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## Advancements in polysaccharide-based carriers for eco-friendly fungicide delivery

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#### ABSTRACT

The demand for sustainable agricultural practices has led to an increased interest in using polysaccharide carriers for the delivery of fungicides. This review provides a comprehensive evaluation of chitosan, alginate, and cellulose as effective delivery systems, focusing on their respective loading capacities and controlled release profiles. Recent advancements in the synthesis and characterization of these biopolymers highlight their potential to improve fungicide efficacy while reducing environmental impact. Comparative analysis of existing studies reveals variability in encapsulation efficiency and release kinetics, which stem from the unique physicochemical properties of each polysaccharide. Additionally, we address ongoing debates regarding the best carrier choice, emphasizing the importance of understanding the interactions between carrier composition, environmental conditions, and fungicide performance. The objective of this review is to clarify the advantages and limitations of polysaccharide-based carriers, identify key factors affecting their effectiveness, and suggest future research directions aimed at developing eco-friendly fungicide formulations. Through this exploration, we aim to contribute valuable insights that will inform the design of sustainable pesticide delivery systems, aligning with the goals of contemporary agriculture and environmental safety.

#### 1. Introduction

Recent studies exploring the impact of various polysaccharide carriers on fungicide loading capacities and controlled release profiles have become increasingly important in the context of sustainable agriculture and environmental protection (Antunes et al., 2024). Polysaccharides such as chitosan, alginate, and cellulose have attracted significant attention due to their biodegradability, biocompatibility, and structural versatility (Tian et al., 2025). These natural polymers can form hydrogels, nanoparticles, or microcapsules, which enable the controlled and targeted release of fungicides, reducing application frequency and minimizing environmental contamination (Zanino et al., 2024). Their

ability to encapsulate active ingredients effectively positions them as promising alternatives to conventional, synthetic carriers in agrochemical formulations (Grazyna et al., 2022; Lihong et al., 2023; Nuo et al., 2023). Since the 1940s, the development of synthetic fungicides has significantly increased crop yields, but concerns about environmental pollution and human health risks have driven research toward eco-friendly delivery systems (Grazyna et al., 2022; Ravinder et al., 2022). Recent advances in nanotechnology and polymer science have facilitated the design of polysaccharide-based carriers that improve pesticide efficacy while reducing residues and toxicity (Hashim et al., 2024; Lihong et al., 2023; Marko et al., 2024). For instance, alginate and chitosan composites have been tailored for pH-responsive release,

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enhancing fungicide bioavailability and minimizing environmental impact (Ludmilla et al., 2023; Nuo et al., 2023; Xiukun et al., 2022).

This review addresses the critical issue of variability in fungicide loading capacities and release kinetics as influenced by the type and structural properties of polysaccharide carriers. While numerous studies have investigated individual carriers, there is still a lack of comprehensive comparative analysis regarding how chitosan, alginate, and cellulose differ in terms of encapsulation efficiency, release behavior, and responsiveness to environmental factors. Understanding these differences is essential for optimizing carrier selection and formulation strategies in the development of effective, environmentally responsive fungicide delivery systems. This gap in knowledge limits the ability to tailor systems for specific agricultural applications and highlights the need for a systematic evaluation (Ritu et al., 2021; Sajjad et al., 2022; Siyu et al., 2023). Controversies exist regarding the optimal carrier choice, as some reports highlight superior loading and sustained release with chitosan-based systems (Farhatun Najat et al., 2020a; Qing et al., 2024), while others emphasize alginate's gel-forming ability and pH sensitivity (Ling et al., 2024; Nuo et al., 2023). Cellulose derivatives have also shown promise in enhancing adhesion and controlled release, but with variable loading capacities (Jingvang et al., 2024; You et al., 2024). This knowledge gap limits the rational design of fungicide formulations that balance efficacy, safety, and environmental sustainability (Lihong et al., 2023; Ravinder et al., 2022).

Conceptually, this review builds on the framework that poly-saccharide carriers act as matrices that encapsulate fungicides through physical or chemical interactions, enabling controlled release governed by diffusion, swelling, or environmental stimuli such as pH and temperature (Ludmilla et al., 2023; Nuo et al., 2023; Zhiyuan et al., 2024). The interplay between carrier composition, crosslinking, and environmental conditions determines loading capacity and release kinetics, which in turn influence antifungal efficacy and ecological safety(Lihong et al., 2023; Ludmilla et al., 2023; Xiukun et al., 2022). Understanding these relationships is crucial for optimizing carrier design to achieve targeted and sustained fungicide delivery.

This review critically examines recent advances in the use of poly-saccharide carriers—specifically chitosan, alginate, cellulose, fucoidan, ulvan, agar, dextran, and pullulan—for fungicide loading and controlled release applications. It aims to provide a comprehensive comparison of their respective advantages and limitations, address current debates, and identify the key factors that govern their performance. By synthesizing the latest research, this review seeks to support the development of sustainable and effective fungicide delivery systems. The focus is on experimental evidence related to loading capacity, release kinetics, and antifungal efficacy. Selected studies emphasize chitosan, alginate, and cellulose-based carriers, with insights organized around material characteristics, formulation approaches, and release mechanisms. The review proceeds with a detailed discussion of each polysaccharide carrier's properties, followed by comparative evaluations and recommendations for future research directions.

## 2. Natural polysaccharide carriers for fungicides: Encapsulation processes and characterization techniques

Natural polysaccharides are increasingly recognized as superior carriers for fungicides and other bioactive compounds, driven by their inherent properties such as biocompatibility, biodegradability, and widespread availability from renewable sources (Detsi et al., 2020; Sun et al., 2020). These biopolymers offer a sustainable and environmentally friendly alternative to synthetic materials in agricultural and environmental applications (Chemat et al., 2020). Encapsulation techniques leverage these properties to protect fungicides from degradation, enhance their stability, improve bioavailability, and enable controlled or targeted delivery, thereby addressing many limitations associated with conventional treatments (Grgić et al., 2020; Su et al., 2020). The ability to tune their properties and controllable degradation makes

polysaccharides highly attractive as local delivery systems. The development of such systems necessitates a thorough understanding of both the encapsulation processes that form these carriers and the characterization techniques vital for evaluating their efficacy and stability (Auriemma et al., 2020).

## 2.1. Primary techniques for the encapsulation of fungicides in polysaccharide-based carries

The encapsulation of fungicides within natural polysaccharide matrices involves several sophisticated techniques, each offering distinct advantages in terms of material properties, desired particle characteristics, and production scalability. These methods are designed to create stable systems that can effectively load active compounds and release them in a controlled manner (Li et al., 2020).

#### 2.2. Ionic Gelation

Ionic gelation is a mild, solvent-free encapsulation method that offers significant advantages for delivering fungicides using polysaccharides like chitosan and alginate. It operates under ambient or slightly elevated temperatures and avoids the use of harsh organic solvents, making it especially suitable for encapsulating heat- or solvent-sensitive fungicides while maintaining their biological activity(Auriemma et al., 2020; Karava et al., 2020). The technique relies on electrostatic interactions between oppositely charged molecules—such as the cationic chitosan and anionic crosslinkers like sodium tripolyphosphate (TPP) to form stable hydrogels, micro, or nanoparticles, typically ranging from 50 to 300 nm in size (Yang et al., 2021). However, the method also presents some limitations. Chitosan's solubility is restricted to acidic pH ranges (typically pH 4-6), which may not be compatible with all fungicides. Additionally, the ionically crosslinked structures can be less stable under varying environmental or field conditions, potentially leading to premature release of the active ingredient. Batch-to-batch variability, low mechanical strength, and limited encapsulation efficiency for highly hydrophobic fungicides are further drawbacks that need to be addressed through careful optimization or combination with other encapsulation strategies (Karava et al., 2020).

#### 2.3. Complex coacervation

Complex coacervation is an effective encapsulation technique that involves liquid-liquid phase separation driven by electrostatic interactions between oppositely charged macromolecules, typically combinations of proteins and polysaccharides (Grgić et al., 2020). This method results in the formation of a dense, polymer-rich coacervate phase that can efficiently entrap active ingredients such as fungicides. One of its key advantages is the ability to fine-tune encapsulation efficiency and release behavior by precisely controlling parameters like pH, ionic strength, and polymer concentration. The pH is commonly adjusted near the isoelectric point of the protein to enhance electrostatic interaction, and the entire process is usually carried out under mild, ambient conditions, which is ideal for preserving the functionality of sensitive bioactives (Becerril et al., 2020; Grgić et al., 2020). After coacervate formation, chemical crosslinkers such as glutaraldehyde or genipin are often used to stabilize the capsules, improving their mechanical strength and controlling the release kinetics (Becerril et al., 2020). However, the use of chemical crosslinkers, especially synthetic ones like glutaraldehyde, may raise toxicity and regulatory concerns depending on the application. Additionally, the system's sensitivity to environmental conditions (e.g., pH and ionic strength) may affect stability during storage or application. Despite these challenges, complex coacervation remains a highly versatile and efficient technique for developing controlled-release formulations in agricultural and pharmaceutical sectors.

