Malaysian Journal of Chemistry, 2026, Vol. 28(2), 110-127

From Encapsulation to Environmental Fate: Chitosan-Based Controlled-Release Nanopesticides for Sustainable Agriculture

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The extensive use of conventional pesticides has created persistent challenges, including residue accumulation in soil and water, bioaccumulation in food chains, and toxicity to non-target organisms. Chitosan-based controlled-release nanopesticides have emerged as a promising strategy to overcome these issues by improving delivery efficiency while reducing ecological risks. This review highlights the encapsulation chemistry and mechanisms of chitosan nanocarriers, focusing on uptake, release behaviour, and bioavailability. Particular attention was given to their environmental fate after application, including interactions with soil and water systems, degradation pathways, and persistence profiles. Compared with conventional formulations, chitosan-based nanoformulations demonstrated reduced volatilization, leaching, and degradation losses, leading to more effective pest control with lower chemical input. Their protective matrix design also reduced their toxicity toward beneficial organisms and minimizes off-target effects. By integrating nanotechnology with sustainable pest management, chitosan-based controlled-release systems offer a practical route toward safer pesticide use, enhanced crop protection, and alignment with global agricultural sustainability goals.

Keywords: Chitosan, controlled release nanoparticles, nanopesticide, sustainable agriculture, green nanotechnology

Received: September 2025; Accepted: January 2026

Pesticides play a critical role in modern agriculture by protecting crops from pests, weeds, and diseases, ensuring food security and high yields. However, the excessive and indiscriminate use of synthetic pesticides has led to significant environmental and health concerns. A major issue is the persistence of pesticide residues in soil, water, and food products, which can have long-term negative impacts on ecosystems and human health. Studies indicate that some applied pesticides remain in the environment, contributing to soil degradation, water contamination, and bioaccumulation in the food chain [1-3]. It was estimated that in 2019, global pesticide consumption was close to 4.2 million metric tons, with many compounds exhibiting slow degradation rates, leading to toxic accumulation in the environment [4]. This shows the fundamental problem with conventional pesticide formulations: they are unable to deliver active ingredients efficiently resulting in excessive use, environmental persistence, and unexpected ecological consequences.

The environmental consequences of pesticide residues are severe. Runoff from agricultural fields contaminates freshwater systems, with studies showing that some global water bodies contain pesticide levels above safety thresholds [5, 6]. Pesticide residues can disrupt soil microbial communities, reduce biodiversity, and negatively affect non-target organisms, including pollinators and beneficial insects [7, 8]. Additionally, the overuse of pesticides has led to the emergence of resistant pest populations, necessitating even higher chemical inputs, which further exacerbates environmental contamination [9]. Human health risks associated with pesticide exposure are also alarming. The World Health Organization (WHO) reports that over 385 million cases of acute pesticide poisoning occur annually, with long-term exposure linked to serious conditions such as cancer, endocrine disruption, and neurological disorders [10, 11]. Many pesticides have been banned worldwide due to their high toxicity, yet some remain in use, contributing to ongoing contamination concerns [12, 13]. Together, these issues highlight an urgent need for safer, more efficient, and environmentally compatible pesticide delivery systems.

To overcome these challenges, nanotechnology-based pesticide delivery systems have emerged as a promising alternative to conventional formulations. Among the various nanocarriers, chitosan is a biodegradable and biocompatible polymer derived from chitin that has gained significant attention for its ability to improve pesticide efficiency while reducing environmental impact. Research on chitosan-based controlled-release nanopesticides has grown rapidly in recent years. Figure 1 shows the number of scientific publications on this topic from 2007 to 2024, which increased notably in the last 3 years, and patent filings from 2000 to date. These highlight several advantages:

i. Targeted and sustained release of pesticides, reducing the need for frequent application;

ii. Lower pesticide residue levels, which help minimize environmental contamination;

iii. Improved stability of active ingredients, protecting them from premature degradation;

iv. Biodegradability that supports safer and more sustainable agricultural practices.

