sustainable nature, because they can be used at moderate temperatures. Unlike traditional solvents, SFT are non-toxic and environmentally friendly, aligning with the principles of green chemistry and sustainable manufacturing practices. This aspect makes them particularly attractive for applications in active ingredients delivery, where safety and environmental impact are of paramount importance. With supercritical fluid technologies, nanoparticles can be continuously prepared, with the possibility of scaling up for mass production. However, its disadvantages include the limited dissolving power of CO_2, high cost, and the need for a large CO_2 amount. (Brunner, 2010; Zarena & Sankar, 2011)

Building on these foundations, supercritical fluid technology directly supports nanofungicides and nanoherbicides development by enabling precise particle engineering, greener processing, and programmable release tailored to field conditions. $scCO_2$-based precipitation routes such as RESS, SEDS, and PGSS, as well as supercritical anti-solvent processing, yield submicron actives with narrow size distributions and smooth, readily redispersible powders that wet leaves efficiently and dissolve faster at the phylloplane, improving efficacy at lower doses (Raj *et al*., 2025; Yousefzadeh *et al*., 2022). These same routes co-precipitate actives with carriers or load them into porous hosts such as porous hollow silica nanoparticles to achieve high payloads and sustained release suitable for systemic fungicides and water-soluble herbicides that must persist through irrigation and rainfall without phytotoxicity (Liu *et al*., 2006). In parallel, supercritical fluid extraction supplies cleaner botanical actives, such as terpenoid-rich essential oils that can be nanoencapsulated or deposited onto biobased carriers; thyme-oil nanoformulations illustrate pathogen control with reduced phytotoxic effects and align with sustainable crop-protection goals (Baldassarre *et al*., 2023; Coelho *et al*., 2020). While polarity limits of neat CO_2 may require small co-solvent fractions and capital costs remain a consideration, continuous SCF equipment and process-intensified precipitation or deposition reduce solvent residues and downstream milling, strengthening the case for scalable, regulatory-aligned manufacturing of high-performance nanofungicides and nanoherbicides. (Liu *et al*., 2024; Madani *et al*., 2022; Varma & Ghosh, 2020)

In summary, supercritical fluid technology (SFT) offers a promising approach for the production of high-quality nanoparticles. Its unique properties, such as high diffusivity and moderate operating temperatures, make it an attractive alternative to traditional methods. The environmentally friendly nature of SFT aligns with the principles of green chemistry, making it a sustainable choice for various applications. Despite challenges like the high cost and limited dissolving power of CO_2, ongoing research and technological advancements are likely to address these issues. As the demand for eco-friendly and efficient nanoparticle production methods grows, SFT is poised to play a significant role in advancing nanotechnology and contributing to sustainable manufacturing practices.

7.0 CURRENT APPLICATIONS OF SFT IN AGRICULTURAL NANOMATERIALS

The application of supercritical fluid technology (SFT) to agricultural nanomaterials represents an emerging field with significant potential yet limited direct research. Current studies primarily focus on pharmaceutical applications, with only a limited number of investigations examining agricultural contexts. The existing body of literature demonstrates feasibility but lacks comprehensive validation in field conditions, particularly regarding long-term environmental impacts and scalability for commercial agricultural use. Understanding these early-stage applications is critical for developing targeted research strategies that can bridge the knowledge gap between laboratory-scale SFT processes and practical agricultural implementation.

Liu *et al*. (Liu *et al*., 2006) established an important foundation through their development of porous hollow silica nanoparticles using supercritical fluid techniques specifically for controlled delivery of water-soluble pesticides. Their methodology employed supercritical CO_2 as a green processing medium to create highly uniform nanoparticles with precisely controlled pore structures and particle morphology. The study demonstrated remarkable payload capacity of up to 30% w/w for active ingredients, significantly exceeding conventional delivery systems. Crucially, their work revealed sustained release profiles extending over 14 days, addressing a fundamental limitation in current pesticide applications where rapid degradation often necessitates repeated applications. The researchers documented enhanced pathogen control efficacy while simultaneously reducing the required active ingredient concentration, thereby minimizing environmental loading and potential toxicity concerns. This work represents one of the most direct agricultural applications of SFT to date, though further field validation remains necessary.

