Carbohydrate Polymer Technologies and Applications 12 (2025) 101009

Contents lists available at ScienceDirect

Carbohydrate Polymer Technologies and Applications

journal homepage: www.sciencedirect.com/journal/carbohydrate-polymer-technologies-and-applications

Polysaccharide polymer-based nanoparticles for nano fertilizer and nano pesticides–A review

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ARTICLE INFO

Keywords:
Polymers
Nanotechnology
Pesticide
Fertilizer
Polysaccharide

ABSTRACT

The increasing global population and escalating threats from plant pathogens demand sustainable strategies for enhancing food security. While conventional fertilizers and pesticides remain essential, their overuse leads to pest resistance, disruption of soil microbiota, and environmental contamination. Smart polymeric materials particularly polysaccharide-based nanoparticles offer a promising approach for controlled and targeted agrochemical delivery. However, most existing reviews provide broad overviews of polymeric carriers without emphasizing the synthesis, mechanistic behaviour, and soil interactions of polysaccharide-derived nanocarriers. While polysaccharide-based nanoparticles are widely studied for agrochemical delivery, this review identifies critical gaps between lab-scale innovation and field applicability. We analyse trade-offs in scalability, environmental persistence, and regulatory barriers, proposing a roadmap for next-generation formulations (marine polysaccharides, enzyme-triggered release). It focuses on their mechanisms of action, structural features, delivery strategies, and highlights the specific challenges and future directions for optimizing their agricultural performance.

1. Introduction

Agriculture is crucial and of global significance, serving as a vital avenue for food supply and a strong driver of economies (Pascoli et al., 2018). The ever-increasing human population exerts substantial pressure on agricultural production. Concurrently, pathogens and pests continue to threaten crop yields and limit output annually. They are among the primary causes of global crop losses, accounting for up to 40 % of total production and resulting in estimated annual economic losses exceeding $220 billion (FAO, 2024; Vagelas et al., 2024; Vagelas et al., 2025). These losses exacerbate global food insecurity (FAO, 2021; Strange & Scott, 2005) and contribute to widespread hunger. To meet the food demands of the growing population and mitigate crop losses due to biotic stressors, enhancing crop production through sustainable and innovative technologies is imperative. This is essential not only for eliminating food insecurity but also for improving human nutritional outcomes (Tilman et al., 2002).

Growing appeal for food has exacerbated use of inputs namely, fertilizers and pesticides. FAO (2012) reported that an enormous 2.5 million tons of agrochemicals are used on cultivable lands every year. However, the inclusion of these inputs has proved unsustainable owing to ecological problems like ecosystem imbalance, pest resistance, health issues, and natural resource exhaustion, coupled with surface and groundwater contamination (Duhan et al., 2017; Fabiyi & Olatunji, 2021; Fabiyi et al., 2024; Oliveira et al., 2014). Subsequently, these unsustainable practices require a move in the direction of a viable and eco-friendly production technique. In anticipation of global human population which is envisioned to be 9 billion by the year 2025, and additionally to minimize and correct accrued environmental effect of fertilizers and agrochemicals, ensuring food safety with new technologies is requisite to shore up crop production by unit area (Max et al., 2019; Mishra et al., 2017).

Primarily, global agriculture is challenged with reducing the quantity of agrochemical and fertilizer use and managing pests and pathogens. Sundry techniques like crop hybrids and edited genes have been used for agricultural development lately. New technologies are evolving with promising potent outcomes (Prasad et al., 2017). One of these is nanotechnology; several nanomaterials are employed in agriculture (Fabiyi, 2021; 2023; 2025), one of which encompasses nano-pesticides that are engineered nano materials containing pesticidal elements

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https://doi.org/10.1016/j.carpta.2025.101009

Available online 18 September 2025

directed at crops for protection against sundry biotic stressors. A group of biopolymers comprising of repeated units containing di and monosaccharides linked by bonds of glycoside to become branched or linear structures, otherwise called polysaccharide polymer (PPs) complements nano pesticides.

Polysaccharide polymers (PPs) are non-polluting materials that have captivated scientists. They are highly prized and employed broadly in dissimilar fields of science like medicine, engineering and physics. Lately, polysaccharide polymers have been applied to materials in aerospace industry owing to their toughness, strength and stiffness. Their high heat resistance quality has put them forward as a functional gradient material gel (Ouyang et al., 2024). Further, their compatibility and safety attributes has enabled them for use in engineering of bones, cartilage and skin (Hu et al., 2024). They serve as nanocatalysts in high-tech chemical techniques and are equally known as good materials in waste water purification (Sharma & Kumari, 2022). Polymer nanomaterials are endowed with characteristics such as bio-decomposability and practicality, that have made them versatile and they can be adapted to agricultural use. Some smart polymer materials are manufactured to respond to stimuli to minimize waste through timely delivery of nutrients and pesticides to crops (Abobatta, 2018; Stuart et al., 2010). This ensures efficiency and cost control with good results while, low dosage of application, environmental risk, and human toxicity are equally brought under check (Choudhary et al., 2017).

Despite multiple reviews addressing individual polysaccharide carriers like chitosan or starch, a comparative and mechanistic synthesis across the most relevant natural polymers for agrochemical delivery is lacking. This review bridges that gap by analyzing shared and divergent features of chitosan, alginate, cellulose, and starch-based systems. Moreover, it presents updated synthesis strategies, highlights underexplored performance determinants, and incorporates original illustrations and comparative tables to consolidate the fragmented literature. In doing so, it offers a field-oriented perspective grounded in synthesis-method-performance relationships-timely given the urgent push for sustainable and precision agriculture. Furthermore, the significance of polymeric nanomaterials in agriculture, polymer types, reactions in soil, applications, physical and chemical attributes are discussed.

2. Polymer types

Polymers are broadly classified into natural and synthetic types, but this review focuses specifically on natural polysaccharide-based polymers due to their environmental compatibility and high potential in nano-fertilizer and nano-pesticide systems. Key polysaccharides include chitosan, starch, cellulose, and alginate, each with distinctive properties for forming nanoparticulate delivery systems (Fig. 1). Their structural versatility and functional groups allow for crosslinking, ionic gelation, and responsive behaviours that are critical in agricultural applications (Fabiyi, 2025).

The diversity in polysaccharide structure, particularly in molecular weight, branching, and functional group availability, influences nanoparticle formation and performance. For instance, chitosan's amine groups facilitate ionic gelation with multivalent anions, while carboxyl groups in alginate promote calcium crosslinking. This review emphasizes how these intrinsic features of polysaccharides govern the design of nano-carriers in agriculture.

3. Synthesis of polymers

Synthesis of polymers is a critical aspect in the progression of polymer-based nanoparticles for nano-fertilizers and nano-pesticides. The method of synthesis not only dictates the molecular architecture of the polymer, it equally impacts size, shape, and functionality of ensuing nanoparticles. Key polymerization techniques used to synthesize polymers for agricultural applications, with a focus on the steps involved and how they relate to the pattern of effective carriage systems for fertilizers and pesticides.

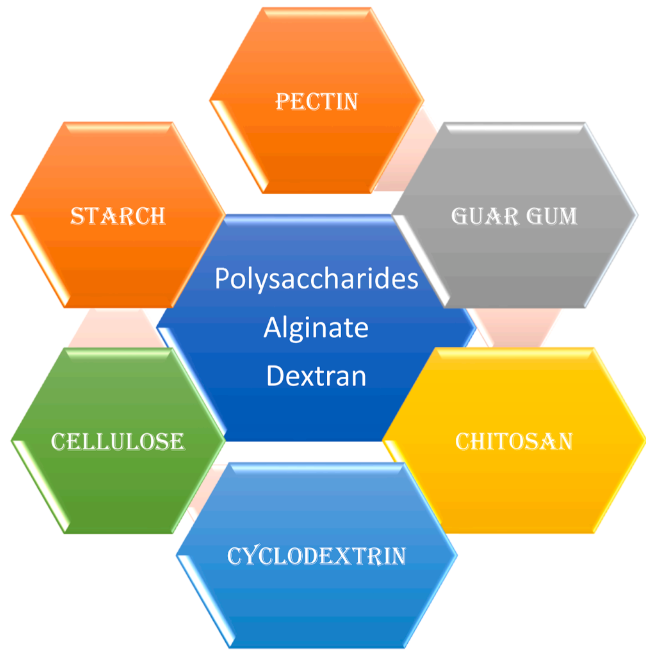


Fig. 1. Polysaccharide polymers (This Fig. was independently designed and created using Microsoft PowerPoint).

3.1. Overview of polymerization techniques

The synthesis of polymeric nanocarriers for agricultural applications leverages a suite of polymerization techniques, each offering distinct advantages in controlling the molecular architecture, composition, and final properties of the polymer. The choice of method directly influences critical nanoparticle characteristics such as biodegradation rate, encapsulation efficiency, and release kinetics. While a vast array of synthetic strategies exists, the most prevalent techniques for formulating agrochemical carriers can be categorized into a few key approaches. Table 1 summarizes these core methods, their fundamental principles, and their specific relevance to the development of advanced nano-fertilizers and nano-pesticides.

3.2. Synthesis of polysaccharide-based nanoparticles

The development of polysaccharide-based nanoparticles (NPs) for agricultural applications hinges on the selection of appropriate synthesis techniques, each tailored to optimize stability, encapsulation efficiency, and controlled release. These methods leverage the unique physicochemical properties of natural polymers such as chitosan, alginate, and starch while addressing challenges like scalability and environmental safety.

One of the most widely used approaches is ionic gelation, which relies on electrostatic interactions to form NPs under mild conditions. For example, chitosan, a cationic polysaccharide derived from crustacean shells, spontaneously cross-links with polyanions like tripolyphosphate (TPP) to create stable nanocarriers. This method has proven particularly effective for encapsulating pesticides; Kumar et al. (2015) demonstrated that chitosan-TPP NPs loaded with imidacloprid reduced leaching losses while prolonging insecticidal activity (Kumar et al., 2022). Similarly, alginate NPs, gelled with calcium ions, have been employed to control the release of herbicides like paraquat, minimizing soil contamination (dos Silva, Cocenza, & Grillo, 2011). The simplicity and solvent-free nature of ionic gelation make it a favoured choice for eco-conscious formulations.

Table 1
Key synthesis methods for agro-nanocarriers from natural and biodegradable polymers.

Synthesis methods	Key characteristics	Relevance to agro-nanocarriers	Example/ applications
Ionic gelation	Simple, mild process; relies on electrostatic interaction between oppositely charged polymers.	Widely used for chitosan nanoparticles encapsulating fertilizers or pesticides under ambient conditions.	Chitosan–TPP nanoparticles for carbendazim delivery (Campos et al., 2015).
Polyelectrolyte complexation	Self-assembly of oppositely charged biopolymers without chemical crosslinkers.	Produces biodegradable nanoparticles with tunable stability and release profiles.	Chitosan–alginate complexes for slow-release insecticides (Kumar et al., 2015).
Emulsion/ nanoemulsion	Dispersion of polymers in aqueous/organic phases; allows control over particle size.	Enables scalable production of nanocapsules and nanospheres for hydrophobic agrochemicals.	Alginate-based nanoemulsions for essential oil pesticides (Suraphan et al., 2020)
Spray-drying	Solvent evaporation under heat; produces dry powders directly.	Facilitates large-scale production and stable formulations suitable for soil application.	Starch nanoparticles encapsulating urea fertilizer for controlled release. (Mondéjar-López et al., 2024)
Ring-opening polymerization (ROP)	Polymerizes cyclic monomers (e.g., lactones); allows control of degradation rates.	Used to create biodegradable carriers tuned to crop growth cycles.	PCL nanocapsules for essential oil bio-pesticide release. (Forim et al., 2013)

For hydrophobic agrochemicals, emulsion solvent evaporation offers a robust alternative. Here, polymers such as poly(lactic-co-glycolic acid) (PLGA) or polycaprolactone (PCL) are dissolved in organic solvents, emulsified in water, and evaporated to form solid NPs. Grillo et al. (2014) utilized this technique to encapsulate atrazine, achieving a tenfold reduction in herbicide dosage while maintaining efficacy against weeds (Grillo et al., 2010). Likewise, PCL nanocapsules have been used to protect volatile essential oils such as neem oil from degradation, enhancing their insecticidal persistence (Forim et al., 2013). Despite its reliance on organic solvents, the method's high encapsulation efficiency and tunable release profiles justify its use for challenging active ingredients.