However, despite this progress, a notable research gap remains. Most existing studies focus on improving encapsulation efficiency, or release profiles without adequately addressing how these systems specifically overcome the fundamental shortcomings of conventional formulations such as low bioavailability, rapid degradation, and uncontrolled release of active ingredients. Furthermore, comprehensive evaluations comparing chitosan-based nanocarriers with traditional formulations in terms of environmental fate, residue reduction, and long-term ecological impact are still limited.

This review examines chitosan-based controlled-release nanopesticides as a sustainable alternative to conventional formulations. It emphasizes the encapsulation chemistry, uptake, and release behaviour of chitosan nanocarriers, showing how these systems enhance bioavailability, enable controlled delivery, and reduce excessive pesticide use. The discussion also addresses the environmental and health risks associated with conventional pesticide residues, including soil and water contamination, bioaccumulation, and toxicity to non-target species, and highlights how chitosan encapsulation mitigates these issues by limiting volatilization, leaching, and premature degradation. Particular attention is given to the environmental fate of chitosan-based nanopesticides after application and their comparatively lower toxicity profiles. Overall, this review positions chitosan nanocarriers as a practical route to reduce pesticide pollution, improve crop protection, and advance sustainable agriculture, in line with global food security and environmental goals.

CHITOSAN AS A NANOCARRIER FOR PESTICIDES

The use of nanotechnology in pesticide delivery has revolutionized agricultural pest management by enhancing efficiency while reducing environmental impact. Among the various nanocarriers available, chitosan, a naturally occurring biopolymer derived from chitin, has gained significant attention due to its unique physicochemical properties. Its ability to encapsulate pesticides, control their release, and minimize toxicity to non-target organisms makes it a promising alternative to conventional pesticide formulations.

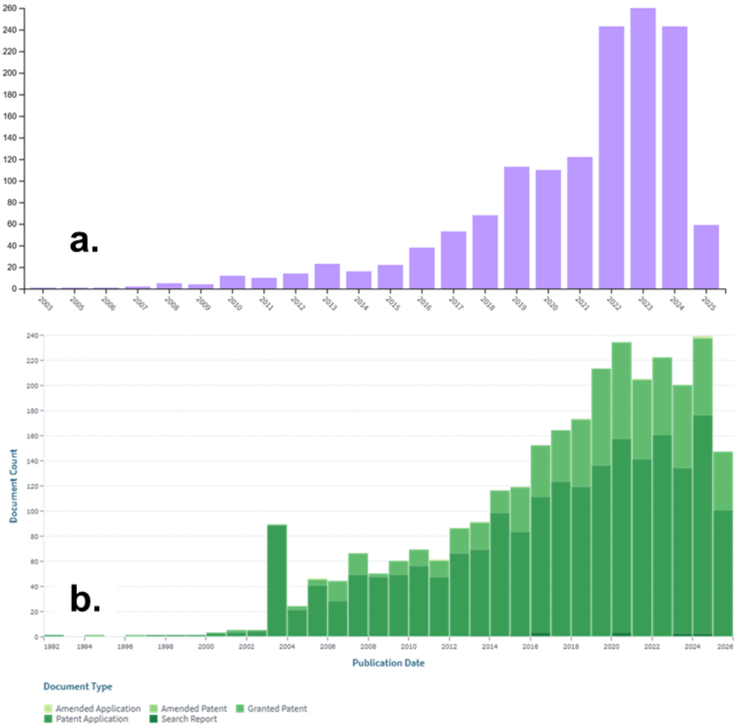

Figure 1. Trends in research on chitosan-based controlled-release nanopesticides in terms of (a) publications, and (b) patent activity, adopted from Web of Science and Lens.Org, respectively.

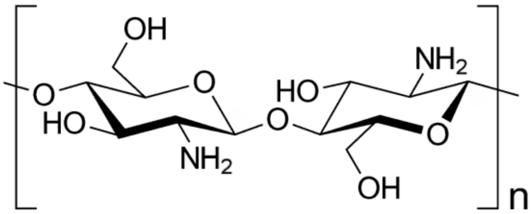

Figure 2. The chemical structure of chitosan.