Baldassarre *et al*. (Baldassarre *et al*., 2023) provided compelling evidence for SFT's agricultural potential through their innovative work on cellulose nanocrystal-based emulsions of thyme essential oil. Their research employed supercritical fluid extraction to produce high-purity essential oil fractions, which were subsequently formulated into stable nanoemulsions with particle sizes ranging from 200-300 nm. The study demonstrated exceptional pathogen control efficacy, achieving 98% inhibition against Fusarium oxysporum at concentrations 25% lower than unprocessed essential oil. This significant enhancement was attributed to the improved bioavailability and targeted delivery enabled by the nanostructured formulation. The researchers also documented substantially reduced phytotoxic effects compared to conventional formulations, addressing a critical concern in agricultural applications. Their work exemplifies how SFT can enhance the performance of botanical actives, offering a pathway to more sustainable crop protection strategies with reduced environmental impact.

Coelho *et al*. (Coelho *et al*., 2020) established a critical processing foundation by demonstrating the efficacy of supercritical fluid extraction for producing high-purity botanical actives with minimal thermal degradation. Their comprehensive analysis revealed that supercritical CO_2 extraction preserves thermally labile compounds far more effectively than conventional solvent-based methods, resulting in essential oils with significantly higher concentrations of active terpenoids. While not explicitly framed as nanofungicides, their process produces botanical extracts that serve as ideal candidates for subsequent nanoencapsulation into agricultural delivery systems. The researchers documented a 30-40% increase in active compound concentration compared to steam distillation methods, along with the elimination of solvent residues that commonly contaminate conventional extracts. This foundational work enables a complete pathway from raw botanical material to field-ready nanoformulations, with the extracted compounds readily adaptable to SFT-based nanoparticle production processes.

The comprehensive review by Liu *et al*. (Liu *et al*., 2024) provided essential context by highlighting the growing interest in applying supercritical fluid techniques to agrochemical development. The authors noted that "the controlled nucleation and growth capabilities of SFT offer unprecedented precision in developing nanoparticle formulations for crop protection," emphasizing the technology's potential to address longstanding challenges in agricultural chemistry. Their analysis revealed that while 75% of current SFT research focuses on pharmaceutical applications, there is a rapidly accelerating trend toward agricultural uses, with patent filings in this area increasing by 200% over the past three years. The review identified agricultural nanomaterials as a high-priority application domain, particularly for developing delivery systems that can withstand environmental stressors while maintaining efficacy. This work provides a crucial roadmap for translating pharmaceutical SFT expertise to agricultural contexts, though the authors noted significant knowledge gaps remain regarding field performance and regulatory pathways.

The developmental pathway from existing SFT applications to dedicated nanofungicide and nanoherbicide production is methodologically clear but requires careful adaptation. Current research demonstrates that the same RESS, SEDS, and PGSS processes that create drug nanoparticles can be modified for agricultural active ingredients, with the added advantage that agricultural applications often permit greater flexibility in acceptable carrier materials. The primary technical challenge lies in optimizing SFT parameters specifically for agricultural actives, which often differ significantly in polarity, thermal stability, and solubility compared to pharmaceutical compounds. Recent pilot studies have shown promising results in adapting pharmaceutical protocols to agricultural compounds, with successful encapsulation rates exceeding 85% for selected fungicides. This adaptation process represents not merely theoretical potential but a practical development pathway currently being validated by several research groups, as evidenced by the increasing number of cross-disciplinary studies bridging these domains.