Nanoprecipitation, a simpler and surfactant-free technique, involves precipitating polymers from a solvent into a non-solvent to form NPs. Starch nanoparticles produced this way have been loaded with thiram fungicides, combining antifungal action with improved water retention in soils (Singh et al., 2008). Cellulose nanocrystals, derived from plant biomass, also exemplify the versatility of this method; their high surface area and biodegradability make them ideal carriers for nutrients and pesticides (Zheng et al., 2022).

In contrast, polyelectrolyte complexation exploits the interaction between oppositely charged polysaccharides to form stable nanocomplexes. Chitosan-alginate systems, for instance, have been engineered to deliver carbendazim, a fungicide that showed enhanced activity against *Fusarium oxysporum* without harming crops (Campos et al., 2015). Similarly, β-cyclodextrin, a cyclic oligosaccharide, forms inclusion complexes with hydrophobic herbicides like chlorpropham, shielding them from photodegradation (Ge et al., 2011). These systems excel in protecting sensitive payloads while responding to environmental triggers like pH or enzymes.

For industrial-scale production, spray drying stands out for its efficiency. By atomizing polymer solutions into fine droplets and rapidly drying them, this method yields uniform micro- and nanoparticles. Alginate-cyclodextrin NPs encapsulating azadirachtin (a botanical insecticide) retained bioactivity longer than conventional formulations, as demonstrated by Jerobin et al., 2012. Similarly, starch-polyvinyl alcohol (PVA) composites have been spray-dried into fertilizer coatings that synchronize nutrient release with crop demand (Han et al., 2009).

Table 2
Natural polymers used in nanofertilizer formulations.

Polymer	Active ingredient	Encapsulation method	Key findings	References
Chitosan	Urea	Ionic gelation with TPP	Prolonged nitrogen release; improved crop yield	Kottegoda et al., 2011, 2017
Alginate	NPK fertilizers	Calcium crosslinking	Reduced leaching; synchronized nutrient release	Wu and Liu, 2008
Starch	Thiram (fungicide)	Nanoprecipitation	Enhanced water retention and antifungal activity	Singh et al., 2008
Cellulose	Phosphates	Hydrogel embedding	Improved soil water retention and nutrient availability	Zhong et al., 2013
Cyclodextrin	Gibberellic acid	Inclusion complexation	Controlled hormone release; boosted plant growth	Pereira et al., 2017

3.3. Limitations and opportunities in synthesis

While significant progress has been made in developing polysaccharide-based nanoparticles for agricultural applications, several critical challenges remain that hinder their widespread adoption. The synthesis methods currently employed each present unique limitation that must be addressed to advance the field. Some encapsulation methods and their key findings are presented in Table 2.

Ionic gelation, despite being one of the most commonly used techniques due to its simplicity and mild conditions, suffers from poor reproducibility when scaled up for industrial production. This limitation stems primarily from its high sensitivity to variations in pH and ionic strength (Sacco et al., 2021) Recent studies suggest that hybrid approaches, such as microfluidic-assisted gelation, could potentially improve nanoparticle uniformity, though these methods come with increased equipment costs and operational complexity that may limit their practical implementation (Li et al., 2025).

The emulsion evaporation method, while effective for encapsulating hydrophobic agrochemicals, presents environmental concerns through its reliance on organic solvents like dichloromethane in PLGA systems. This dependence contradicts the fundamental principles of green chemistry that motivate the development of polysaccharide-based delivery systems. Emerging alternatives such as supercritical CO_2-based techniques show promise in addressing this issue, though their energy requirements and scalability need further evaluation (Sakkaravarthy et al., 2025).

Perhaps most fundamentally, the inherent variability in polysaccharide purity poses significant challenges to consistent nanoparticle production. Commercial chitosan, for instance, exhibits batch-to-batch differences in degree of deacetylation and molecular weight that directly impact nanoparticle stability and performance. While the use of crude algal extracts has been proposed as a cost-effective alternative, these materials require rigorous standardization and quality control measures before they can be reliably employed in agricultural applications (Rampim et al., 2025).

These synthesis challenges present not just obstacles, but opportunities for innovation. Addressing them will require interdisciplinary collaboration between polymer chemists, process engineers, and agricultural scientists to develop scalable, environmentally benign, and economically viable production methods for polysaccharide-based nanoformulations.

4. Mechanistic insights into polymer nanoparticles

Understanding the mechanistic behaviour of polymer-based nanoparticles is crucial to optimizing their performance in agricultural systems. These mechanisms govern encapsulation, release dynamics, systemic mobility, and environmental interaction, which collectively determine efficacy and sustainability.

4.1. PEGylation and surface functionalization

Polyethylene glycol (PEG) is commonly used to modify nanoparticle surfaces (PEGylation), imparting hydrophilicity, steric hindrance, and biocompatibility (Abhinay and Kumar, 2024). PEGylation enhances nanoparticle stability by preventing aggregation and shielding against enzymatic degradation (Fig. 2a). In agricultural contexts, PEGylated nanoparticles exhibit prolonged soil residence, slower nutrient or pesticide release, and minimized burst release effects (Nazeer et al., 2023). Del Prado-Audelo et al. (2022) showed that PEG-modified PLGA nanoparticles enhanced the systemic mobility of agrochemicals and reduced their premature release (Del Prado-Audelo et al., 2022). Similarly, Memarizadeh et al. (2014) demonstrated that ABA block copolymers (PEG-PCA) loaded with imidacloprid offered high insecticidal efficiency with significantly lower LC_{50} values (Memarizadeh et al., 2014).

While PEGylation reduces nanoparticle aggregation, its non-biodegradability risks soil accumulation. Recent alternatives include lignin-based coatings (Shu et al., 2021), though adhesion to polysaccharides remains challenging.

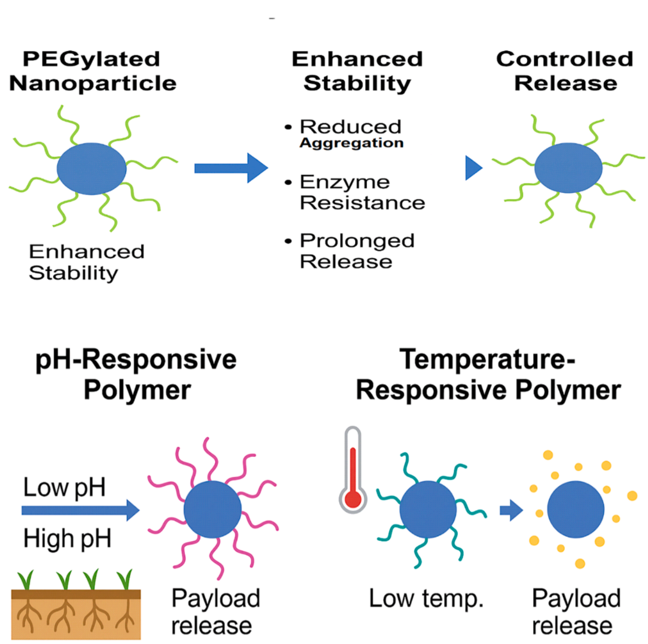


Fig. 2. a: PEGylation mechanism. **b:** Responsive polymer behaviour mechanism. (These figures were independently designed and created using Microsoft PowerPoint and Inkscape).

4.2. Responsive polymer behaviour

Responsive polymers go through physicochemical alterations in reaction to environmental cues like pH, temperature, ionic strength, or enzymatic activity. These behaviours are harnessed for on-demand agrochemical delivery (Fig. 2b). Examples of some stimuli-responsive polymers are presented in Table 3.

a. pH-Responsive Polymers: Polymers like poly(methacrylic acid) or carboxymethyl chitosan deliver their payload in reaction to pH changes in rhizosphere (Singh & Kumar, 2023). Pereira et al. (2017) formulated pH-sensitive chitosan/γ-polyglutamic acid nanoparticles that released over 69 % of their payload at pH 8.5.

b. Temperature-Responsive Polymers: Poly(N-isopropylacrylamide) (PNIPAm) demonstrates lower critical solution temperature (LCST) behaviour, allowing temperature-triggered release. Xu et al. (2020) used PNIPAm-capped nanoparticles to achieve temperature-controlled delivery of active compounds under field-relevant thermal conditions (Xu et al., 2020). pH/temperature-responsive systems often fail in field conditions due to soil heterogeneity. For instance, PNIPAm's LCST (∼32 °C) is rarely reached in temperate soils, necessitating polymers with tunable transition thresholds

4.3. Controlled degradation and release kinetics

Polymer degradation via hydrolysis, enzymatic cleavage, or environmental breakdown is a central mechanism for sustained release.

a. Hydrolytic Degradation: PLA and PLGA degrade via ester bond hydrolysis, with rates tunable by copolymer ratios and molecular weights. Suraphan et al. (2020) showed that co-delivery nanoparticles composed of PLA enabled gradual nutrient availability over several weeks [Fig. 3 (a)].

b. Enzyme-Mediated Degradation: Natural polymers like chitosan or alginate are susceptible to soil enzyme activity (da Rocha et al., 2024). Mawale & Giridhar. (2024) demonstrated that chitosan nanoparticle degradation matched plant uptake windows, enhancing nutrient utilization [Fig. 3 (b)].

c. Crosslinking Density: Strongly crosslinked matrices release actives more slowly. The work by Kumar et al. (2015) is representative of the early wave of research focusing on ionic gelation, a technique that remains popular due to its simplicity but, as discussed in Section 3.7, faces significant reproducibility challenges at scale [Fig. 3 (c)].

4.4. Diffusion and swelling mechanisms

Hydrophilic polymer matrices (e.g., starch-based hydrogels) swell in moist soils, creating diffusion channels for agrochemical release (Fig. 4a). The rate depends on polymer molecular structure, soil moisture content, and ionic strength (Maksimova, Shchetko, & Maksimov, 2023). Grillo, Rosa, and Fraceto (2014) found that nanocapsules made from poly(ε-caprolactone) released atrazine more gradually than nanospheres due to limited swelling and diffusion through the dense shell. Bortolin et al. (2013) demonstrated similar control in fertilizer release using methylcellulose matrices

4.5. Encapsulation mechanism and stability

The encapsulation technique, emulsion, nanoprecipitation, or spray-drying, affects particle morphology, porosity, and encapsulation efficiency, which ultimately shape release kinetics and field stability (Fig. 4 b). High encapsulation efficiency ensures prolonged bioavailability and reduces environmental contamination (Mondéjar-López et al., 2024). Campos et al. (2015) encapsulated carbendazim in chitosan-pectin nanoparticles and observed improved antifungal performance with lower environmental toxicity compared to non-encapsulated formulations.

Table 3
Stimuli-responsive natural polymer formulations.