#### 2.4. Spray-drying

Spray-drying is a widely recognized and economically viable technique for the encapsulation and stabilization of active ingredients such as fungicides in agrochemical formulations. One of the most significant advantages of spray-drying is its cost-effectiveness and scalability, making it particularly suitable for industrial-scale applications in sectors like pharmaceuticals, food, and agriculture (Mohammed et al., 2020; Piñón-Balderrama et al., 2020). The method efficiently converts liquid feed solutions—composed of fungicides and polysaccharide wall materials such as maltodextrin or alginate—into dry micro- or nanoparticles through atomization in a heated chamber (Mohammed et al., 2020). The process involves atomizing a feed solution—which typically has a total solids content between 10% and 30% and includes the fungicide and wall materials such as maltodextrin or alginate—into a hot drying chamber (Mohammed et al., 2020). However, despite these advantages, spray-drying does present several critical limitations. One of the primary concerns is the thermal sensitivity of fungicides. The high inlet temperatures typically required for efficient drying (ranging from 140°C to 180°C) can lead to thermal degradation of heat-sensitive fungicides, thereby compromising their bioactivity. Therefore, careful optimization is required to balance drying efficiency with fungicide stability (Piñón-Balderrama et al., 2020).

#### 2.5. Emulsification

Emulsification is a widely used encapsulation technique that involves the formation of stable emulsions, typically either oil-in-water (O/W) or water-in-oil (W/O), where fungicides whether hydrophobic or hydrophilic are confined within the dispersed phase (Becerril et al., 2020). This method is particularly versatile, allowing for the encapsulation of a broad range of active ingredients, and is adaptable to various formulation requirements. Emulsions are typically formed through intense mechanical stirring or high-shear homogenization, often at speeds between 1,000 and 10,000 rpm, which enables the production of uniform droplets of desired size. These emulsified droplets can then be stabilized using ionic or chemical crosslinking, especially when polysaccharide carriers like alginate or chitosan are involved. Critical factors such as emulsifier concentration, temperature, and pH must be carefully controlled, as they significantly influence the encapsulation efficiency, droplet stability, and particle size. A major advantage of emulsification is its ability to protect sensitive fungicides from degradation while enabling controlled or sustained release, making it highly suitable for agricultural applications. However, the method can be energy-intensive due to the need for high-speed mixing, and droplet coalescence or phase separation may occur if emulsifiers or stabilizing conditions are not adequately optimized (Becerril et al., 2020).

#### 2.6. Nanoprecipitation

Nanoprecipitation is a bottom-up technique used to produce polymeric nanoparticles by rapidly precipitating polysaccharides from a solvent into a non-solvent, leading to spontaneous formation of nanoparticles that encapsulate fungicides (Gericke et al., 2020; Lammari et al., 2020). In this process, a solution containing both the polysaccharide and fungicide in a good solvent is quickly introduced into a non-solvent, causing the polymer to precipitate and trap the fungicide within the newly formed nanoparticles. This method is especially beneficial for encapsulating sensitive natural products like essential oils, as it is performed at room temperature, thus protecting thermosensitive compounds from degradation and evaporation (Gericke et al., 2020; Lammari et al., 2020). The particle size can be finely tuned, typically ranging from tens to hundreds of nanometers, by adjusting parameters such as polymer concentration, solvent-to-non-solvent ratio, injection speed, and stirring rate (Gericke et al., 2020; Lammari et al., 2020). Nanoprecipitation offers controlled release properties and ensures adequate protection of volatile and sensitive fungicides, making it a promising approach for developing efficient fungicide delivery systems.

The table below summarizes the primary encapsulation processes, highlighting their mechanisms, typical parameters, and general outcomes:

outcomes:	75 1 1 /		m · 1
Encapsulation Technique	Mechanism/ Principle	Key Process Parameters	Typical Outcomes/ Advantages
Ionic Gelation  Complex Coacervation	Electrostatic interaction between charged polysaccharide and multivalent counter-ions (e. g., TPP for chitosan).  Liquid-liquid phase separation due to electrostatic	Polysaccharide concentration (0.1-2% w/v), crosslinker type/ ratio (e.g., chitosan:TPP 5:1 to 10:1), pH (acidic for chitosan), agitation speed. pH (near protein isoelectric point), temperature (ambient).	Mild conditions, high biocompatibility, tunable particle size (50-300 nm), controlled release (Auriemma et al., 2020; Karava et al., 2020).  Forms dense polymer-rich phase, good for sensitive
Canan Daving	interaction between oppositely charged biopolymers (e. g., polysaccharide- protein).	biopolymer concentrations, agitation conditions.	compounds, often requires post- stabilization (Becerril et al., 2020; Grgić et al., 2020)
Spray-Drying	Conversion of liquid emulsion/ suspension into dry powder via hot air stream.	Inlet temp (140- 180 °C), outlet temp (80-90 °C), feed flow rate, atomization air flow, total solids (10-30%).	Economical, scalable, produces dry powders, protects against oxidation/volatilization, versatile for various wall materials (Mohammed et al., 2020; Piñón-Balderrama et al., 2020).
Emulsification	Creation of oil- in-water or water-in-oil emulsions followed by solidification/ crosslinking.	Emulsifier concentration, temperature (ambient/ controlled), pH, mechanical stirring/ homogenization speed (1,000-10,000 rpm).	Versatile for different solubilities, can be combined with other solidification methods, protects active agents (Becerril et al., 2020).
Nanoprecipitation	Rapid precipitation of polymer upon mixing solution with non- solvent.	Polymer concentration, solvent:non- solvent ratio, injection speed, stirring rate.	Produces small, uniform nanoparticles, suitable for thermosensitive compounds, offers controlled release (Gericke et al., 2020; Lammari et al., 2020).

## 3. Characterization techniques for polysaccharide-fungicide systems

#### 3.1. xxxx

Thorough characterization is indispensable for understanding the physical, chemical, and functional properties of polysaccharide-based fungicide carrier systems, ensuring their efficacy, stability, and predictable release kinetics (Vigata et al., 2020). A combination of physicochemical, structural, morphological, spectroscopic, and thermal

analysis techniques provides a comprehensive profile of these complex systems.

#### 3.1.1. Physicochemical characterization

Physicochemical properties are fundamental to the performance of encapsulated systems, influencing their stability, interaction with the environment, and release behavior.

#### 3.1.2. Particle size analysis (PSA) and size distribution

Particle size is a critical parameter, directly impacting the carrier's ability to encapsulate fungicides, its stability in suspension, and the rate and duration of fungicide release (Gericke et al., 2020; Karava et al., 2020; Skiba et al., 2020; Topal et al., 2021). Techniques like Dynamic Light Scattering (DLS) are routinely used to determine the hydrodynamic size and polydispersity index (PDI) of nanoparticles in solution. DLS measures the Brownian motion of particles and relates it to their size, providing insights into size uniformity, which is crucial for reproducible performance.

#### 3.1.3. Zeta potential measurement

Zeta potential serves as a critical electrokinetic parameter that quantifies the surface charge of particles in colloidal systems, providing vital insights into their stability, aggregation behavior, and interactions within biological contexts (Ahmed et al., 2020; Karava et al., 2020; Skiba et al., 2020; Yu et al., 2024). In sustainable agriculture, the rising demand for more efficient pesticide utilization has driven the innovation of advanced delivery systems, with polysaccharide-based carriers emerging as particularly effective solutions (Zhang, 2024). These natural biopolymers are favored due to their cost-effectiveness, abundance, safety, and functional versatility, making them suitable for encapsulating and delivering active agrochemicals such as fungicides. The precise measurement and understanding of zeta potential are essential for optimizing the design and performance of these carriers, facilitating efficient fungicide delivery, controlled release, and reduced environmental impact. For example, Pyraclostrobin (Pyr) has been successfully encapsulated within lignin nano/microcapsules (Pyr@LNCs), demonstrating high encapsulation efficiency, tunable sizes, excellent UV shielding, and pH/laccase-responsive targeting against Botrytis disease (Yu et al., 2024). Similarly, tebuconazole has been loaded into fully degradable polyphosphoester cubosomes, exhibiting high antimycotic activity against Botrytis cinerea, notable adhesion to leaves after simulated rainfall, and a continuous release profile. It has also been incorporated into zein/polydimethyl diallyl ammonium (PDADMAC) nanoparticles, resulting in a lower release rate compared to the technical concentrate while enhancing antifungal efficacy (Azhdari et al., 2024). The zeta potential significantly influences the physical and chemical characteristics of nano-drug delivery systems, affecting their stability, aggregation behavior, release rates, and interactions with biological targets (Zhang, 2024). A high absolute value of zeta potential, whether positive or negative, is generally associated with enhanced colloidal stability, as a significant surface charge fosters greater electrostatic repulsion between particles, thereby preventing aggregation and maintaining a stable dispersion (Zhang, 2024). For instance, posaconazole-loaded mixed micelles exhibited a desirable zeta potential of -25.3  $\pm$  2.8 mV, which contributed to the long-term stability of the lyophilized formulation (Patil et al., 2024; Yu et al., 2024).