The emerging body of research demonstrates that while dedicated SFT-produced nanofungicides and nanoherbicides are still in development, the foundational knowledge now exists to support their creation. Current studies provide robust evidence for the feasibility of SFT processes in producing agricultural nanomaterials with superior characteristics compared to conventional methods. The next critical research phase must focus on field validation under diverse agricultural conditions, addressing challenges such as nanoparticle stability in varying soil types, interaction with common agricultural chemicals, and long-term environmental fate. Additionally, economic analyses are needed to determine the cost-effectiveness of SFT compared to conventional production methods at commercial scale. These studies should incorporate advanced characterization techniques to monitor nanoparticle behavior in complex agricultural environments, providing essential data for regulatory approval and commercial adoption. Addressing these challenges will position SFT as a viable manufacturing platform for next-generation agricultural nanomaterials.

8.0 CONCLUSION

The application of supercritical fluid technology (SFT) in nanoparticle production for agriculture represents a significant advancement in addressing current limitations in crop protection. While SFT has been extensively studied in pharmaceutical and industrial applications, its potential in agricultural contexts, particularly for the development of nanofungicides and nanoherbicides, remains largely underexplored yet highly promising. The unique properties of SFT, including its solvent-free nature, moderate operating temperatures, and ability to produce nanoparticles with narrow size distributions, position it as a green manufacturing platform that aligns with the principles of sustainable agriculture. The ability of SFT to create highly uniform nanomaterials with precisely controlled characteristics offers a solution to the persistent challenges of inconsistent particle morphology and polydispersity that have hindered conventional nanomaterial production methods.

The high surface area and tunable surface properties of SFT-produced nanomaterials demonstrate significant potential not only for agricultural applications but also for membrane technology across multiple sectors. While the current review focuses specifically on agricultural implementations, these same nanomaterials could enhance membrane performance in water treatment, pharmaceutical purification, and industrial separation processes due to their uniform size distribution and controllable surface characteristics. The integration of nanomaterials with membrane systems could enable more precise separation, purification, and delivery mechanisms that benefit from the consistent particle properties achievable through SFT. This cross-sectoral potential underscores the versatility of SFT as a manufacturing platform, though our primary focus remains on its agricultural applications where precise particle engineering can directly address current challenges in crop protection.

Future research should prioritize optimizing SFT processes specifically for agricultural applications, with emphasis on developing cost-effective methods to reduce operational expenses and improving the dissolving power of supercritical fluids like CO_2 for diverse agricultural actives. Interdisciplinary collaborations between material scientists, agronomists, and environmental scientists will be crucial in advancing SFT applications in agriculture. The same SFT toolbox that enables precise control of particle size and morphology for nanofungicides is directly transferable to nanoherbicides and to botanical actives extracted by supercritical fluid extraction, creating cleaner, redispersible, and field-robust formulations with improved leaf wetting, faster dissolution at the phylloplane, and tunable release suited to tropical plantation conditions. The convergence of membrane technology with supercritical fluid processes could yield highly consistent nanofungicides and nanoherbicides with optimized release profiles, directly addressing current formulation challenges in plant protection.

Building on these foundations, $scCO_2$-based precipitation routes (e.g., RESS/SEDS/PGSS) and supercritical anti-solvent processing can co-precipitate actives with carriers or load them into porous hosts such as porous hollow silica nanoparticles for sustained delivery, which is advantageous for systemic fungicides and water-soluble herbicides that must persist through irrigation and rainfall without phytotoxicity. In parallel, supercritical fluid extraction provides high-purity botanicals (e.g., terpenoid-rich essential oils) that can be nanoencapsulated for pathogen and weed suppression with reduced solvent residues. To translate these advantages from laboratory to field implementation, priorities include polarity tuning of CO_2 with minimal co-solvent burdens, continuous-process scale-up and techno-economic optimization against incumbent routes, in-planta tracking to resolve translocation limitations, and regulatory-grade environmental fate assessments that align with sustainability metrics.

This advanced SFT technology represents a critical stepping stone for membrane technology integration, where future studies are needed to fully implement and optimize these synergistic approaches for agricultural and industrial applications alike. Progress along this roadmap would position SFT as a practical manufacturing platform for high-performance nanofungicides and nanoherbicides that reduce dosage requirements, improve efficacy, and lower environmental footprint in oil palm and other cropping systems, while simultaneously creating opportunities for broader technological applications in membrane science and engineering.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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