Polymer	Stimulus	Agrochemical	Response mechanism	Application	References
Chitosan/γ-PGA	pH	Nematicide	Swelling at high pH (69.5 % release at pH 8.5)	Targeted delivery in alkaline soils	Liang et al., 2018
Carboxymethyl Chitosan	Light	Methomyl (insecticide)	UV-triggered bond cleavage	On-demand pest control	Sun et al., 2014
Alginate/Silica	pH	Herbicide	Faster release at higher pH	Weed management in variable soils	Gao et al., 2019
PNIPAm-PDA	Temperature	General pesticides	Thermal-responsive polymer collapse	Field-temperature-dependent release	Xu et al., 2017

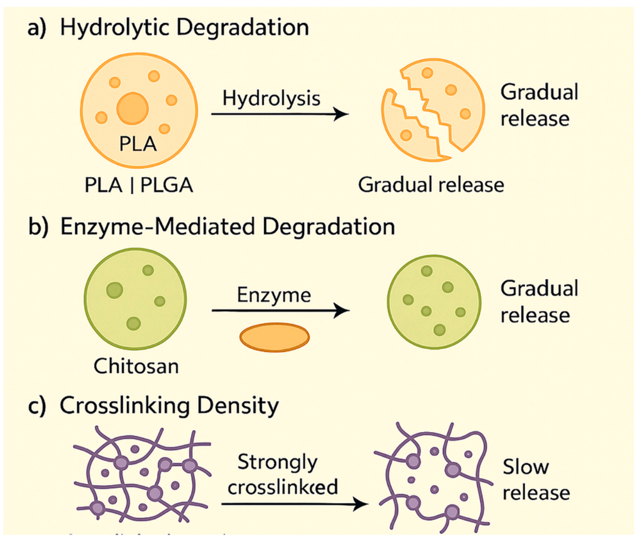


Fig. 3. a, b, c: Controlled degradation and release kinetics mechanism (These figures were independently designed and created using Microsoft PowerPoint and Inkscape).

4.6. *Comparative performance of polymeric nanocarriers*

While the preceding sections have detailed the synthesis, mechanisms, and applications of polysaccharide-based nanoparticles in isolation, a critical, comparative analysis is essential to translate these findings into practical design principles. This subsection synthesizes the literature to evaluate key performance metrics, including encapsulation efficiency, release kinetics, and degradation profiles, across the most prominent polymer systems. This comparative framework moves beyond descriptive summary to identify clear trade-offs, synergies, and data-driven guidelines for selecting nanocarriers for specific agricultural applications.

The performance of any nano-formulation is dictated by the interplay between the active ingredient (A.I.), the polymer carrier, and the synthesis method. A critical first step is matching the hydrophobicity of the A.I. with an appropriate encapsulation strategy. As summarized in Table 4, ionic gelation excels for hydrophilic compounds like fertilizers (e.g., urea, nitrates), achieving high encapsulation efficiency (>85 %) through water-based, eco-friendly processes. Conversely, hydrophobic A.I.s, which constitute most pesticides (e.g., imidacloprid, atrazine) and fungicides, require alternative methods. Emulsion solvent evaporation, despite its environmental drawbacks from organic solvent use, remains indispensable for these compounds, routinely achieving efficiencies >90 % by creating a compatible oil-core environment for the water-repelling active ingredient.

Beyond encapsulation, the temporal dynamics of A.I. release and carrier degradation are paramount for efficacy. The performance data in Fig. 5 provides a visual comparative framework based on consolidated literature trends. The degradation profiles (Fig. 5a) highlight a fundamental design choice: chitosan-TPP systems offer a shorter service life (simulated half-life of ~10 days), ideal for seasonal crops or short-duration pest threats, while alginate-Ca^{2+} carriers provide longer-lasting structural integrity (simulated half-life of ~23 days), suitable for perennial systems or extended nutrient delivery.

This degradation rate directly governs release kinetics (Fig. 5b). Starch-based nanoparticles, with their high swelling capacity, exhibit a significant burst release (>50 % within 24 h), beneficial for immediate pest knockdown but potentially wasteful and environmentally hazardous for nutrient delivery. In contrast, chitosan and alginate provide a more linear, sustained release profile, crucial for maintaining effective dosages, improving nutrient use efficiency, and minimizing leaching and environmental contamination. The choice of polymer thus directly influences application frequency and environmental impact.

5. Stability and quality of polymer nanoparticles

The stability and quality of polymer nanoparticles are crucial factors that determine their effectiveness as carriers for nano fertilizers and nanopesticides. Stability refers to potential of nanoparticles to maintain structural reliability, size, alongside functionality under various environmental conditions, while quality encompasses the consistency, purity, and performance of the nanoparticles.

5.1. *Physicochemical stability*

Physicochemical stability is essential for ensuring that polymer nanoparticles retain their size, shape, and encapsulated contents during storage, handling, and application.

-Factors Affecting Physicochemical Stability:

- Polymer Composition: Chemical structure of polymer, inclusive of hydrophilicity, molecular weight, as well as degree of cross-linking, plays a pivotal part in determining stability of nanoparticles. To illustrate, polymers with high crystallinity and cross-linking tend to form more stable nanoparticles (Zhang, et al., 2014).
- Environmental Conditions: Exposure to light, temperature fluctuations, and pH changes can influence the stability of polymer nanoparticles. Thus, nanoparticles fashioned out from poly(lactic-co-glycolic acid) (PLGA) may hydrolyse under acidic or basic conditions, leading to premature degradation (Wang et al., 2022).
- Encapsulation Efficiency: The method and efficiency of encapsulating active ingredients (e.g., fertilizers or pesticides) within the nanoparticles influence their stability. Poorly encapsulated nanoparticles may release their contents prematurely, reducing their effectiveness (Castro et al., 2022).

Stable polymer nanoparticles ensure that the encapsulated agrochemicals are delivered to the target site at the desired rate (Del Prado-Audelo et al., 2022). For example, nanoparticles that degrade too quickly may release fertilizers too early, leading to nutrient loss and reduced plant uptake. Conversely, overly stable nanoparticles may release their contents too slowly, limiting their efficacy.

5.2. *Colloidal stability*

Colloidal stability is the ability of polymer nanoparticles to remain

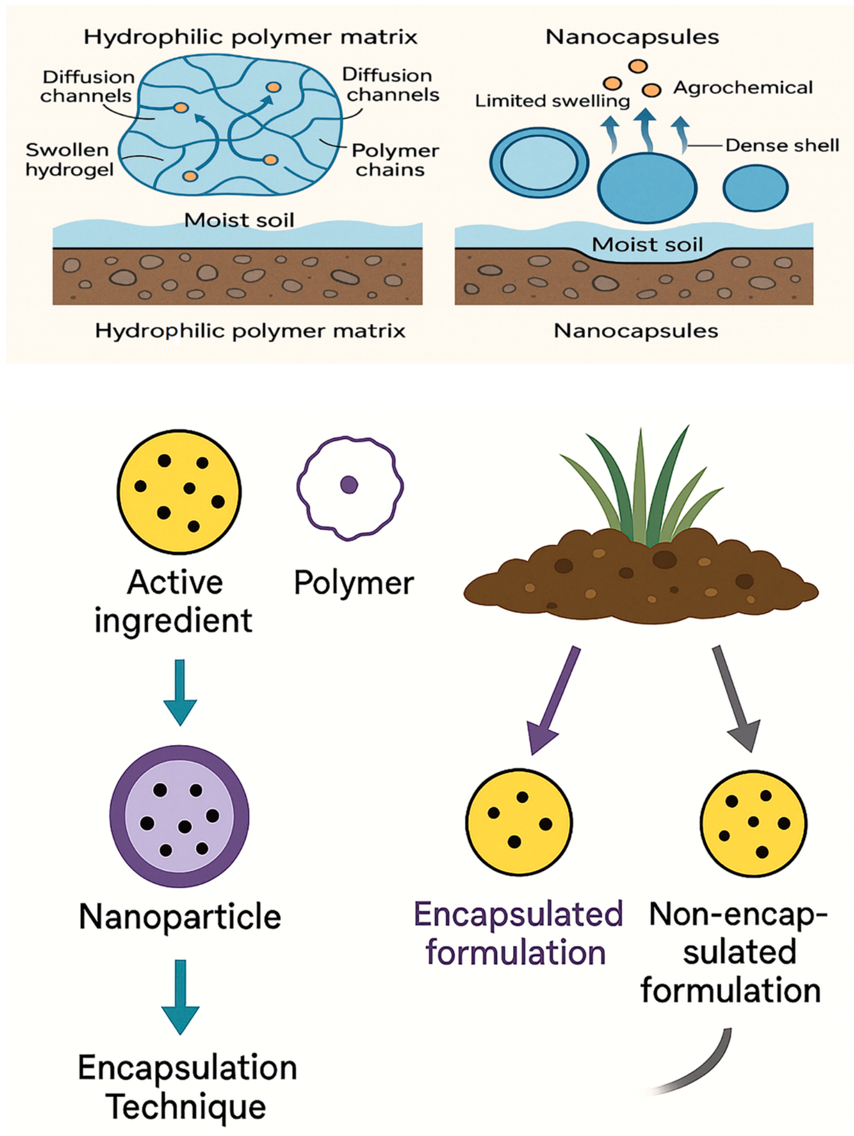


Fig. 4. a: Diffusion and swelling mechanisms. **b:** Encapsulation mechanism and stability. (These figures were independently designed and created using Microsoft PowerPoint and Inkscape).

Table 4
Critical appraisal of selected case studies on polysaccharide-based nanoformulations.

References	Polymer systems	Active ingredient (A.I.)	Key results	Encapsulation efficiency	Critical analysis / limitations
Kumar et al. (2015)	Chitosan-Alginate	Acetamiprid (insecticide)	Extended release to 36h, reduced leaching	85 %	**Strength:** Excellent sustained release. **Limitation:** Lab-scale only; no field validation.
Grillo, Rosa, and Fraceto (2014)	PCL	Atrazine (herbicide)	10x dose reduction, reduced toxicity	>90 %	**Strength:** High efficacy & reduced env. impact. **Limitation:** Use of organic solvent (DCM).
Pereira et al. (2017)	Chitosan/γ-PGA	Gibberellic acid (PGR)	Improved plant growth, pH-responsive release	78 %	**Strength:** Smart release mechanism. **Limitation:** Complex synthesis may hinder scalability.
Wu and Liu (2008)	Chitosan-based hydrogel	NPK Fertilizer	75 % release in 30 days, improved water retention	N/R	**Strength:** Dual function (release + water retention). **Limitation:** Encapsulation efficiency not reported.

uniformly dispersed in a medium without aggregation or precipitation.
- Factors Affecting Colloidal Stability:

- Surface Charge: The surface charge of nanoparticles, typically measured by zeta potential, influences their ability to repel each other and remain dispersed. Nanoparticles with high zeta capability (either positive or negative) are likely to remain stable in suspension (Midekessa et al., 2020).
- Surfactants and Stabilizers: The use of surfactants and stabilizers during nanoparticle synthesis can enhance colloidal stability by preventing aggregation. As an illustration, polyethylene glycol (PEG) is recurrently used to coat nanoparticles, providing steric stabilization (Gref et al., 2012).