In contrast, systems with zeta potential values between -10 mV and +10 mV are indicative of lower stability and a higher aggregation propensity, influenced by factors such as bacterial presence, electrolyte concentration, and pH (Yu et al., 2024). Polysaccharide-based coatings, such as  $\beta$ -glucan on mesoporous silica nanoparticles, utilize zeta potential measurements to confirm surface modifications and predict stability (Yu et al., 2024). At the same time, lignin nano/microcapsules exemplify how surface charge regulation can enhance stability. Beyond stability, zeta potential plays a decisive role in determining release kinetics, adhesion to target surfaces, and overall biological efficacy of

fungicide carriers (Azhdari et al., 2024). The interaction dynamics between carriers and their environments can be engineered for stimuli-responsive or sustained release. Lignin nano/microcapsules, for instance, exhibit pH/laccase-responsive targeting against Botrytis disease, allowing for intelligent release of pyraclostrobin, whereas fully degradable cubosomes provide continuous fungicide release with distinct kinetics over several days. The flexible topology of the pyraclostrobin-loaded lignin nano/microcapsules further enhances retention and adhesion on foliar surfaces (Vogel et al., 2024). At the same time, tebuconazole-loaded polyphosphoester cubosomes maintain adhesion to Vitis vinifera Riesling leaves even after simulated rain. For nanoparticle-based fungicide delivery, parameters such as contact angle and surface adhesion energy, influenced by surface charge, are critical to the efficacy of the encapsulated fungicide (Vogel et al., 2024). Additionally, zeta potential is crucial for drug targeting and absorption across biological membranes. Nanogels functionalized with phosphoric acid 2-hydroxyethyl acrylate (PHA) demonstrated improved adhesion to hyphal surfaces and successful internalization into Aspergillus fumigatus hyphae, which was attributed not only to the increased negative surface charge but also to the functional characteristics of the quencher, leading to enhanced therapeutic outcomes (Vogel et al., 2024).

#### 3.1.4. Encapsulation efficiency (EE) and loading capacity (LC)

Encapsulation efficiency determines the percentage of the initial fungicide successfully loaded into the polysaccharide matrix (Abukhadra et al., 2020; Machado et al., 2020). Loading capacity indicates the mass of fungicide encapsulated per unit mass of the carrier. These parameters are typically assessed by separating the free (unencapsulated) fungicide from the encapsulated form through centrifugation or filtration, followed by quantification of the fungicide in the supernatant or within the dissolved particles. Analytical methods such as UV-Vis spectroscopy or High-Performance Liquid Chromatography (HPLC) are commonly employed for precise quantification. Lignin-based micro and nanocapsules, as well as lignin-surfactin coacervates, demonstrate impressive EE, often exceeding 90% and reaching up to 95% when optimized. In applications involving fungicides, lignin-based systems report EE values ranging from 70% to 99%, primarily influenced by the solubility of the drug and specific formulation details (Wang et al., 2024; Yu et al., 2024). Alginate systems generally achieve high EE values, with instances approaching 90% or nearly 100% when combined with other polymers in various forms such as beads or hydrogels (Hazra et al., 2023; Korbecka-Glinka et al., 2022). Conversely, chitosan-based nanoparticles typically exhibit EE ranging from approximately 42% to about 80-90%, depending on factors such as crosslinking, derivatization, and the methods used for their preparation (Zhou et al., 2024). Starch and its derivatives also show promise for high loading efficiencies, with one study noting curcumin loading efficiency at around 78% in optimized formulations (Pang et al., 2015).

In contrast, literature on loading capacities (LC) varies significantly, with rates of about 15 mg/g or higher based on specific formulations. Additionally, composite and hybrid polysaccharide carriers—including cellulose-polydopamine composites and polysaccharide-metal-organic frameworks-can achieve notable EE and LC, with some examples reporting drug loading ratios of up to 35 wt% and an LC around 46% when MOF cores are coated with polysaccharides (Wang et al., 2024; Yang et al., 2021). Several mechanistic factors influence the efficiency of encapsulation. The interactions between the carrier and the fungicide, such as hydrophobic interactions, electrostatic attraction, hydrogen bonding, and  $\pi$ - $\pi$  stacking, play a crucial role in determining the retention and efficiency of the fungicide. Moreover, the wall-to-core ratio and the concentration of the carrier have a significant impact; increasing the wall material typically enhances EE while potentially decreasing LC per unit of carrier mass (Hazra et al., 2023). The type and degree of crosslinking—whether with calcium ions for alginate or TPP for chitosan-affect the material's porosity and permeability, thus impacting both EE and release behavior. Environmental conditions

during the encapsulation process, such as pH, temperature, and solvent composition, can alter polymer solubility, ionization, and diffusion rates, which also play a crucial role in EE and LC outcomes (Meng et al., 2024). Finally, the size and topology of the particles are important, as nanoscale carriers often exhibit different EE and LC trade-offs compared to their microscale counterparts, with varying proportions impacting release speed and effective EE in multiscale systems (Wang et al., 2024; Yang et al., 2021; Yu et al., 2024).

#### 3.1.5. Release profile determination

Evaluating the release kinetics of the fungicide from the poly-saccharide carrier is crucial for understanding its controlled delivery capabilities (Malik et al., 2020; Vigata et al., 2020). *In vitro* release studies are conducted by immersing the encapsulated system in a relevant dissolution medium (e.g., simulated physiological or environmental conditions) at controlled temperature and pH. Periodical sampling and subsequent analytical quantification of the released fungicide allow for the construction of a release profile over time. Mathematical models, such as the Korsmeyer-Peppas model, are often applied to the release data to elucidate the release mechanisms, which can include diffusion, erosion, or a combination of both (Malik et al., 2020; Vigata et al., 2020).

#### 3.2. Structural and morphological characterization

These techniques provide visual and quantitative information about the physical form, surface features, and internal architecture of the encapsulated systems.

#### 3.2.1. Scanning electron microscopy (SEM)

SEM is used to visualize the external morphology of polysaccharide-based carriers, providing high-resolution images of their surface topography, particle shape, and overall size distribution (Alqaheem & Alomair, 2020; Malik et al., 2020; Venkateshaiah et al., 2020; Yadav et al., 2020). SEM images can reveal the spherical shape, surface roughness, and porous structure of microparticles or nanoparticles, which are important for understanding their interaction with target sites and their mechanical stability (Kim et al., 2020; Maruyama et al., 2020).

#### 3.2.2. Transmission electron microscopy (TEM)

TEM offers insights into the internal structure and morphology of nanoparticles at the nanoscale, revealing details not visible with SEM (Auriemma et al., 2020; Venkateshaiah et al., 2020; Yadav et al., 2020). TEM can confirm the presence of core-shell structures, the uniform dispersion of the fungicide within the matrix, or the formation of nanofibrillar networks, which are critical for encapsulation integrity.

#### 3.2.3. Atomic force microscopy (AFM)

AFM is a surface-sensitive technique that provides three-dimensional topographical maps of the particle surface at nanoscale resolution (Alqaheem & Alomair, 2020; Venkateshaiah et al., 2020). It allows for the measurement of surface roughness, adhesion forces, and precise particle dimensions, complementing the information obtained from SEM and TEM.

#### 3.2.4. X-ray diffraction (XRD)

XRD is primarily used to determine the crystallinity and phase composition of the polysaccharide carrier and the encapsulated fungicide (Alqaheem & Alomair, 2020; Venkateshaiah et al., 2020). Changes in the diffraction patterns upon encapsulation can indicate alterations in the crystallinity of the polysaccharide or the fungicide (e.g., conversion from crystalline to amorphous state), which may influence loading efficiency, stability, and release behavior.

#### 3.2.5. Spectroscopic and chemical analysis

These methods are crucial for understanding the chemical

composition, functional groups, and molecular interactions within the polysaccharide-fungicide system.

#### 3.2.6. Fourier-transform infrared spectroscopy (FTIR)

FTIR is a powerful tool for identifying the functional groups present in the polysaccharide, the fungicide, and the final encapsulated system (Malik et al., 2020; Mostafa et al., 2020; Węgrzynowska-Drzymalska et al., 2020). By comparing the spectra of the individual components with that of the encapsulated product, FTIR can confirm successful encapsulation, detect chemical modifications to the polysaccharide, and identify specific interactions (e.g., hydrogen bonding, ionic interactions) between the carrier and the fungicide.

#### 3.2.7. Nuclear magnetic resonance (NMR) spectroscopy

NMR, particularly <sup>H</sup> NMR, provides detailed structural information about the polysaccharide backbone and any chemical modifications or grafting reactions that occur during the encapsulation process (Alqaheem & Alomair, 2020; Mostafa et al., 2020). It can also offer insights into the molecular environment of the fungicide within the matrix, helping to understand its dispersion and interactions.