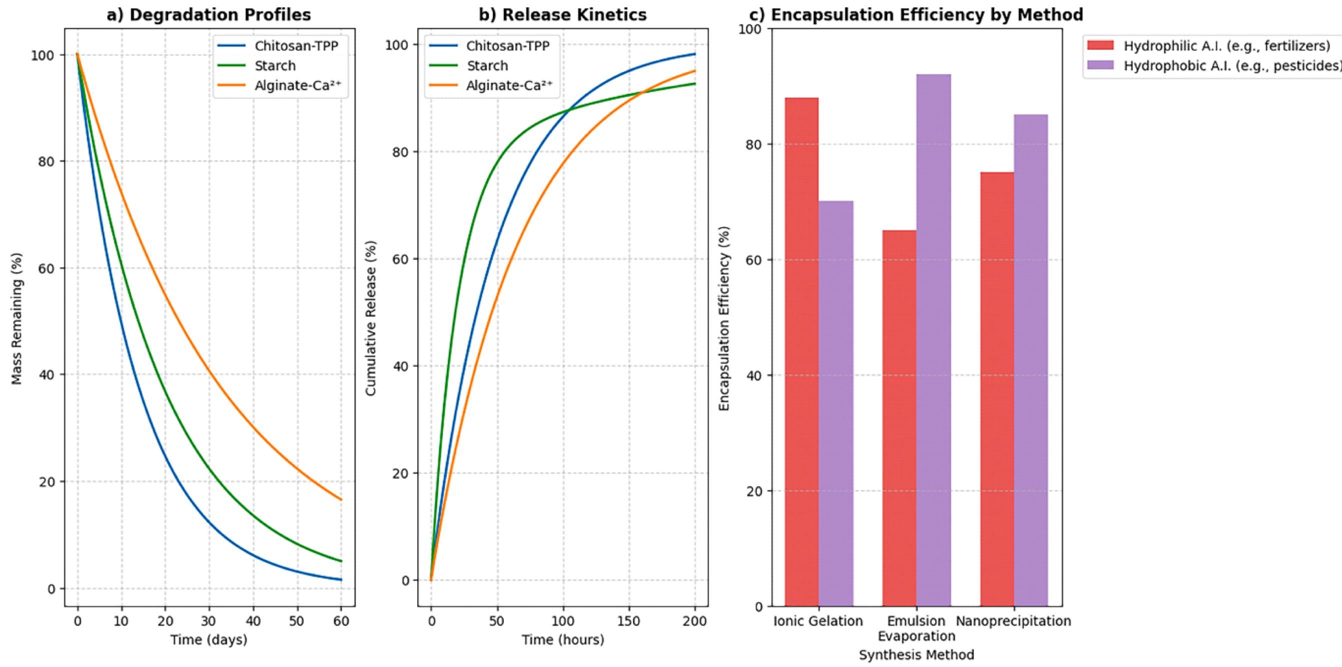


Fig. 5. Panel diagram summarizing representative case studies of polysaccharide-based nanocarriers. (a) Soil degradation profiles. (b) release kinetics of a model active ingredient. (c) encapsulation efficiency across different polymer formulations. Data are redrawn and adapted from published studies (Kumar et al. (2015), Grillo, Rosa, and Fraceto (2014), and Pereira et al. (2017) to illustrate comparative performance. This Fig. integrates encapsulation efficiency, degradation behavior, and release trends to highlight key findings across case studies relevant to agricultural applications. (Figures by authors using Matplotlib 3.10.0). However, this analysis also reveals significant gaps in the current research landscape. While chitosan is the most extensively studied polymer, its instability in acidic soils remains a major constraint for widespread field application. Conversely, cellulose nanocrystals, despite their abundance, superior mechanical properties, and potential for slow release remain critically underexplored (Section 9). Furthermore, the literature is heavily biased toward laboratory-scale proof-of-concept studies. A severe deficit exists in multi-season, field-scale trials that quantitatively assess the long-term agronomic efficacy, soil health impact, and ultimate environmental fate of these materials. The encapsulation efficiency of many commercial fertilizers in polysaccharide matrices also remains poorly reported and standardized, hindering comparative analysis and reproducibility.

- Ionic Strength: Ionic strength of surrounding medium can affect stability of nanoparticles (Lin & Wiesner, 2012). High ionic strength may reduce the electrostatic repulsion between particles, leading to aggregation.

Colloidal stability is particularly important for nanoparticles used in foliar applications, where they must remain stable in solution for uniform distribution on plant surfaces (Beckers et al., 2021). Aggregated nanoparticles may clog sprayers or settle out of suspension, reducing their effectiveness.

5.3. *Chemical stability*

Chemical stability refers to the resistance of polymer nanoparticles to chemical reactions that could alter their structure or functionality.

- Factors Affecting Chemical Stability:

- Oxidation and Hydrolysis: Polymers susceptible to oxidation or hydrolysis, such as polyesters, may degrade when exposed to oxygen, moisture, or reactive species. This can lead to the collapse of polymer matrix and liberation of embedded agrochemicals.
- Cross-Linking: Cross-linked polymers tend to have higher chemical stability due to their robust network structure. For example, cross-linked poly (acrylic acid) hydrogels are resistant to hydrolysis, making them suitable for controlled-release applications (Song & Wang, 2020).
- Protective Coatings: Applying protective coatings, such as PEGylation, can enhance the chemical stability of nanoparticles by shielding them from reactive species and environmental conditions (Shi et al., 2021).

Chemical stability is vital for ensuring that polymer nanoparticles maintain their integrity until they reach the target site. In the case of nano-fertilizers, chemically stable nanoparticles can prevent the premature release of nutrients, ensuring that they are available to plants when needed (Jakhar et al., 2022).

5.4. *Biological stability*

Biological stability pertains to the ability of polymer nanoparticles to resist degradation by biological agents, such as enzymes or microorganisms.

- Factors Affecting Biological Stability:

5.4.1. *Biodegradability*

Polymers like PLGA are constructed to degrade over time through hydrolysis of their ester bonds. Rate of biodegradation can be controlled by modifying polymer composition and molecular weight. However, overly rapid degradation may reduce the effectiveness of the nanoparticles.

5.4.2. *Enzymatic degradation*

Enzymes present in the soil or on plant surfaces can degrade polymer nanoparticles. The susceptibility of the polymer to enzymatic attack depends on its chemical structure and the existence of specific functional groups.

5.4.3. *Microbial interactions*

Soil microorganisms can interact with polymer nanoparticles, conceivably occasioning their degradation. The impact of microbial activity on nanoparticle stability hinges on factors including the polymer type, surface modification, as well as environmental conditions

(Levard et al., 2012).

While some level of biodegradability is desirable for environmental sustainability, polymer nanoparticles must remain stable long enough to deliver their active ingredients effectively. Balancing biological stability while, need for controlled degradation is key to developing successful agricultural nanoparticles (Singh et al., 2021).

5.5. Quality control and characterization

Ensuring the quality of polymer nanoparticles involves rigorous characterization and testing to confirm that they meet the required specifications for size, distribution, encapsulation efficiency, and stability (Marques & Segundo, 2024). High-quality polymer nanoparticles with consistent characteristics are essential for achieving reliable and reproducible results in agricultural applications. Effective quality control ensures that the nanoparticles perform as expected, providing targeted and controlled agrochemical delivery (An et al., 2022). Stability alongside the quality of polymer nanoparticles is fundamental to their success as delivery systems for nano-fertilizers and nano-pesticides (Babu et al., 2022). By carefully selecting polymer types, optimizing synthesis methods, and implementing rigorous quality control measures, researchers can develop stable, efficient, and environmentally friendly nanoparticles. These considerations are critical for advancing the usage of polymer-based nanoparticles in sustainable agriculture, where consistent performance alongside controlled delivery of potent ingredients is key to augmenting crop yields and lessening environmental fallouts.

Development of techniques for testing with optimal standards, plus the assessment of risk associated with nano use, comes with complexity. Nano-polymer behaviour in the environment is premised on surface characteristics, size, and shape. These are good pointers to any prospective associated risk. Thus, unforeseen outcomes call for applicable moderation and observance efforts in the environment. Instituting a general worldwide benchmark including guidelines via cross-country accord will ensure accountable production of high-quality nanomaterials for agricultural use (Abdul Wahab et al., 2024).

6. Reaction of polymers in soil

Understanding adaptability and reactions of polymers in soil is critical for assessing environmental influence and efficacy of polymer-based nanoparticles employed in agriculture, particularly in formulation of nano-fertilizers and nano-pesticides. Interaction of these polymers with soil components influences their stability, degradation, and the release of encapsulated agrochemicals.

6.1. Polymer degradation in soil

This is a complex process determined by sundry environmental components, including temperature, moisture, pH, and existence of microorganisms. The degradation rate and mechanism are premised on chemical structure of polymer, and its molecular weight, alongside the presence of additives or fillers. Polymer components lose cohesion by exercise of microorganisms such as bacteria, fungi, and algae. This process involves enzymatic hydrolysis, oxidation, and other microbial activities that cleave polymer chains into smaller fragments, eventually transforming them into carbon dioxide, water, and biomass (Pathak & Navneet, 2017). The biodegradability of a polymer is influenced by its chemical composition. For example, natural polymers like chitosan, alginate, and starch are readily biodegradable, while synthetic polymers like PLA and PLGA degrade more slowly depending on their crystallinity and molecular weight. Biodegradable polymers are exceptionally valuable in agricultural utilization because they minimize the accumulation of persistent plastic residues in soil. Controlled degradation of these polymers ensures that they release their active ingredients over time, matching the crop's nutrient or pesticide requirements (Serrano-Ruiz et al., 2021).

a. Photodegradation: Photodegradation exist when polymers are exposed to ultraviolet (UV) radiation, leading to the breakdown of polymer chains through photo-oxidation. This process can initiate the degradation of polymers even before they are introduced into the soil. Polymers with chromophoric groups or unsaturated bonds are more susceptible to photodegradation. However, soil coverage often limits the exposure of polymers to sunlight, reducing the significance of this process in soil environments. While photodegradation is less significant in soil due to limited light penetration, it can play a role in the pre-application phase or surface-exposed agricultural films and coatings. Ensuring that polymers degraded under UV exposure can help in reducing plastic waste in open-field conditions (Rizzarelli et al., 2021).

b. Chemical Degradation: Chemical degradation in soil involves the hydrolysis, oxidation, or other chemical reactions that break down polymer chains. Hydrolysis is particularly relevant for polymers with ester or amide bonds, such as PLA and PLGA, which degrade through the cleavage of these bonds in presence of water. Soil pH in conjunction with catalysts like metal ions can accelerate chemical degradation. Acidic or basic conditions can enhance hydrolysis, while oxidative degradation is facilitated by the presence of oxygen or other reactive species. Chemical degradation contributes to the progressive malfunction of polymer nanoparticles, ensuring controlled release of agrochemicals. Understanding the chemical stability of polymers in different soil types is integral for predicting their behaviour and optimizing their use in agriculture (Singh et al., 2020).

-Interaction with Soil Components: The interaction of polymers with soil particles, organic matter, and microorganisms influences their behaviours and effectiveness as carriers for fertilizers and pesticides.

c. Adsorption and Desorption: Polymers can adsorb onto soil particles, such as clay minerals and organic matter, via physical adsorption or chemical bonding. Degree of adsorption is reliant on the polymer's surface properties, namely charge and hydrophilicity, and the nature of soil components. Polymers with a high affinity for soil particles may experience reduced mobility, while those with low adsorption may remain more available for plant uptake or microbial degradation. Desorption, the reverse process, is determined by soil moisture, pH, and ionic strength. Adsorption to soil particles can affect the bioavailability of encapsulated agrochemicals, influencing their release profile and effectiveness. In the case of nano-pesticides, strong adsorption may reduce leaching but also limit the reach of the active ingredients to target pests (Alimi et al., 2018).

6.2. Soil microorganisms

Soil microorganisms act a dual role in interacting with polymers they can contribute to the biodegradation of polymers, and they can also be distressed by presence of polymer nanoparticles. The extent of microbial degradation depends on availability of biodegradable polymers and activity of microbial community. Polymers that do not degrade may accumulate, potentially affecting soil health and microbial diversity. Interaction of polymers with soil microorganisms is vital for ensuring that biodegradation occurs at a controlled rate. Understanding these interactions helps in designing polymer nanoparticles that are compatible with soil ecosystem and do not disrupt microbial activity (Lim & Thian, 2022).

6.3. Impact on soil structure

Polymers, particularly those used as soil conditioners or mulch films, can affect soil structure by altering its porosity, water holding, and aeration. Physical presence of polymer nanoparticles in soil influence aggregation of soil particles. The impact on soil structure hinges on concentration and apportionment of polymers in soil. High concentrations of non-degradable polymers may lead to soil compaction or reduced permeability, while biodegradable polymers may improve soil structure over time. The effect of polymers on soil structure is an important consideration in sustainable agriculture. Polymers that enhance soil structure can improve water retention and root penetration, while those that negatively impact soil properties should be avoided or used with caution (Tian et al., 2019).