#### 3.2.8. Differential scanning calorimetry (DSC)

DSC measures the heat flow associated with thermal transitions (e.g., glass transition, melting, crystallization) in materials as a function of temperature (Ahmed et al., 2020; Topal et al., 2021). For encapsulated systems, DSC can assess the thermal stability of the composite material, detect potential interactions between the polysaccharide and the fungicide, and determine the physical state (crystalline or amorphous) of the encapsulated fungicide. A shift in transition temperatures or the disappearance of a fungicide's characteristic peak can indicate successful encapsulation or amorphous dispersion within the carrier (Ahmed et al., 2020; Topal et al., 2021).

#### 4. Polysaccharide carriers in fungicide delivery systems

This section will highlight how different polysaccharide carriers (e. g., chitosan, alginate, cellulose (Fig. 1 (Islam et al., 2017; Salisu et al., 2015)) affect fungicide loading capacities and controlled release profiles, encompassing a diverse range of experimental designs and analytical techniques (Islam et al., 2017). The studies primarily focus on the synthesis, characterization, and evaluation of polysaccharide-based delivery systems for fungicides, with an emphasis on encapsulation efficiency, releasing kinetics under varying environmental conditions, and bioactivity against phytopathogens. The geographic and disciplinary scopes encompass agricultural sciences, materials chemistry, and environmental toxicology, reflecting the interdisciplinary nature of sustainable pesticide delivery research. This comparative analysis addresses key research questions by benchmarking loading capacities, release behaviors, environmental safety, molecular interactions, and antifungal efficacy across chitosan, alginate, cellulose, and their composites and summarized in Table 1 and overview of advantages of polysaccharide carriers in fungicide delivery systems in Fig. 2.

#### 5. Encapsulation efficiencies

Encapsulation efficiencies and loading capacities of polysaccharide carriers have garnered significant interest due to their potential applications in agricultural biotechnology, particularly in the delivery of fungicides and other agrochemicals. Polysaccharides, such as chitosan, alginate, and cellulose, are favored as carriers because of their biodegradability, biocompatibility, and ability to form stable complexes with various active ingredients. Recent studies have reported a wide range of encapsulation efficiencies and loading capacities achieved through different formulations tailored for specific agrochemical applications. Chitosan, a deacetylated derivative of chitin, stands out for its exceptional properties as an encapsulating matrix. For instance, Wei et al.

Fig.1. Structure of Chitosan, Cellulose, alginic acid, fucoidan, carageena, agaran, laminaran(Gunathilaka, Keertihirathna, & Peiris, 2022), pullulan (Nagamoto et al., 2024) and dextran (Díaz-Montes, 2021). Reproduced permission from ref.(Islam et al., 2017). Copyright 2017 Springer and sodium alginate. Reproduced permission from ref.(Salisu et al., 2015). Copyright 2016 Elsevier.

(2023) reported a loading capacity of 9.03% with an encapsulation efficiency of 68.64% using a chitosan-based formulation (Nuo et al., 2023). This system exhibited pH-responsive release characteristics, demonstrating accelerated release in alkaline conditions, which is particularly useful for controlling wheat crown rot. The favorable biocompatibility of this formulation with non-target organisms is an added advantage, highlighting the environmentally friendly nature of chitosan encapsulation. Similarly, alginate has been explored extensively for microencapsulation. Vinceković et al. (2023) developed alginate/chitosan microparticles with demonstrated antifungal activity against Botrytis cinerea, although the quantitative loading capacity was not specified (Marko et al., 2023). Alginate's inherent ability to form gel-like structures enables controlled release mechanisms, often governed by Fickian diffusion, resulting in a slower release profile that enhances the longevity of the active components. Another noteworthy example is the composite system reported by Yang et al. (2023), which achieved a 46.27% loading capacity of the fungicide boscalid within a metal-organic framework coated with polysaccharides (Xiukun et al., 2022). This formulation showcased a pH-triggered release, peaking at acidic conditions with a remarkable efficiency of 68.87% at pH 5. The hybrid polysaccharide coating not only improved adhesion but also enhanced stability and efficacy, establishing new benchmarks in

fungicidal performance compared to conventional methodologies.

In contrast, Zhou et al. (2024) reported an impressive encapsulation efficiency of 80% for a hydrophobic fungicide using N-succinyl chitosan (Oing et al., 2024). The controlled release characteristics coupled with improved solubility significantly increased bioavailability and demonstrated notable biocompatibility, ultimately leading to enhanced plant disease resistance. The unique self-assembling nature of the polymer contributed to the stability of the encapsulated active ingredient, resulting in superior efficacy against pathogens such as Rhizoctonia solani. Furthermore, some studies have highlighted the importance of cross-linking agents in improving encapsulation efficiencies (Qing et al., 2024). For instance, Sánchez-Hernández et al. (2023) achieved a loading capacity of approximately 20% for carvacrol in chitosan-CMC-alginate nanocarriers(Eva Aurora et al., 2024). The controlled release through hollow nanospheres (~114 nm) allowed for effective inhibition of multiple phytopathogens. The cross-linking agents used in this formulation not only stabilized the nanocarriers but also played a crucial role in reducing the required dosage of fungicides, which has implications for sustainable agricultural practices.

Incorporating multifunctional aspects, the work by Zheng et al. (2023) demonstrated a biodegradable delivery system with a fungicide covalently conjugated within an alginate-lignin network (Ling et al.,

 Table 1

 Overview of Polysaccharide-Based Delivery Systems for Fungicides: This table presents encapsulation efficiency, release kinetics under diverse environmental conditions, and bioactivity results against various phytopathogens.

Loading Capacity Efficiency	Release Kinetics Profile	Environmental Safety Assessment	Carrier-Fungicide Interaction Strength	Antifungal Efficacy Outcomes	References
9.03% loading, 68.64% encapsulation efficiency	pH-responsive release: faster in alkaline, slower in acidic	Good biocompatibility with non-target organisms	3D crosslinked mesh structure enhances encapsulation	Improved control of wheat crown rot vs. technical fungicide	(Nuo et al., 2023)
Metal ion loading in alginate/ chitosan microparticles;	Fickian diffusion- controlled release; slower	Environmentally friendly metal ion carriers	Complex molecular interactions confirmed by	High antifungal activity against <i>Botrytis cinerea</i>	(Marko et al., 2023)
quantitative loading not specified	from microcapsules		FTIR-ATR		
Indoxacarb loaded in polyurethane-alginate nanoemulsions; loading not	Alkaline-responsive swelling and release; persistent effect	Reduced toxicity to non- target insects	Polymer blend improves adhesion and release control	Effective against Spodoptera litura with reduced toxicity	(Shiying et al., 2020)
specified 46.27% loading of boscalid in MOF coated with polysaccharides	pH-triggered release; highest at acidic pH (68.87% at pH 5)	Low toxicity to plants and non-target organisms	Hybrid polysaccharide coating enhances adhesion and stability	Superior fungicidal activity vs. conventional formulations	(Yang et al., 2025)
80% encapsulation of	Controlled release with	Biocompatible carrier with	Self-assembling polymer	Higher control efficiency	(Qing et al.,
hydrophobic fungicide in N- succinyl chitosan	improved solubility and bioavailability	enhanced plant disease resistance	improves encapsulation stability	against Rhizoctonia solani than commercial fungicide	2024)
~20% loading capacity for carvacrol in chitosan-CMC-	Controlled release with hollow nanospheres; size	Safe for postharvest application; reduced	Cross-linking agents stabilize nanocarriers	Effective inhibition of multiple phytopathogens in vitro	(Eva Aurora et al., 2024)
alginate nanocarriers 14% loading, 57% entrapment	~114 nm Controlled release	fungicide dose Potential for reduced	Ionic gelation forms stable	Promising for commercial	(Sajjad et al.,
efficiency for chloridazon in alginate-chitosan nanocapsules	demonstrated by dialysis and UV spectroscopy	environmental impact	polyelectrolyte complexes	herbicide formulations	2022)
Drug release ratio controlled by polysaccharide type; cellulose lowest release	Release rate varies by polysaccharide; MMT reduces release	Biocompatible films with transdermal potential	Polysaccharide-mineral interactions modulate release	Sustained release over 2 days demonstrated	(Ji Ha et al., 2023)
Clotrimazole loaded in chitosan- g-PEG/starch beads; loading not specified	Slow release with zero- order kinetics; swelling decreases with pH	Potential for in vivo application; biodegradable	Crosslinking modulates release and swelling behavior	Novel microparticles for slow drug release	(Akakuru et al 2019)
Fungicide covalently conjugated in alginate-lignin network; loading not quantified	Redox-responsive release triggered by environmental reductants	Biodegradable with soil remediation potential	Covalent bonding controls release and metal ion complexation	Effective against Fusarium oxysporum in seeds	(Ling et al., 2024)
Copper ions loaded in alginate microspheres; loading efficiency not specified	Controlled copper ion release with swelling behavior	Eco-friendly fungicide with reduced environmental impact	Ionic gelation forms stable microspheres	Significant inhibition of multiple phytopathogenic fungi	(Marko et al., 2024)
Fungicide encapsulation efficiency up to 95% in lignin- surfactin coacervates	Stable deposition and controlled release on hydrophobic leaves	Biobased, eco-friendly with antifungal properties	Synergistic antifungal and carrier functions	Broad-spectrum fungicidal activity and reduced fungicide use	(Zhichen et al. 2024)
Prochloraz loading in ethyl cellulose nanoparticles;	Reduced burst release; improved photostability	Lower acute toxicity to zebrafish	Tannic acid modification enhances membrane interaction	Enhanced antifungal activity against Fusarium	(Yao et al., 2023)
loading not specified High entrapment efficiency (>90%) for thiram in agar-	Swelling and release influenced by polymer	Biodegradable and environmentally safe beads	Crosslinking controls swelling and release	graminearum Effective slow delivery of fungicide thiram	(Singh et al., 2013)
alginate beads Hexaconazole loaded in chitosan	composition Sustained release up to 86	Smaller particles show	dynamics Crosslinking agent	Enhanced control of	(Farhatun
nanoparticles; loading not specified	h at pH 5.5	higher antifungal activity	concentration controls particle size	Ganoderma boninense	Najat et al., 2020b)
Alginate-coated chitosan nanoparticles ~60 nm; loading not specified	Release profiles over days; core-shell structure controls release	Biocompatible nanoparticle system	Electrostatic coating stabilizes encapsulation	Controlled release of biomolecules demonstrated	(Körpe et al., 2014)
Chitosan-based nanocomposites carry various active	Controlled release and nutrient delivery	Enhances environmental sustainability and reduces	Multiple mechanisms including antimicrobial	Improved plant defense and reduced chemical inputs	(Hashim et al. 2024)
substances; loading varies Chitosan/O-CMCS nanoparticles loaded with tebuconazole;	Enhanced foliar adhesion and controlled release	pesticide use Biocompatible with selective fungal targeting	action Nanoparticles aggregate around pathogens for	Superior antifungal activity against strawberry	(Jian et al., 2023)
loading not specified  Posaconazole loaded in alginate- chitosan glutamate cryogels;	Freeze-thaw improves viscosity and prolongs	Enhanced bioadhesiveness and antifungal activity	targeted delivery Cryogel structure stabilizes drug release	anthracnose Better inhibition of Candida species than traditional	(Marta et al., 2022)
loading not specified Dual fungicide loading in	release Sustained release with	Enhanced antifungal	Crosslinking agent	hydrogels Improved control of	(Maluin et al.,
chitosan nanoparticles;	particle size control	efficacy with reduced	concentration modulates particle size and release	Ganoderma boninense basal stem rot	2019)
loading not specified MCPA loaded in chitosan- alginate-oil granules; loading not specified	Slow, controlled release with floating properties	environmental impact Targeted delivery reduces spray drift and non-target damage	Crosslinking and embedding stabilize granules	Enhanced control of water hyacinth with environmental safety	(Ruiquan et al 2021)
Actinomycetes encapsulated in alginate-chitosan composites; loading 50-88%	Encapsulation protects viability during drying	Biocompatible and functional for agricultural use	Composite matrices maintain cell viability and function	Supports sustainable agriculture via microbial delivery	(María et al., 2024)

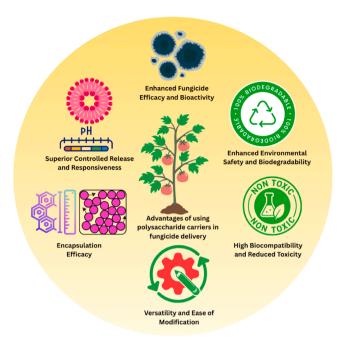


Fig. 2. Advantages of using polysaccharide carriers in fungicide delivery.

2024). However, the specific loading capacity was not defined. The redox-responsive release mechanism, activated by environmental reductants, facilitated controlled delivery, showcasing the potential of polysaccharide-based systems in enhancing the effectiveness of seed treatments against pathogens such as Fusarium oxysporum. Finally, Xiong et al. (2024) achieved a remarkable encapsulation efficiency of up to 95% for a fungicide within lignin-surfactin coacervates (Zhichen et al., 2024). This formulation is characterized by stable deposition and controlled release on hydrophobic leaf surfaces, further demonstrating the versatility of polysaccharide carriers in adapting to diverse agricultural environments. In conclusion, the advances in encapsulation efficiencies and loading capacities of polysaccharide carriers reflect their growing importance in agrochemical applications. By optimizing formulation strategies, researchers continue to enhance the performance and efficacy of fungicides while aligning with sustainable agricultural practices. These developments pave the way for innovative solutions to combat plant diseases effectively while minimizing environmental impact.

#### 6. Controlled release profiles for polysaccharide carriers

Polysaccharide carriers have emerged as a pivotal class of materials in the realm of controlled release systems, offering unique advantages in drug delivery and agricultural applications due to their biocompatibility, biodegradability, and ability to exhibit tunable release profiles. The development of these carriers is often underscored by their structural characteristics, which enable a nuanced modulation of release kinetics in response to various external stimuli, notably pH, ionic strength, and environmental conditions. Fundamentally, the release mechanisms associated with polysaccharide carriers can be categorized primarily into diffusion-controlled and swelling-related processes. The Korsmeyer-Peppas model is commonly used as a framework for assessing release kinetics, with release patterns influenced by the morphology of the polymer network and the nature of the encapsulated agent(Al-barudi et al., 2024). Evidence suggests that polysaccharide carriers, such as alginate and chitosan, tend to demonstrate slower release profiles under acidic conditions, primarily due to reduced swelling and increased density of the polymer matrix. This behavior is particularly advantageous in targeted delivery systems, where stability and controlled release at physiological pH levels are crucial. For instance, recent studies

(Ling et al., 2024; Nuo et al., 2023) highlight how nanoparticle formulations derived from polysaccharides can achieve sustained release profiles by leveraging pH-responsive swelling behaviors. While many systems are designed to provide sustained release, some studies reveal a biphasic release pattern characterized by an initial burst followed by a slower release phase. Akakuru et al. (2020) documented such burst kinetics, which can be crucial in scenarios requiring rapid therapeutic action (Akakuru & Onyido, 2021). This initial release is often attributed to the diffusion of surface-bound or loosely associated drug molecules. In contrast, the subsequent sustained release is controlled by matrix degradation or diffusion through the polymeric network.

Cross-linking undoubtedly plays a pivotal role in dictating the release profiles of polysaccharide carriers. Cross-linked networks generally exhibit greater stability and slower release kinetics compared to their non-crosslinked counterparts. For instance, research conducted by Akakuru et al. (2019) indicates that the release dynamics of chitosan-g-PEG/starch beads exhibit zero-order kinetics, with release rates decreasing as the pH increases (Akakuru et al., 2019). This highlights the significance of network integrity and cross-linking density in modulating release behaviors. Moreover, the incorporation of additional functionalities—such as metal-organic frameworks (MOFs) or surfactants—into polysaccharide matrices further enhances the versatility of these carriers. Yang et al. (2025) reported a successful formulation using polysaccharide-coated MOFs for the loading of boscalid, which exhibited a pH-responsive release profile peaking at pH 5. Such hybrid systems not only improve stability and adhesion but also expand the therapeutic window of fungicides while ensuring low toxicity to non-target organisms (Yang et al., 2025). Equally noteworthy is the advancement in polysaccharide combinations to achieve tailored release profiles. Zhou et al. (2024) achieved an impressive encapsulation efficiency of 80% for a hydrophobic fungicide using N-succinyl chitosan, demonstrating its potential for controlled release and improved bioavailability (Qing et al., 2024). The self-assembling nature of this polymer significantly enhances encapsulation stability, underscoring the value of tailoring polysaccharide structures to optimize delivery functionalities.

Ongoing research continues to explore novel polysaccharide formulations and cross-linking strategies to achieve desired release profiles. For example, Sánchez-Hernández et al. (2023) developed chitosan-CMC-alginate nanocarriers that demonstrated controlled release via hollow nanospheres, highlighting their potential for agricultural applications with reduced fungicide dosages(Eva Aurora et al., 2024). Such innovations pave the way for formulations with minimized environmental impacts while maintaining efficacy. In conclusion, the versatility and tunability of control release profiles in polysaccharide carriers underscore their potential in both pharmaceutical and agricultural contexts. By leveraging the intrinsic properties of polysaccharides and employing strategic modifications, researchers can engineer sophisticated delivery systems that provide controlled, sustained, and targeted release of active compounds. Ongoing exploration in this area promises further advancements in the design of effective, environmentally friendly delivery systems that meet the evolving needs of modern therapeutic and agricultural practices.