7. Preparation plus delivery mechanism of polymer-based pesticide and fertilizer

7.1. Nonbonding packing and encapsulation

This is a technique for converting nutrient ratio levels and limiting material waste. Coated polymeric materials are employed in controlled release mechanisms for fertilizer and pesticide release (Fabiyi et al., 2020; Sampathkumar et al., 2020). Embedded pesticides or fertilizers are solubilized, and the quantity used at the target site is limited, thus checking issues that may arise from unchecked delivery systems. Derivatives of starch, such as cyclodextrins with hydrophobic inner lining and hydrophilic outer cover, give a superb complexation in water medium with minimal soluble molecules (Sampathkumar et al., 2020). Essential oils with insecticidal characteristics have been delivered with the aid of cyclodextrins (Campos et al., 2018). The shelf life of the volatile compounds was extended in the environment. Similarly, another set of essential oil was encapsulated with zein, this prevented compound degradation, disallowed resistance development in target organisms, minimised lethal concentration, while compound release time was extended (Oliveira et al., 2019). A combination of chitosan and polyelectrolyte plus alginate was prepared to arrest quick release of acetamiprid active ingredient, the polymer combination extended release up to 36 hours, a length of time that cannot be achieved via conventional means of application (Kumar et al., 2015). Hydroxyapatite-urea cast nanoparticles prepared by Kottegoda et al. (2011) with controlled technique method employed cellulose and lignin in stem of wood to serve as nano fertilizer receptacle. The composite maitained release of fertlizer sustainably for over a 60 day period. Field trials with rice plants using nano hybrids of hydroxyapatite-urea composite under controlled technique saw yield increase of rice, while only 50 % quantity of fertilizer in relation to conventional method was used (Kottegoda et al., 2017).

Adak et al. (2012) in their report on controlled release preparations used aggregate strings of combined polymer of amphiphilic nature prepared from PEG-b-poly(aliphatic acid) with controlled release mechanism. This was employed for imidacloprid delivery, using PEG of different units that served as water loving components while aliphatic acids are headgroup of hydrophobic nature. They discovered that rate of release was gradual in comparison with ready-made formulations. A preparation involving poly(lactic-co-glycolic acid) diblock of amphiphilic nature whose size ranges between 6–10 μm revealed that using dispenser of micro size significantly minimised quantity of pesticide needed (Meyer et al., 2015). The utilisation of combined triblock polymers has also been documented. Combined polymers consisting of poly (citric acid) (PCA) serving as A block dendrimer and linear B block made of poly(ethylene glycol) (PEG) thus forming ABA linear triblock. The combined trio polymer self-built nanoparticles were packed with imidacloprid via hydrophobic means. The preparation led to notably high mortality of *Glyphodes pyloalis* larvae with significantly minimal 50 % lethal concentration as opposed to regular pesticide preparation (Memarizadeh et al., 2014).

Pesticide discharge rate in the controlled discharge system is a function of polymer type. For example, cross-linker type can remarkably influence release rate characteristics of polymer matrices. Cross-linker modifications altered balance of hydrophilicity or hydrophobicity, which in turn impacts release rate (Urbano-Juan et al., 2019). To achieve sustainable release of atrazine, multiple dissimilar microparticles of biodegradable nature were prepared via solvent evaporation/emulsion method. The hydrophobic main materials used for packing were poly (hydroxybutyrate) (PHB) and poly-(hydroxybutyrate-valerate) (PHBV). For solubility in aqueous state poly(vinyl alcohol) served as a homogenizer. The authors noted a high rate of discharge in PHBV relative to PHB (Grillo et al., 2011). Poly(ε-caprolactone) nanospheres and nanocapsules were made via oil in water singly with polymer and a blend of triglyceride capric surfactant, respectively. The nanocapsules were not as stable as nanospheres. The two were packed with atrazine by encapsulation, and both had very high efficiency, with long discharge time and were significantly less toxic than regular atrazine (Pereira, Grillo, Mello, Rosa, & Fraceto, 2014).

7.2. Bonding polymers

To guide against unstable situations after encapsulation and other occurrences such as untimely pesticide/fertilizer discharge stemming from packaging deficiencies, a pesticide and polymer conjugate mode of preparation was designed. Preparation of nanopolymer via copolymerization was carried out by Shang et al. (2013) by employing the polymerization emulsion method. Monomer of N-acylated emamectin benzoate blended with butyl acrylate plus methyl methacrylate. Photostability was achieved, and pesticidal action of the polymer conjugate was commendable. Similarly, herbicide conjugation with polymers was prepared by Kwiecien et al. (2018), the conjugated matrices presented a gradual discharge, and weeds were removed totally.

7.3. Responsive polymers

Progressive development in nanotechnology brought about smart polymers that reacts and regulates relative to environmental factors. Blending between chitosan and γ-polyglutamic acid complex, plus nonbonding cross-connect with TPP hinged on electrostatic interplay was prepared by Liang et al. (2018), to function as pH reactive system in nematicide delivery. Stability was displayed with low pH level achieved through strong electrostatic synergy displayed by carboxyl functional groups contained in γ-polyglutamic acid which invariably reduces with high pH level. Without reliance on pH, release rate was 20 % and at pH 8.5, 69.5 % of content was released (Fig. 6a). In the same vein, Sun et al. (2014) prepared pH reliant release mechanism for armyworm larvae management. The procedure involved encapsulation of methomyl in hydrophilic state in capsule of photo-cross-linked azidobenzaldehyde-operationalized amphiphilic carboxymethyl chitosan, complete linking was achieved through irradiation of membrane with UV. Nanocapsule efficiency was 90 % with pH level 4. This was premised on existing hydrogen bond between the materials used. However, with increase in pH level to 6, the bond gave way and controlled rate of insecticide release was accomplished (Fig. 6b). Conjugation of functional groups of 2-nitrobenzyl with carboxymethyl chitosan premised on light sensation. Without element of light, release was super controlled, while sustainable release was maintained all through an 8-hour period during light exposure and pH level 7 (Ye et al., 2015). Furthermore, another pH reliant release mechanism prepared by Gao et al. (2019) was premised on silica NPs while poly(glycidyl methacrylate-acrylic acid) served as copolymer. The release rate profile increased with higher pH level. A temperature reliant carrier was formulated by Xu et al. (2017). The temperature reactive nature of poly(N-isopropylacrylamide) (PNIPAm)-capped poly(dopamine) (PDA) allowed gradual content delivery with temperature increase.

7.4. Foliar application

Foliar route has been employed extensively to manage diverse diseases of plants, and chitosan, a wholesome polycarbohydrate, has played a great role expansively in this regard. Enhancement of growth in okro plants with chitosan treatments at 120 ppm was detailed by Muñoz-Bonilla et al. (2013). Chitosan nanoparticles applied to leaves of 15-day old *Withania somnifera* (L) seedlings at 2.5 mg/mL^{-1} acted as

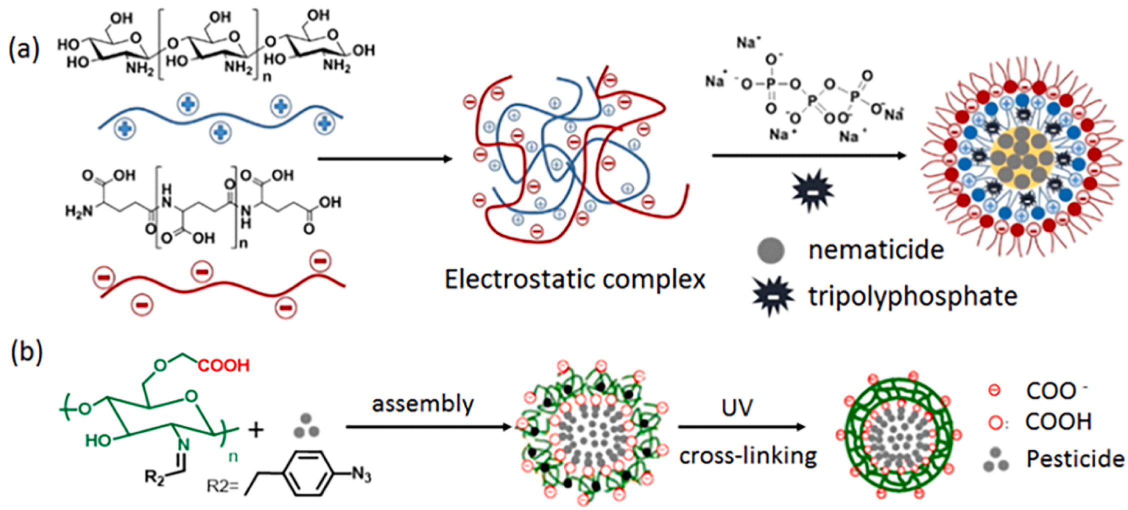


Fig. 6. pH-reliant polymers **(a):** Formation of nanoparticles by electrostatic bonding. Culled from Liang et al. 2018. [Licence no: 5975360939535] **(b):** Process of methomyl packing cross-string nanoparticles. Culled from Sun et al., 2014. [Licence no:5975370171762].

growth enhancer. Parameters such as leaf breadth, area, length, and height of plant all increased significantly (Jacob et al., 2023). In a different study, foliar use of chitosan impacted resistance on barley plants to *Blumeria graminis* f. sp. hordei, while infection was minimised up to 55.5 %. Further, an increase in water use efficiency was observed with chitosan foliar application on pepper plants up to 43 % while yield and plant biomass were unaffected (Bittelli et al., 2001). Comparably, Sajid et al. (2020) reported potency of chitosan 1 % foliar treatment on peach trees. Incidence of disease was significantly limited, with an increase in fruit weight. El Amerany et al. (2020) in their research concluded that foliar treatment of tomato plants influenced flower and biomass growth positively.

Nanosilicon embedded in tripolyphosphate (TPP) chitosan protected wheat plants against salt-induced stress via foliar application. There was a balance in root and leaf H_2O_2 as opposed to untreated plants under stress of excess salt (Hajihashemi et al., 2022). The salt stress alleviation capacity of chitosan was also evaluated by Attia et al. (2021) on tomato plants. The researchers discovered that chitosan ameliorated salt stress effectively worked with a significant increase in antioxidant factors, osmoprotectant elements, and photosynthetic characters. Likewise, Farouk & Ramadan (2012) established that chitosan foliar treatment on cowpea plants prevented damage to water-stressed cowpea plants. There was a substantial increase in quantity and quality of yield, thus subduing the effect of water stress. Finally, Mondal et al. (2013) noticed that the morphological, physiological, and harvest index of maize plants were significantly enhanced with application of chitosan via foliar route. Seed yield was noted to be high at 125 ppm treatment.

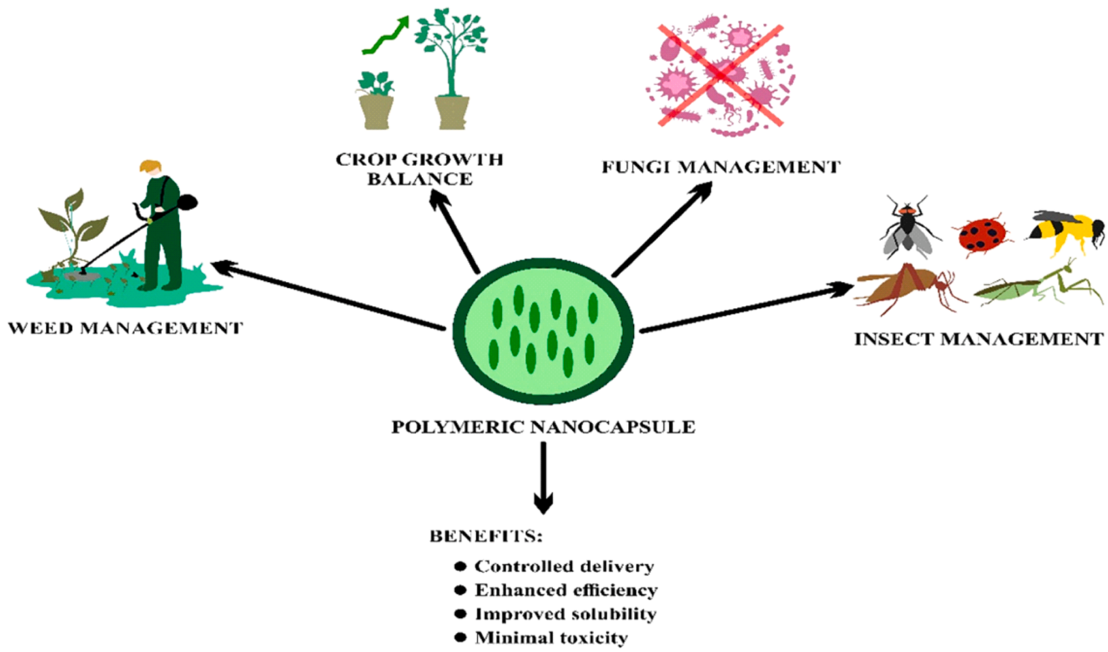
Most delivery systems rely on passive diffusion or degradation-triggered release, but the temporal synchronization between release rate and plant uptake windows remains underexplored. Moreover, encapsulation methods lack standardization across studies, making comparative assessments difficult. Future work should prioritize dynamic, stimuli-responsive systems tuned to crop phenology and soil conditions.

8. Nanopolymer application in agriculture

Several classes of pesticides could be loaded into polymeric materials (Fig. 7a). Many reports of agrochemical encapsulations abound, as summarized in Table 5. The threat of plant pathogenic diseases is alarming, with sizeable crop loss; in some cases, 90 % of crops are damaged (Yamini, Singh, Antar, & El Sabagh, 2025). To inhibit fungi penetration and entry into crop plants, fungicides are applied, and these applications could be greatly enhanced by nano material encapsulation for good efficiency. Nano polymers are applicable carriers, and some have the characteristics of killing pests (Kashyap et al., 2015). An illustration of this could be seen in chitosan nanoparticles (NPs), which exhibited antifungal properties on *Fusarium graminearum* by reducing radial mycelial development. Chitosan combined hexaconazole NPs were reported by Kumar et al. (2015) to be more active than a non-nano formulated compound in the management of *Rhizoctonia solani.* The effect of control on non-targeted areas was greatly reduced (Kheiri et al., 2016; Kumar et al., 2015). PCL nano capsules encapsulated tebuconazole and carbendazim exhibited significantly reduced toxicity against treated common bean in comparison with regular fungicides. Carbendazim encapsulated into chitosan-pectin NPs demonstrated higher activity on *Aspergillus parasiticus* and *Fusarium oxysporum* in relation to direct fungicide application. Studies with tomato, maize, and cucumber revealed that NPs loaded with carbendazim did not alter seed germination and root development of test plants (Campos et al., 2015; Sandhya Kumar et al., 2017). *In vitro* inhibitory action of PEG loaded azomethine on *Rhizoctonia solani, Sclerotium rolfsii,* and *Rhizoctonia bataticola* was increased remarkably. Significantly reduced plant mortality was recorded in nano-fungicide-treated mung bean plants as against direct application of regular azomethine (Mondal et al., 2017).

A primary factor of significant importance is the insect group. They contribute immensely to field and storage damage of crops, and this necessitates application of synthetic insecticides. However, the high toxicity of synthetic reactions on non-targets and the need to curtail losses further necessitates carrier media. Encapsulated insecticides have been introduced in place of direct conventional formulations. Polyethylene glycol and poly citric acid (PEG and PCA) were employed in imidacloprid encapsulation into NPs. High mortality of *Glyphodes pyloalis* larvae was recorded; the LC_{50} was minimal in comparison with direct application of insecticides (Memarizadeh et al., 2014). Reports by Sun et al. (2014) on chitosan NPs encapsulated methomyl established that greater efficiency was achieved with enhanced insecticidal action on armyworm larvae as against direct insecticide usage. PEG-encapsulated acephate was discovered to be excellent on *Sitophilus oryzae* through acetylcholinesterase inhibition, larval mortality, and malformation of pupae (Pradhan et al., 2013).

The advantages of nano-polymeric materials have also been employed in encapsulation of bio pesticides. The active principles derived from plants for insecticidal activity are prone to degradation by sunlight. Thus, nano-encapsulation is used to control application of botanical insecticides. Polymeric carriers have been adopted for the delivery of essential oils from *Allium sativum*. High insecticidal performance was noted in *Tribolium castaneum* mortality compared to non-



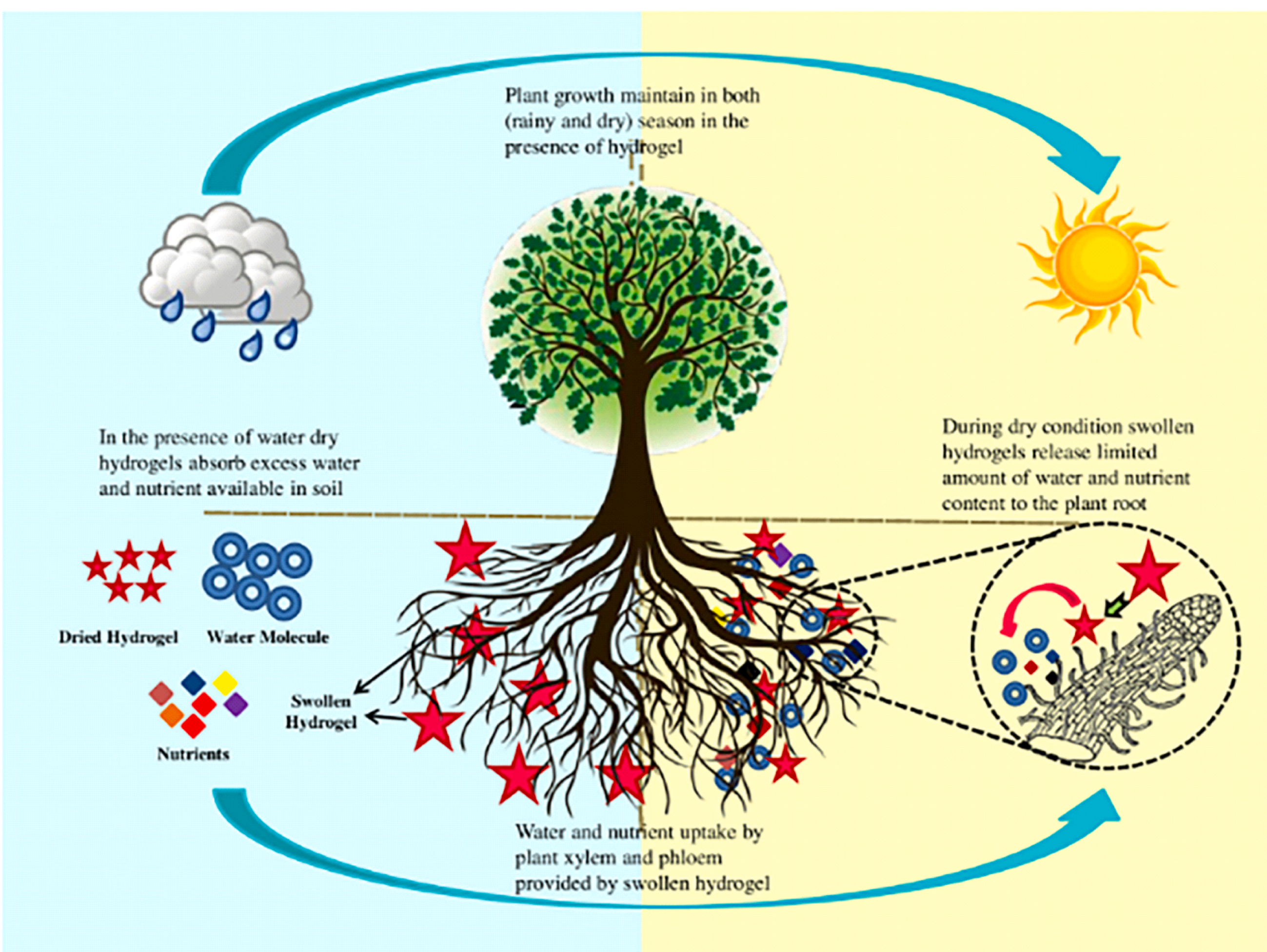


Fig. 7. a: Polymer applications in agriculture. Culled with permission from Springer Nature. Pascoli et al., 2018. [Licence no: 5975540617624]. **7b:** Delineation of hydrogel discharge in wet and dry situations. Culled with permission from Elsevier. Singh et al. 2021. [Licence no: 6012550813322].

Table 5
Natural polymers in nanopesticide formulations.

Polymer	Pesticide	Encapsulation method	Target pest/pathogen	Advantages	References
Chitosan	Imidacloprid	Ionic gelation with alginate	*Martianus dermestoide* (storage pest)	Extended release (8 × slower)	Guan et al., 2008
Alginate	Azadirachtin	Spray drying	General insect pests	UV protection; prolonged efficacy	Jerobin et al., 2012
Starch	Carbofuran	Cross-linked hydrogels	Soil-dwelling pests	Reduced environmental toxicity	Shukla et al., 1991
Pectin	Essential oils	Emulsion solvent evaporation	*Tribolium castaneum* (beetle)	Enhanced stability of volatile compounds	Campos et al., 2018
β-Cyclodextrin	Pyrimethanil	Inclusion complexation	*Fusarium oxysporum* (fungus)	Improved solubility and photostability	Fernandes et al., 2014

nano preparation (Yang, Li, Zhu, & Lei, 2009). In the same vein, EO from *Azadirachta indica, Geranium maculatum,* and *Citrus bergamia* EO were loaded in chitosan and PEG polymeric NPs. Weight of pupal, activity of larvae, and feeding of *Helicoverpa armigera* were significantly arrested, while high effectiveness was achieved against *Culex pipiens* respectively (Duraipandiyan, Baskar, Muthu, Ignacimuthu, & Al-Dhabi, 2015). Further, *A. indica* essential oils were encapsulated with PCL nano carriers for high effectiveness on *Plutella xylostella*, good mortality was achieved relative to direct application (Forim et al., 2013). Decomposition of emamectin benzoate was prevented through formulation with polyacrylate NPs. The emulsion polymerization process conferred photostability on emamectin benzoate.

Aside from insects and fungi, weeds are equally responsible for yield reduction. They compete for nutrients with crops, thus lowering yield. To minimise the negative impact of herbicides in the environment, polymeric carrier mediums have been applied promisingly. Controlled and minimal release of triazines, diuron, paraquat, and a combination of imazapyr and imazapic has remarkably prevented contamination of the environment from various herbicides (Maruyama et al., 2016). The action of herbicides on target plants increased considerably without effect on adjoining crops. Nano-capsule loaded atrazine effectively controlled pre-emergence weeds in *Brassica juncea* in comparison with normal atrazine mode of application (Oliveira et al., 2015). The researchers reported x10 reduction in herbicide atrazine dose with action intact. *Zea mays* physiological parameters were persistently retained with PCL-encapsulated atrazine. Minimal soil sorption, high bioavailability was noticed in PCL encapsulated atrazine relative to normal application (Pereira et al., 2014). PLGA and PEG carrier medium for metolachlor, enhanced solubility. Uptake of *Oryza sativa* and *Digitaria sanguinalis* gave rise to enhanced herbicidal action. Minimal toxicity in human cells was equally recorded (Tong et al., 2017).