#### 7. Advancements in polysaccharide-based carriers for ecofriendly fungicide delivery

The development of polysaccharide-based carriers for fungicide delivery has garnered significant attention in recent years due to their potential to enhance the efficacy, stability, and environmental safety of agrochemical formulations. The interaction strength between polysaccharide carriers and fungicides is crucial for optimizing these formulations, ultimately enhancing their controlled release profiles and bioavailability in agricultural applications. Polysaccharides, including alginate, chitosan, and cellulose, exhibit unique properties that make them suitable for use as carriers in fungicide delivery systems. Their natural abundance, biocompatibility, and biodegradability contribute to

reduced environmental impact compared to synthetic polymers. Moreover, the chemical structure and functional groups of these polysaccharides facilitate strong molecular interactions with fungicides, primarily through hydrogen bonding, electrostatic interactions, and hydrophobic effects. These interactions are crucial for enhancing encapsulation stability, as they prevent the premature release of active ingredients and ensure that fungicides are delivered effectively to the target site. Recent studies have elucidated the significance of these interactions in the design of effective delivery systems. For instance, Wei et al. (2023) and Wu et al. (2023) reported that the integrity of polysaccharide-fungicide complexes plays a vital role in their performance. Strong interactions not only stabilize the encapsulated fungicides but also influence the kinetics of their release (Nuo et al., 2023; Siyu et al., 2023). Enhanced adhesion to leaf surfaces facilitated by polysaccharide formulations can contribute to prolonged fungicidal activity, reducing the frequency of application and lowering overall pesticide use.

One innovative approach to strengthening these interactions is the chemical modification of polysaccharide structures. Modification techniques, such as quaternization, graft copolymerization, and the introduction of functional groups, can significantly enhance the affinity of the carrier for fungicides. Niu et al. (2023) demonstrated that chemically modified polysaccharides exhibited superior retention capabilities and controlled release profiles (Junfan et al., 2024). This strategy not only increases loading efficiency but also enables the formulation to respond to environmental conditions, thereby optimizing fungicide delivery when needed. Characterizing the interactions between polysaccharides and fungicides is essential for understanding their encapsulation mechanisms. Fourier Transform Infrared Spectroscopy (FTIR) and other spectroscopic techniques are routinely employed to elucidate these molecular interactions. For example, Vinceković et al. (2023) demonstrated that alginate/chitosan microspheres utilize complex molecular interactions to enhance antifungal activity against pathogens such as Botrytis cinerea. The study emphasized the ability of these formulations to create stable microenvironments that favor fungicide efficacy (Marko et al., 2023).

Another promising avenue in polysaccharide-based delivery systems is the incorporation of metal-organic frameworks (MOFs). Research by Yang et al. (2025) revealed that polysaccharide-coated MOFs can achieve high fungicide loading efficiencies and exhibit pH-responsive release mechanisms (Yang et al., 2025). This particular formulation demonstrated that a significant loading capacity, along with low toxicity to beneficial organisms and plants, allows for tailored delivery that aligns with agronomic needs. Encapsulation efficiency remains a critical parameter in the development of these systems. Zhou et al. (2024) achieved an 80% encapsulation efficiency using N-succinyl chitosan, resulting in improved controlled release, enhanced solubility, and increased bioavailability. Functionalization of polysaccharide carriers can enhance their role in increasing plant resistance to diseases caused by pathogens like Rhizoctonia solani, thereby presenting a dual benefit of promoting crop health while ensuring effective disease management (Qing et al., 2024).

The overarching challenge in this field lies in forging a balance between improving the interaction strength between polysaccharide carriers and fungicides while ensuring environmental sustainability. As regulatory scrutiny of chemical pesticides increases, the exploration of polysaccharide-based delivery systems becomes increasingly relevant. Future research should focus on unraveling the intricate molecular mechanisms that govern these interactions and enhancing the chemical and physical stability of fungicide formulations. In summary, the strength of polysaccharide carrier-fungicide interactions is pivotal for developing advanced, eco-friendly fungicide delivery systems. By leveraging the unique properties of polysaccharides and exploring innovative modification strategies, researchers can create formulations that not only enhance efficacy and stability but also align with sustainable agricultural practices. Continued investigation in this area

promises to deliver novel solutions for adequate crop protection, contributing to food security and environmental stewardship.

#### 8. Environmental safety assessment

Polysaccharide carriers are widely acclaimed for their biodegradable nature and biocompatibility, exhibiting low toxicity levels toward nontarget organisms, thus contributing positively to environmental safety (Hashim et al., 2024; Jingyang et al., 2024; Nuo et al., 2023; Yang et al., 2025; Zhichen et al., 2024). Numerous studies highlight their potential to mitigate toxicity and improve ecological profiles, particularly when compared to conventional formulations (Junfan et al., 2024; Yao et al., 2023). However, specific formulations reveal varying degrees of ecotoxicity, which can be influenced by the choice of composite materials or the introduction of metal ions. For instance, while copper or silver-loaded formulations may exhibit antimicrobial properties, they also raise significant environmental concerns that merit careful consideration (Marko et al., 2023; Marko et al., 2024). The extent of environmental impact assessments presents noticeable discrepancies; some studies lack comprehensive long-term toxicity evaluations (Lihong et al., 2023). These differences can be attributed to factors such as the inclusion of metal ions, the use of synthetic polymers, and the absence of standardized ecotoxicity testing methodologies across various studies. Furthermore, the form of the carrier and the rate at which substances are released play critical roles in determining environmental exposure and potential ecological consequences.

#### 8.1. Antifungal efficacy outcomes

Polysaccharide carriers have emerged as a pivotal advancement in the realm of fungicide delivery systems, significantly enhancing antifungal efficacy outcomes. These biopolymers are gaining traction due to their favorable biocompatibility, biodegradability, and ability to improve the solubility and stability of fungicides. The incorporation of polysaccharide carriers enables the tailored release kinetics of fungicides, which is crucial for maximizing their antifungal potency. For instance, studies have shown that polysaccharide-based carriers can exhibit pH-responsive release profiles, offering rapid release in alkaline conditions and sustained release in acidic environments (Nuo et al., 2023). This feature not only facilitates optimized delivery in varying environmental conditions but also minimizes the potential for harmful side effects, as demonstrated by the reduced toxicity of formulations using biodegradable materials, such as chitosan (Qing et al., 2024). Efficiency in loading capacity and encapsulation is another crucial factor that polysaccharide carriers address. Research has shown that specific polysaccharide matrices, like chitosan and alginate, can achieve remarkable loading efficiency, enabling higher concentrations of active fungicides (Marko et al., 2023; Yang et al., 2025). The three-dimensional crosslinked structures of these carriers enhance encapsulation, leading to a stronger carrier-fungicide interaction and enabling prolonged antifungal activity (Hashim et al., 2024). Moreover, the presence of bioactive components within these polysaccharides can synergistically improve fungal inhibition beyond the inherent efficacy of the fungicides alone, as observed with chitosan's antimicrobial properties (Zhichen et al., 2024). An important aspect of utilizing polysaccharide carriers in fungicide delivery is their environmental safety. Many studies have highlighted that these carriers exhibit good biocompatibility with non-target organisms, thereby mitigating the ecological risks traditionally associated with chemical fungicides (Sajjad et al., 2022). For instance, the study showcases coacervates made from lignin and surfactin, natural substances with potent antifungal properties, which enhance the efficacy of fungicides while reducing their dosage. The carriers achieve up to 95% encapsulation efficiency and effectively adhere to hydrophobic leaves. They demonstrate broad-spectrum activity against eight common phytopathogens and can function as standalone biofungicides. Encapsulating 0.30 mM pyraclostrobin (Pyr)

results in an 87.0% inhibition rate, like that of 0.80 mM Pyr alone, and exhibits a 53% preventive effect against tomato gray mold, outperforming commercial adjuvants. This innovative approach highlights the potential of using biosurfactants and biomass for environmentally safe fungicide delivery (Fig.3a) (Wang et al., 2024). Developing functional nanocarriers for the effective delivery of pesticides to plants is challenging. This study presents a pH-triggered pesticide formulation (BUCC) that encapsulates boscalid (Bos) within UIO-66-NH2 nanoparticles, which are then coated with a polysaccharide layer of carboxymethylcellulose (CMC) and chitosan quaternary ammonium salt (CQAS). The UIO-66-NH2 nanocarriers have a size of approximately 60 nm and a Bos loading capacity of 46.27%. The BUCC exhibits excellent pH-responsive release and enhanced fungicidal activity against Sclerotinia sclerotiorum (EC50 = 0.14 mg/L), surpassing that of conventional Bos granules (EC50 = 0.84 mg/L). It effectively reaches various parts of rapeseed plants through leaf spray or root immersion, exhibits 1.9-fold better photostability than Bos WG, and adheres well to leaf surfaces. The formulation also demonstrates low toxicity to rapeseed and various non-target organisms, making it a promising eco-friendly solution for sustainable pest and fungal disease management(C. Yang et al., 2025) (Fig.3b). For example, formulations that employ metal ions in alginate/chitosan carriers have demonstrated both high antifungal activity against pathogens and a minimized environmental footprint (Marko et al., 2024). This positions polysaccharide carriers not only as effective delivery systems but also as environmentally responsible choices in agriculture and horticulture. However, the effectiveness of these delivery systems is contingent upon numerous variables, including the type of fungicide, its dosage, the specific fungal species targeted, and the precise characteristics of the polysaccharide carrier(Eva Aurora et al., 2024). Variations in experimental protocols—ranging from in vitro assays to in planta evaluations—also impact the measured antifungal efficacy. In this context, a comprehensive understanding of the mechanistic interactions between the carrier and the fungicide is crucial for optimizing formulations for practical applications in various agricultural settings (Jun-Wei et al., 2023). Therefore, polysaccharide carriers represent a transformative approach in the delivery of fungicides, significantly enhancing their antifungal efficacy through improved loading efficiency, controlled release, and favorable environmental profiles. The ongoing research into optimizing these carrier systems promises to address the growing challenges posed by fungal pathogens while supporting sustainable agricultural practices. Continued exploration of the nuances of carrier-fungicide interactions and environmental implications will undoubtedly yield innovative solutions for crop protection in the future.