Substances for modulating plant growth development, namely auxins, abscisic acid, brassinosteroid, and cytokinins, are prone to quick degradation from high field temperature, making them lose potency fast. Hence, controlled use of growth hormones is also important (Campos et al., 2024; Kah & Hofmann, 2014). Some reports on encapsulation of plant growth hormones include microspheres of chitosan infused with brassinosteroid, gibberellin-chitosan coupling, and O-naphthylacetyl chitosan pair (Quinones, García, Curiel, & Covas, 2010; Liu et al. 2013; Tao et al. 2012). Gibberellic acid encapsulated alginate/chitosan NP carrier for common bean plants was described by Pereira et al. (2017). Photosynthetic pigment area increased with leaf area in relation to conventional hormones.

9. Polysaccharide composite carriers in agriculture

Sundry natural polysaccharide materials serve as carriers for delivery of potent substances in agriculture. This is to regulate use of active substances to the precise quantity needed and minimise pollution. Several techniques of encapsulation are employed, either as single polysaccharide or composite materials as summarised in Table 6. Combination of materials strengthens the matrix and eliminates active ingredient loss to weakened material or premature release of content. Release rate is often dependent on ratio of polysaccharides to cross-linkers, additives or other materials (Roy, Bajpai, & Bajpai, 2009). Enzymes in soil, microorganisms, and moisture are also of significance where active ingredient discharge is concerned. The encapsulated substances may serve as herbicides, insecticides, fungicides, or fertilizers, depending on active principle of the substance in question, while in some cases a single matrix may contain two to three active principles of insecticide/herbicide or insecticide/fertilizer (Johnson, Pepperman, & Selim, 1998). Some polysaccharides serve as pollutant removals and water retainers with the potentiality of remediating pesticide-polluted mediums and alleviating drought stress in crop production systems (Fig. 7b). Soil water holding capability ensures uniform seed germination and conservation of nutrients through crop growth cycle. Polysaccharide introduction into soil has been reported to promote retention of water up to 402 % from 171 % (Woodhouse & Johnson, 1991). Polysaccharide materials like alginate have been implicated in positive crop development, germination enhancement, and root growth

Table 6
Polysaccharide polymers in agriculture.

Herbicides	Polysaccharide polymer	Active ingredient	Action	References
	Bentonite/Alginate	Isoproturon	Minimised herbicide movement in soil	Fernández-Pérez et al., 2000
	Alginate spheres	Chloridazon and metribuzin	Release minimised	Flores Céspedes et al., 2007
	Ethylcellulose matrix	Chlorsulfuron	Leaching managed in calcite/chalky soil	Flores-Cespedes et al., 2009
	Ethylcellulose capsule	Norflurazon	Release minimised	Sopeña et al., 2007
	Chitosan/alginate matrix	Paraquat	Reduction in soil sorption profile	dos Silva et al., 2011
	β- cylodextrin	Chlorpropham	Improved solubility	Ge et al., 2011
	Clay/chitosan	Clopyralid	Removal of herbicide from water	Celis et al., 2012
Insecticides	Chitosan/alginate spheres	Imidacloprid	Release minimised	Guan et al., 2008
	Alginate	Azadirachtin	Release time extended	Jerobin et al., 2012
	Alginate	Azadirachtin	Consistent release	Kulkarni et al., 2000
	Cashew gum/chitosan composite	Essential oil	Release time extended	Paula et al., 2010
	Chitosan matrix	Rotenone	Improved solubility	Lao et al., 2010
Fungicides	Starch hydrogels	Thiram	Water retention	Singh et al., 2007; Singh et al., 2008
	β-cyclodextrin.	Pyrimethanil	Improved solubility	Fernandes et al., 2014.
Fertilizer	Poly(acrylic acid-co-acrylamide and chitosan	NPK	Gradual release retention of water	Wu and Liu 2008.
	Poly(acrylic acid-co-acrylamide) and ethylcellulose	Urea	Gradual release and retention of water	Ni et al. 2009
	Polyvinyl alcohol (PVA) and starch	Fertilizer	Gradual release	Han et al. 2009

functions (Abd El-Rehim, 2006).

9.1. Polysaccharide matrix for herbicides

In research conducted by Fernández-Pérez et al. (2000), bentonite was combined with alginate to encapsulate isoproturon herbicide to check the movement in soil. The polysaccharide composite significantly minimised herbicide movement in soil relative to non-encapsulated direct herbicide use. Thus, establishing significance of polysaccharide materials in minimising herbicide leaching in soil and eliminating the risk of water below ground contamination with herbicide. Alginate spheres composed with dissimilar adsorbents impacted delivery of chloridazon and metribuzin. The rate of herbicide delivery was minimal and well controlled by the polysaccharide material. In the same vein leaching of chlorsulfuron in calcite/chalky soil was managed with ethylcellulose matrix (Flores Céspedes et al., 2007), a high efficiency of herbicidal activity was achieved. The mobility of norflurazon in soil was assessed through encapsulation in ethylcellulose. Discharge from ethylcellulose capsule was slow, and release into soil was minimal relative to direct use of herbicide. The active ingredient from encapsulated material lasted in the top soil for some time with good concentration for management of weeds (Sopeña et al., 2007). Further, the herbicidal action of paraquat was supported by chitosan/alginate matrix. Herbicide release was notably minimal from the polysaccharide carrier in respect to unencapsulated paraquat. A reduction in sorption profile of soil was equally observed (dos Silva, Cocenza, & Grillo, 2011). Solubleness of chlorpropham herbicide was enhanced with β- cylodextrin complexation. The interaction also afforded stability of herbicide in presence of light (Ge et al., 2011). Clay/chitosan composite was employed by Celis et al. (2012) for clopyralid cleaning from water medium, with a higher percentage of chitosan adsorption rate of herbicide from medium increased. The composite reduced herbicide movement and could minimise the danger of herbicide pollution.

9.2. Polysaccharide matrix for insecticides

The combination of chitosan and alginate spheres provided a strong carrier medium for imidacloprid. Adult *Martianus dermestoide* served as a test organism; insecticidal release time from encapsulation was eight times delayed in comparison with unencapsulated insecticide (Guan et al., 2008). Superiority of alginate concentration over starch in polysaccharide composite encapsulation of chlorpyrifos was evaluated by Roy et al. (2009). They established that a matrix with a higher percentage of alginate over starch had a lower profile of insecticide release, while 50 % of direct application of chlorpyrifos was release under 24 hours; the same quantity of encapsulated content went through five days of gradual release with a high percentage of alginate in the material. Accordingly, emphasising the importance of controlled release rate of insecticides to minimise pollution. Similarly, alginate encapsulation of azadirachtin was evaluated by Jerobin et al., 2012. An additional coating of the encapsulation medium was done with a mixture of polyethylene glycol and starch. The length of active ingredient release was facilitated by coating. Furthermore, alginate encapsulation medium was employed as a carrier for azadirachtin by Kulkarni et al. (2000), and a consistent release of active ingredient was recorded. The insecticidal capacity of *Lippia sidoides* essential oil (EO) encapsulated in the tree gum of cashew and chitosan composite was examined by Paula et al. (2010) against larvae of *Aedes aegypti*. A prolonged release time of EO was noted with remarkable insecticidal activity. Mortality of *A. aegypti* larvae was 100 % after observation for 72 % hours. Thus, affirming polysaccharide's ability to function as capsule for insecticides. Rotenone solubility was greatly enhanced up to 1,300 times more through encapsulation in a derivatized chitosan matrix, which supported sustainable release of insecticide in in vitro experiment. Consequently, polysaccharide encapsulations could be applied in use of non-soluble pesticidal formulations (Lao et al., 2010). Similarly, azadirachtin solubility was facilitated by chitosan carboxy methyl composite blend carrier. The matrix is self-built in aqueous medium, and was capable of releasing azadirachtin for 11 days (Feng & Peng, 2012). Encapsulation matrix premised on starch prepared by Shukla et al. (1991) for carbofuran also had a minimal release rate with an increase in water retention capability of soil.

9.3. Polysaccharide matrix for fungicides

Fungicide pyrimethanil action was supported and improved with inclusion of β-cyclodextrin. Pyrimethanil solubility was enhanced five times more than regular application. Light stability in aqueous medium was equally improved (Fernandes et al., 2014). Hydrogels premised on starch were reported by Singh et al. (2007,Singh et al., 2008 as a suitable carrier for thiram with efficient water retention capability.

9.4. Polysaccharide matrix for fertilizers

Fertilizer encapsulation with poly(acrylic acid-co-acrylamide and chitosan was made by Wu and Liu (2008). Gradual release of fertilizer (75 %) was achieved within 30 days of observation. The water retention capability of soil was enhanced by encapsulation material employed. Comparably, combination of poly(acrylic acid-co-acrylamide) with ethylcellulose as a conveyor for urea yielded positively. After 30 days of experiment, urea release was about 75 %, and significance of polysaccharide materials for water holding in soils was noted. Implying that such materials and techniques could be employed for crops under drought stress (Ni et al., 2009). Coating of fertilizer with polyvinyl alcohol (PVA) and starch to form a matrix film, which was biodegradable and permeable, was investigated by Han et al. (2009), and the researchers established that film composite degraded naturally and was permeable for fertilizer release. Polysaccharides have been applied in removal of herbicides from water. The incorporation of phosphate fertilizer into sulfonated polysaccharide carrier medium by Zhong et al. (2013) afforded good water retention and steady discharge of fertilizer, as summarized in Table 8. Thus, establishing the potentiality of such formulations for arid area crop production. Polysaccharide hydrogels are highly efficient materials for retaining water and holding nutrient concentration for precision release, thus guiding against wastage in the field. Methylcellulose matrix was employed by Bortolin et al. (2012; 2013) for potassium phosphate and ammonium sulfate fertilizers. Elongation of release time, quantity released, and amount of fertilizer contained in the matrix was facilitated by methylcellulose.

While composite polysaccharide carriers improve mechanical properties and modulate release rates, very few studies quantify synergistic effects or interaction mechanisms between polymer constituents. Additionally, the long-term environmental fate and biodegradability of composite materials under field conditions remain insufficiently studied. There's a need to move beyond proof-of-concept and validate these systems in multi-season field trials with agronomic performance metrics as identified in Table 7.

Table 7
Trade-offs in polysaccharide selection.

Polymer	Advantages	Limitations	Unresolved questions
Chitosan	Cationic, antimicrobial	Unstable above pH 6.5	Can chitosan derivatives tolerate alkaline soils?
Alginate	Mild gelation (Ca^{2+})	Low mechanical strength	How to prevent premature dissolution in rainwater?
Starch	Low cost, edible	High swelling → burst release	Can crosslinking reduce swelling without hindering degradation?
Cyclodextrin	Enhances solubility	Low payload capacity	Are toxic byproducts formed during inclusion?

Table 8
Applications and encapsulation methods of polysaccharide polymers in agriculture.

Agrochemical	Polysaccharide polymer	Encapsulation method	Application	References
Herbicides	Bentonite/Alginate	Ionic gelation	Minimized herbicide movement in soil	Fernández-Pérez et al., 2000
	Alginate spheres	Ionic gelation with adsorbents	Controlled release of chloridazon and metribuzin	Flores Céspedes et al., 2007
	Ethylcellulose matrix	Solvent evaporation	Reduced leaching of chlorsulfuron in calcareous soil	Flores-Cespedes et al., 2009
	Chitosan/Alginate matrix	Polyelectrolyte complexation	Reduced soil sorption of paraquat	dos Silva et al., 2011
	β-Cyclodextrin	Inclusion complexation	Improved solubility and photostability of chlorpropham	Ge et al., 2011
Insecticides	Chitosan/Alginate spheres	Ionic gelation	Extended release of imidacloprid	Guan et al., 2008
	Alginate/PEG/starch	Coating	Prolonged release of azadirachtin	Jerobin et al., 2012
	Cashew gum/Chitosan composite	Emulsion	Controlled release of essential oils for insecticidal activity	Paula et al., 2010
	Chitosan matrix	Derivatization	Enhanced solubility of rotenone	Lao et al., 2010
Fungicides	Starch hydrogels	Cross-linking	Improved water retention and thiram delivery	Singh et al., 2007, Singh et al., 2008
	β-Cyclodextrin	Inclusion complexation	Enhanced solubility and light stability of pyrimethanil	Fernandes et al., 2014
Fertilizers	Poly(acrylic acid-co-acrylamide)/Chitosan	Cross-linking	Gradual release of NPK fertilizers and improved water retention	Wu and Liu, 2008
	Polyvinyl alcohol (PVA)/Starch	Spray drying	Biodegradable coating for controlled fertilizer release	Han et al., 2009
Growth Regulators	Chitosan/Alginate NPs	Ionic gelation	Controlled release of gibberellic acid for plant growth enhancement	Pereira et al., 2017

10. Advantages and disadvantages of polysaccharide polymer materials

Primarily, the use of polysaccharide matrix as carriers has possibility to correct nutrient, herbicide, and insecticide leaching, especially in extremely porous soils. They can nurture crops and provide nutrients with precision, while their water holding capability will provide a futuristic solution to drought issues in arid environments. Polysaccharide carriers are pivotal materials for controlled release. They can also serve as remediating materials for removing pesticides from soil and water. Although remarkable advancements have been made in the usage of polysaccharide polymer materials in agriculture, yet some grey areas exist. There is a strict regulation on use of polymer materials owing to the cost of fabrication. Aside from this, premature release of contents from materials is a challenge, and at times, release of contents may fail at peak period of demand from crops. Another challenge has to do with nutrient impact evaluation, because of unavailability of a standard evaluation process. The chemistry of polymeric nano materials in soil is an important factor that has to be considered. Several environmental and soil parameters are significant factors to be assessed regarding use of polysaccharide carriers. Similarly, shelf life and stability of polymer carriers is equally important and has to be examined. Further, blending of polysaccharides or modification with chemicals for use in matrices may bring about disposal challenges. Addition with synthetics predispose polysaccharides to incomplete or partial degradation in the eco-environment. Full degradation requires microbes, water, temperature and other requisite elements of eco-environment. Intricate and complex polysaccharide materials become recalcitrant and slow to mineralisation. Hence understanding decomposition of materials prior to blending with polysaccharide polymers is of utmost importance. A probable way to surmount these challenges is to amend polysaccharide bonds via linking with natural materials for physicochemical characteristics enhancement.

11. Bibliometric and trend analysis

To quantitatively address the evolution of this research field, a bibliometric analysis was conducted using Google Scholar (data accessed August 2025) for key terms central to polysaccharide-based nano-agrochemicals over the last decade. The results, summarized in Table 9 and Fig. 8, reveal not just growth but a striking shift in research intensity and focus, moving from foundational concepts to applied nanotechnology.

The analysis reveals a stark contrast in scale and momentum. The overarching field of "controlled release" is vast and mature, with over 54,000 publications. However, the applied sub-fields of "nanofertilizer" and "nanopesticide" are experiencing explosive, hyper-growth. Remarkably, over half (52.6 %) of all research on nanopesticides and nearly half (47.3 %) on nanofertilizers has been published since just 2022. This indicates a dramatic acceleration of interest, aligning with global pressures for sustainable agriculture and precision farming

Table 9
Analysis of recent growth in key research areas.

Search query	Total publications (All Time)	Publications since 2013	Publications since 2017	Publications since 2022	Publications since 2024	Approx. % of work in last 3 years
Core nano-agrochemical concepts						
allintitle: "nanofertilizer"	315	284	266	149	80	47.3
allintitle: "nanopesticide"	152	144	136	80	44	52.6
allintitle: "controlled release"	54,000	14,600	10,200	4,240	2,030	7.9
Key polysaccharide polymers						
allintitle: "chitosan" "nanoparticle"	1,870	1,490	1,160	549	303	29.4
allintitle: "alginate nanoparticle"	72	57	45	25	18	34.7
allintitle: "starch nanoparticle"	100	79	69	37	20	37.0
allintitle: "cellulose nanocrystal"	2,850	2,640	2,200	963	425	33.8

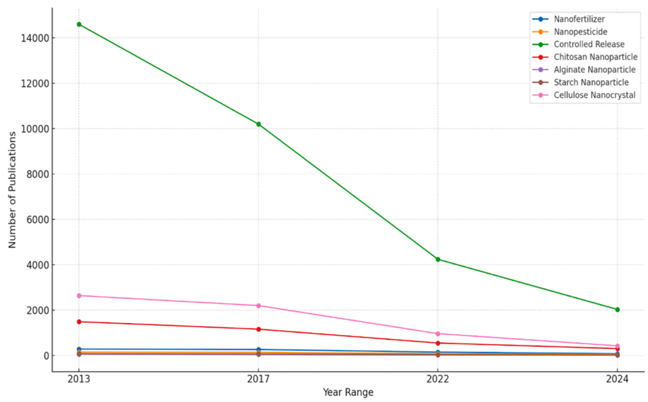


Fig. 8. Publication trends on polysaccharide nanoparticles. (Figure by authors using Origin Viewer 9.9.5).

techniques.

This applied research is underpinned by vigorous innovation in specific polysaccharide nanomaterials. Chitosan-based nanoparticles dominate the polymer landscape in absolute volume, accounting for over 1,870 publications, and remain highly active with 29.4 % of its research output in the last three years. This is largely due to its well-documented biocompatibility, antimicrobial properties, and straightforward synthesis via ionic gelation. However, the most intense recent focus is on alternative polymers. Alginate and starch nanoparticles, while having a lower total output, show the most rapid recent acceleration, with 34.7 % and 37.0 % of their respective literature published since 2022. This highlights them as emerging, promising materials for encapsulation and nutrient release. In contrast, cellulose nanocrystals, despite being the second-largest polymer category by publication volume (2,850) and showing robust recent activity (33.8 % since 2022), remain relatively underrepresented given their natural abundance and superior mechanical properties, indicating a significant opportunity for further exploration.

Narrative Insights:

- The field is bifurcated: massive growth in nano-agrochemical applications is being driven by rapid innovation in polysaccharide materials.
- While chitosan remains the workhorse polymer, there is a clear and accelerating pivot towards exploring alginate and starch, suggesting a diversification of material strategies.
- A significant research gap exists in fully leveraging cellulose, the world's most abundant natural polymer, for advanced delivery systems.
- The data suggests a field that is rapidly moving from proof-of-concept studies to optimized formulation and application, though a translation gap to large-scale field trials remains a critical barrier.

Research Gaps Identified:

- Comparative Material Studies: A lack of systematic, comparative studies evaluating the performance of chitosan, alginate, starch, and cellulose carriers under identical conditions.
- Scalability and Environmental Fate: The literature is dominated by lab-scale synthesis and efficacy studies, with a severe deficit of multi-season field trials assessing agronomic efficacy, soil health impact, and long-term environmental fate.
- Soil Biome Interactions: Minimal investigation into how these nanocarriers influence soil microbial biodiversity, nutrient cycling, and rhizosphere dynamics; factors critical for sustainable deployment.
- Protocol Standardization: The absence of standardized protocols for synthesis, characterization, and testing hinders direct comparison between studies and slows collective progress.

These quantitative trends highlight both the remarkable momentum in the field and the critical gaps that must be addressed. The future of polysaccharide-based nano-agrochemicals lies in bridging this divide, moving from lab-scale innovation to scalable, environmentally benign, and societally accepted field applications.

12. Future research

Research into new molecules of polysaccharides can be done via exploration of biomass materials that are less utilized. Of significance are marine sources like seaweeds and green, red, brown and grey algae, utilization of these can be done with enhancement of structures. Polysaccharide materials can be studied at supramolecular level. Gene can be altered for cell wall modifications for aggregation of carbohydrates. Layering of structures and scaffolds can be managed for interaction of polysaccharides with other materials, especially solvents. Interaction of electrostatics or helices can be developed via novel modelling and numerical computation. Extraction techniques are to be upgraded to green novel ways, while there is a need to study fundamentals of ionic and hydrogen linkage dissolution in the steps of extraction. Existing techniques of characterizing polysaccharides should be fixed up for upgrade; enzyme supportive cleavage tool may be employed to identify polysaccharides when swollen or at gelling state. relationship between small molecules and layers of surface will facilitate clearer understanding of porosity and swelling viz a viz the structural bonds. Incorporation of sensors into polysaccharide polymers for swift delivery of products is suggested. Missing knowledge in the highlighted points may be further developed.

In addition to technical research directions, broader systemic challenges must be addressed to enable translation into practice. Regulatory barriers remain significant, as most countries lack harmonized frameworks for approval of nano-enabled agrochemicals. Without clear guidelines for safety testing, commercialization remains uncertain. Cost and scalability are equally limiting, since many nanoparticle synthesis routes are not yet feasible for large-scale, low-cost agricultural deployment, particularly in developing regions. Ecotoxicological impacts, including effects on microbial biodiversity, soil invertebrates, and water systems are insufficiently studied, raising concerns about long-term accumulation and non-target risks. Future research must therefore integrate regulatory compliance, techno-economic assessments, and comprehensive ecotoxicity studies alongside laboratory innovation.

12.1. Next-generation innovations: the frontier of smart delivery

Beyond current applications, several emerging innovations could redefine the role of polysaccharide-based nanoparticles in sustainable agriculture. Biohybrid nanocarriers, combining polysaccharides with biomolecules such as peptides, proteins, or even engineered microbes, offer opportunities for multifunctional delivery systems that integrate nutrient supply with pathogen resistance or stress signalling. These hybrid carriers could enable targeted release triggered by plant–microbe interactions in the rhizosphere, advancing precision agriculture (Noman et al., 2025).

Another promising frontier is CRISPR-activated release systems, where gene-editing platforms (e.g., CRISPR-Cas) are conceptualized to act as molecular switches. Such systems could enable "on-demand" delivery of pesticides or nutrients in response to plant genetic stress signals or pathogen invasion, although this remains largely at the conceptual and proof-of-principle stage (Javaid et al., 2024).

Finally, AI-driven optimization represents a powerful tool to accelerate the design of polysaccharide nanoparticles. Machine learning algorithms can predict optimal synthesis conditions, release kinetics, and soil–crop compatibility, significantly reducing the reliance on trial-and-error experimentation. By integrating computational modelling with experimental data, AI could streamline the development of customizable, field-ready formulations (Sun et al., 2025). Together, these innovations highlight future pathways for polysaccharide-based nanocarriers that move beyond laboratory-scale encapsulation toward smart, adaptive, and sustainable agricultural systems.

13. Conclusion

Polysaccharide nanoparticles offer a compelling alternative to conventional agrochemicals, but their potential is overstated without addressing scalability, environmental fate, and socioeconomic barriers. Future research must prioritize: (1) low-cost, standardized synthesis; (2) in-field tracking technologies; (3) regulatory harmonization; and (4) stakeholder engagement to ensure adoption. Only then can these materials transition from academic curiosity to agricultural mainstays. Understanding the degradation mechanisms, interactions with soil components, and environmental implications of these polymers is essential for designing materials that are effective, safe, and sustainable. By selecting biodegradable and environmentally friendly polymers, agricultural practices can benefit from the advantages of nanotechnology while minimizing negative effects on soil health alongside the broader ecosystem. Stimuli-reliant polymer discharge mechanisms are advantageous to suit various field situations. As research continues to step forward in this field, the progression of polysaccharide polymers fashioned for specific soil conditions and agricultural needs will be key to promoting sustainable and responsible farming practices.

Funding

This research was funded by ANID Chile, grant number Fondecyt Postdoctoral 3240059.

CRediT authorship contribution statement

Oluwatoyin A. Fabiyi: Writing – review & editing, Writing – original draft, Conceptualization. **Ayorinde V. Ogundele:** Writing – review & editing, Writing – original draft, Funding acquisition. **Hector S. Mella:** Funding acquisition.

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.

Acknowledgments

The authors thank Universidad de La Frontera for its financial support to cover the APC cost.

Data availability

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

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