## 9. Standardizing assessment protocols for polysaccharide carriers in fungicide delivery: Addressing challenges and impacts

The variability in loading capacities and encapsulation efficiencies of polysaccharide carriers poses significant challenges for consistent fungicide delivery. This subsection examines the necessity for standardized assessment protocols, emphasizing the consequences of methodological inconsistencies on performance benchmarking, environmental impact, and the development of optimized polysaccharide-based carrier systems in agricultural applications and summarized in Table 2.

#### 9.1. Standardized assessment of loading capacities

The loading capacities and encapsulation efficiencies of polysaccharide carriers exhibit significant variability due to inconsistent reporting metrics and a lack of standardized protocols across studies. To address these discrepancies, it is crucial to establish and implement standardized methodologies for quantifying fungicide loading and encapsulation efficiency. This should encompass uniform units of measurement and consistent experimental conditions. Such standardization is vital for facilitating direct comparisons and benchmarking the performance of different carriers, as the current methodological heterogeneity hampers effective evaluations (Jun-Wei et al., 2023; Ritu et al., 2021; Sajjad, Danial, Iraj, Naser, Elham, & Muhammad, 2022).

### 9.2. Advancing carrier performance: challenges and opportunities in standardization and environmental impact

The molecular interaction mechanisms between carriers and fungicides, such as hydrogen bonding and electrostatic forces, arpe frequently described qualitatively, lacking a robust quantitative correlation to release kinetics and bioactivity. This study aims to conduct systematic and quantitative investigations that elucidate the link between specific molecular interactions within polysaccharide matrices and their resultant controlled release profiles and fungicide bioavailability. By employing advanced spectroscopic techniques and modeling approaches, we seek to gain insights into these intricate interaction mechanisms. An in-depth understanding will facilitate the rational design of carrier systems with customized release characteristics and enhanced efficacy profiles (Marko et al., 2023; Ren et al., 2024; Sajjad et al., 2022).

#### 9.3. Long-term environmental impact and biodegradation pathways

There is a paucity of data regarding the long-term environmental fate, biodegradation byproducts, and ecotoxicological repercussions of polysaccharide-based fungicide carriers in real-world applications. It is essential to conduct extensive field-based ecotoxicological evaluations and biodegradation studies to assess these carriers and their decomposition products over prolonged periods. This should encompass an analysis of their effects on soil microbiota and non-target organisms. A comprehensive understanding of the long-term ecological impacts, extending beyond initial biocompatibility assessments, is crucial for ensuring environmental safety and sustainability (Heny et al., 2023; Jun-Wei et al., 2023; Ren et al., 2024).

## 9.4. Influence of structural variability in polysaccharides on release profiles

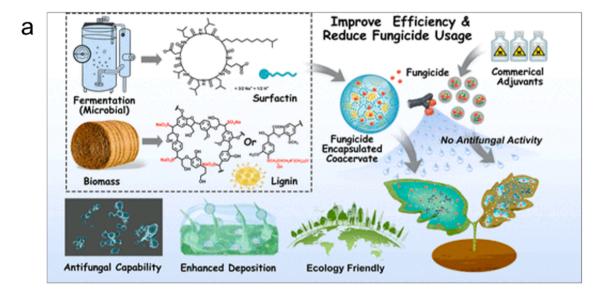
The impact of polysaccharide molecular weight, degree of substitution, and structural heterogeneity on the loading and release kinetics of fungicides is an area that has not been thoroughly investigated. It is essential to explore how variations in the physicochemical properties of polysaccharides affect encapsulation efficiency, matrix porosity, swelling dynamics, and release kinetics, utilizing well-characterized polymer batches. The structural variability of these carriers significantly influences their performance, yet it remains inadequately defined. This limitation poses challenges for reproducibility and optimization in application(Fernando et al., 2023; Morozkina et al., 2022).

#### 9.5. Field validation of antifungal efficacy and release behavior

While many studies have established the antifungal efficacy and release profiles of these compounds under in vitro or controlled pot conditions, field trials validating their practical performance are notably scarce. It is crucial to design and implement multi-location field trials to assess the efficacy, release behavior, and environmental safety of polysaccharide-based fungicide carriers under realistic agricultural conditions. Such field validation is necessary to confirm laboratory findings and evaluate the real-world applicability and scalability of these methods (Eva Aurora et al., 2022; Jian et al., 2023; Nuo et al., 2023) .

#### 9.6. Optimization of composite and hybrid polysaccharide systems

Hybrid systems that integrate polysaccharides with inorganic or



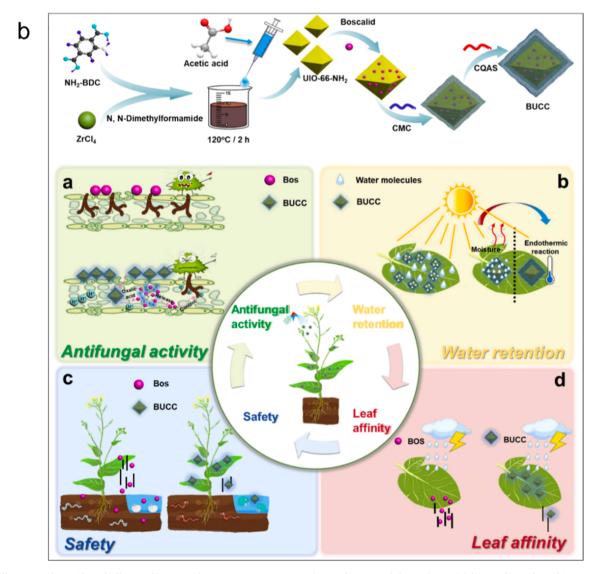


Fig. 3. (a)Illustrating the antifungal efficacy of lignin-surfactin coacervates against phytopathogens and their enhanced delivery of pyraclostrobin. Reproduced with permission from ref.(Wang et al., 2024). Copyright 2024 American chemical society (b) pH-triggered BUCC formulation using UIO-66-NH2 nanoparticles enhances boscalid delivery and efficacy against Sclerotinia sclerotiorum with low toxicity. Reproduced with permission from ref. (C. Yang et al., 2025). Copyright 2025 Elsevier.

**Table 2**Challenges and Future Research Directions.

Challenging area	Limitations	Possible solutions	Comments
Standardized Quantification of Loading Capacities	Loading capacities and encapsulation efficiencies vary widely across studies with inconsistent reporting metrics and lack of standardized protocols for polysaccharide carriers.	Develop and adopt standardized methodologies for quantifying fungicide loading and encapsulation efficiency across polysaccharide carriers, including uniform units and experimental conditions.	Standardization is essential to enable direct comparison and benchmarking of carrier performance, which is currently hindered by methodological heterogeneity (Nuo et al., 2023; Ritu et al., 2021; Sajjad et al., 2022).
Comparative Mechanistic Studies of Carrier- Fungicide Interactions	Molecular interaction mechanisms (e.g., hydrogen bonding, electrostatic forces) are often qualitatively described without quantitative correlation to release kinetics or bioactivity.	Conduct systematic, quantitative studies linking specific molecular interactions within polysaccharide matrices to controlled release profiles and fungicide bioavailability using advanced spectroscopic and modeling techniques.	Understanding precise interaction mechanisms will enable rational design of carriers with tailored release and efficacy profiles(Jingyang et al., 2024; Marko et al., 2024; Sajjad et al., 2022).
Long-Term Environmental Impact and Biodegradation Pathways	Limited data exist on the long-term environmental fate, biodegradation products, and ecotoxicological effects of polysaccharide- based fungicide carriers under field conditions.	Perform comprehensive field-based ecotoxicological assessments and biodegradation studies of polysaccharide carriers and their degradation products over extended periods, including effects on soil microbiota and non-target organisms.	Ensuring environmental safety and sustainability requires understanding long-term impacts beyond initial biocompatibility assays (Heny et al., 2023; Jun-Wei et al., 2023; Xiukun et al., 2022).
Influence of Polysaccharide Structural Variability on Release Profiles	The effects of polysaccharide molecular weight, degree of substitution, and structural heterogeneity on fungicide loading and release kinetics remain underexplored.	Investigate how variations in polysaccharide physicochemical properties influence encapsulation efficiency, matrix porosity, swelling behavior, and release kinetics using well-characterized polymer batches.	Structural variability critically affects carrier performance but is insufficiently characterized, limiting reproducibility and optimization( Fernando et al., 2023; Morozkina et al., 2022).
Field Validation of Antifungal Efficacy and Release Behavior	Most studies demonstrate antifungal efficacy and release profiles under in vitro or controlled pot conditions, with scarce field trials validating practical performance.	Design and implement multi-location field trials to evaluate polysaccharide-based fungicide carriers' efficacy, release behavior, and environmental safety under realistic agricultural conditions.	Field validation is necessary to confirm laboratory findings and assess real-world applicability and scalability(Eva Aurora et al., 2024; Siyu et al., 2023).
Optimization of Composite and Hybrid Polysaccharide Systems	Hybrid systems combining polysaccharides with inorganic or synthetic components show promise but introduce complexity and unclear synergistic mechanisms.	Systematically optimize composite formulations to elucidate synergistic effects on loading capacity, release control, and bioactivity, employing factorial design and mechanistic studies.	Clarifying the role of hybrid components will improve formulation efficiency and environmental compatibility(Junfan et al., 2024; Zhichen et al., 2024).
Controlled Release under Variable Environmental Conditions	Release kinetics are often studied under limited pH or temperature conditions, lacking comprehensive evaluation under fluctuating field-relevant environmental parameters.	Develop dynamic release studies simulating variable pH, temperature, humidity, and soil/water interactions to better predict carrier performance in diverse agroecosystems.	Realistic environmental simulations are critical for designing carriers with robust and predictable release profiles (Jun-Wei et al., 2023; Ludmilla et al., 2023).
Scalability and Cost- Effectiveness of Polysaccharide Carrier Production	Few studies address the economic feasibility, scalability, and manufacturing challenges of polysaccharide-based fungicide carriers for commercial agricultural use.	Investigate scalable synthesis routes, cost analysis, and process optimization for polysaccharide carriers, including raw material sourcing and green chemistry approaches.	Commercial adoption depends on cost-effective and scalable production methods, currently underreported (You et al., 2024; Zan et al., 2023).
Impact of Carrier Properties on Targeted Delivery and Adhesion	The relationship between carrier surface properties, adhesion to plant surfaces, and targeted fungicide delivery efficacy requires further elucidation.	Explore how modifications in carrier surface chemistry, charge, and morphology affect foliar adhesion, rainfastness, and targeted delivery using advanced imaging and adhesion assays.	Enhanced adhesion improves fungicide bioavailability and reduces environmental loss, yet mechanistic understanding is limited (Jian et al., 2023; C. Yang et al., 2025).
Resistance Development and Fungicide Dose Reduction Potential	The potential of polysaccharide carriers to reduce fungicide doses and mitigate resistance development in phytopathogens is insufficiently studied.	Conduct longitudinal studies assessing fungicide dose reduction, resistance evolution in target fungi, and synergistic effects of carriers with fungicides.	Demonstrating dose reduction and resistance management benefits will support sustainable disease control strategies(Grazyna et al., 2022; Hashim et al., 2024; Zhichen et al., 2024).

synthetic components demonstrate significant potential; however, they introduce complexity and obscure synergistic mechanisms. A systematic optimization of composite formulations is needed to elucidate the synergistic effects on loading capacity, release control, and bioactivity, employing factorial design and mechanistic studies. Clarifying the role of hybrid components is vital for enhancing formulation efficiency and environmental compatibility (Junfan et al., 2024; Ritu et al., 2021; Zhichen et al., 2024).

#### 9.7. Controlled release under variable environmental conditions

Release kinetics are frequently evaluated under constrained pH or temperature conditions, yet a comprehensive assessment is often lacking under dynamically changing, field-relevant environmental parameters. It is necessary to develop dynamic release studies that simulate variable pH, temperature, humidity, and interactions between soil and water to predict carrier performance across diverse agroecosystems better. Realistic environmental simulations are critical for designing carriers with robust and predictable release profiles (Jingyang et al., 2024; Jun-Wei et al., 2023; Ludmilla et al., 2023).

## 9.8. Scalability and cost-effectiveness of polysaccharide carrier production

Limited investigations have been conducted into the economic viability, scalability, and manufacturing hurdles associated with polysaccharide-based fungicide carriers for commercial agricultural deployment. It is essential to explore scalable synthesis methodologies, conduct comprehensive cost analyses, and optimize production processes for these carriers, taking into account raw material procurement and green chemistry approaches. The commercial adoption of these carriers depends on establishing cost-effective and scalable manufacturing strategies, which are currently underrepresented in the literature (You et al., 2024; Zan et al., 2023).

#### 9.9. Impact of carrier properties on targeted delivery and adhesion

The interplay between the surface characteristics of carriers, their adhesion to plant surfaces, and the efficacy of targeted fungicide delivery necessitates further exploration. A detailed investigation into how alterations in carrier surface chemistry, charge, and morphology impact foliar adhesion, rainfastness, and targeted delivery is warranted,

utilizing advanced imaging techniques and adhesion assays. Improved adhesion is crucial for enhancing fungicide bioavailability and minimizing environmental losses, yet the underlying mechanisms have yet to be fully elucidated (Jian et al., 2023; Siyu et al., 2023; C. Yang et al., 2025).

#### 9.10. Resistance development and fungicide dose reduction potential

The capacity of polysaccharide carriers to decrease fungicide application rates and address resistance development in phytopathogens remains underexplored. Longitudinal studies are necessary to evaluate the potential for reducing fungicide doses, track the evolution of resistance in susceptible fungal populations, and investigate the synergistic interactions between carriers and fungicides. Establishing the benefits of dose reduction and effective resistance management will be critical in supporting sustainable disease control strategies (Grazyna et al., 2022; Hashim et al., 2024; Zhichen et al., 2024).

#### 10. Conclusion

This review presents compelling evidence that polysaccharide carriers, such as chitosan, alginate, and cellulose, substantially influence fungicide loading capacities and controlled release profiles, thereby enabling more efficient and environmentally sustainable plant disease management. Loading capacities vary widely across polysaccharide types and formulations, with starch-based systems demonstrating exceptionally high loading potential, while chitosan and alginate composites frequently achieve moderate to high encapsulation efficiencies. Amphiphilic modifications and nanocomposite formulations further enhance loading efficiencies, particularly for hydrophobic fungicides, underscoring the importance of carrier chemical structure and composite design in optimizing encapsulation. Controlled release behaviors from these polysaccharide matrices exhibit strong environmental responsiveness, most notably pH-sensitive release, where alkaline conditions accelerate the liberation of the fungicide, while acidic environments retard it. Release kinetics typically conform to diffusioncontrolled mechanisms, including Fickian and non-Fickian models, which are often modulated by factors such as crosslinking density, polymer composition, and carrier architectures, including multilayer beads, hydrogels, and aerogels. The use of hybrid systems and nanostructures enables fine-tuning of release profiles to achieve sustained delivery, reduce burst release, and address field-specific requirements.

Molecular interactions between carriers and fungicides are primarily governed by electrostatic forces, hydrogen bonding, and, in some cases, covalent conjugation, which stabilize encapsulation and influence release rates and bioavailability. Carrier modifications and composite formation enhance these interactions; however, there remains a need for more quantitative mechanistic studies that correlate molecular-level phenomena with functional outcomes. Structural properties, such as porosity, particle size, and surface charge, critically impact adhesion, swelling behavior, and ultimately, antifungal efficacy. Polysaccharidebased carriers consistently enhance antifungal bioactivity compared to technical fungicides, often allowing for lower dosages and targeted delivery that improves adhesion to plant surfaces and pathogen specificity. Furthermore, intrinsic antifungal properties of some carriers or synergistic effects with bioactive additives contribute to enhanced pathogen suppression. However, most efficacy evaluations are confined to in vitro or greenhouse trials, highlighting the necessity for expanded field-level validation. Environmental safety assessments affirm the biocompatibility and biodegradability of polysaccharide carriers, with reduced toxicity to non-target organisms and potential for minimized environmental residues compared to conventional formulations. Nonetheless, comprehensive long-term ecotoxicological studies and fate analyses of degradation products are insufficient and warrant further investigation. The scalability and cost-effectiveness of advanced carrier modifications also require more thorough evaluation to facilitate practical agricultural applications.

Overall, this review highlights that the selection of polysaccharide carriers, molecular design, and formulation strategies significantly influence fungicide loading efficiency, release dynamics, and bioactivity, collectively affecting sustainable pest management outcomes. Future research should prioritize standardized methodologies, in-depth mechanistic elucidation, and comprehensive environmental impact assessments to advance the development of optimized polysaccharide-based fungicide delivery systems suitable for commercial deployment and ecological stewardship.

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#### Generative artificial intelligence

During the preparation of this manuscript, the authors used ChatGPT4.0 (OpenAI) to improve language clarity and readability, particularly for phrase restructuring and draft polishing. After using the tool, all generated text was thoroughly reviewed, edited and verified by the authors, who take full responsibility for the final content.

#### CRediT authorship contribution statement

Sathish Kumar Venkatachalam: Validation, Software, Resources. Dharmaraj Senthilkumar: Software, Resources. Nallusamy Duraisamy: Resources, Project administration. Thangaraj Sheela: Software, Resources. Meivelu Moovendhan: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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No data was used for the research described in the article.

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