As shown in Figure 2, chitosan ($[C_6H_{11}NO_4]_n$) is a linear polysaccharide composed of β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine units. It is obtained through the deacetylation of chitin, the second most abundant biopolymer in nature, primarily sourced from crustacean shells, fungal cell walls, and insect exoskeletons [14]. The degree of deacetylation (DD) and molecular weight influence its solubility, viscosity, and functional properties, making it adaptable for various applications in agriculture. Unlike most natural polysaccharides, chitosan carries a positive charge due to protonated amino groups at acidic pH, enabling strong electrostatic interactions with negatively charged biological membranes which enhances adhesion to plant surfaces and pests, improving the efficiency of pesticide formulations [15]. Additionally, chitosan exhibits film-forming ability, providing protective coatings around pesticides to prevent premature degradation and enhance stability [16]. Its mucoadhesive properties facilitate prolonged retention on plant leaves and insect exoskeletons, increasing the effectiveness of pesticide delivery [17].

Chitosan is well known for its biodegradability and biocompatibility, making it an environmentally friendly alternative to synthetic polymer-based pesticide carriers. Unlike conventional pesticide formulations that often lead to soil and water contamination, chitosan-based nanopesticides degrade naturally into harmless byproducts, such as glucosamine, which can further act as a soil conditioner by promoting beneficial microbial activity [15]. Moreover, chitosan is non-toxic to humans, animals, and beneficial insects such as bees and butterflies [18]. Studies have shown that chitosan-based formulations reduce pesticide drift and residue accumulation in food crops, thereby lowering health risks associated with pesticide exposure [8]. Due to its antimicrobial properties, chitosan also helps suppress plant pathogens, offering dual benefits of pest and disease control [17].

To optimize chitosan as a nanocarrier for pesticide delivery, functionalization strategies are designed to regulate intermolecular interactions, polymer chain mobility, and mass transport within the carrier system. As illustrated in Figure 3, grafting chitosan with hydrophobic moieties modifies the amphiphilic character of the polymer, enhancing hydrophobic interactions between the carrier and poorly water-soluble pesticides such as pyrethroids and organophosphates (Figure 3a) [19]. These interactions promote the formation of hydrophobic domains that serve as preferential pesticide-binding sites, increasing loading capacity and reducing premature diffusion. However, excessive hydrophobic substitution can disrupt hydrogen bonding and electrostatic interactions along the chitosan backbone, leading to reduced colloidal stability and particle aggregation. This highlights the importance of controlling the degree of substitution to balance encapsulation efficiency with dispersion stability.

Ionic crosslinking using multivalent anions such as sodium tripolyphosphate ($Na_5P_3O_{10}$, Na-TPP) governs the structural integrity and transport properties of chitosan nanoparticles by introducing electrostatic bridges between protonated amino groups (Figure 3b) [20, 21]. Increasing crosslink density restricts polymer chain mobility, decreases effective pore size, and lowers the diffusion coefficient of encapsulated pesticides, thereby suppressing burst release and enabling sustained, diffusion-controlled release. Conversely, insufficient crosslinking results in loosely associated chains that permit rapid solvent penetration and uncontrolled release. Precise control of chitosan molecular weight, degree of deacetylation, and the chitosan-to-TPP ratio is therefore critical for achieving reproducible physicochemical properties and predictable release behaviour.

Stimuli-responsive release mechanisms introduce environmentally triggered changes in polymer conformation and transport pathways (Figure 3c) [22]. pH-responsive behaviour arises from protonation–deprotonation of chitosan amino groups, which alters electrostatic repulsion between chains, leading to reversible swelling, pore enlargement, and increased diffusivity of the encapsulated pesticide. Enzyme-responsive systems rely on cleavage of glycosidic bonds within the chitosan backbone, progressively reducing molecular weight and increasing matrix permeability through polymer erosion. From a materials perspective, pesticide release in such systems is governed by coupled diffusion, swelling, and degradation processes, where release kinetics depend on both polymer physicochemical properties and environmental conditions.

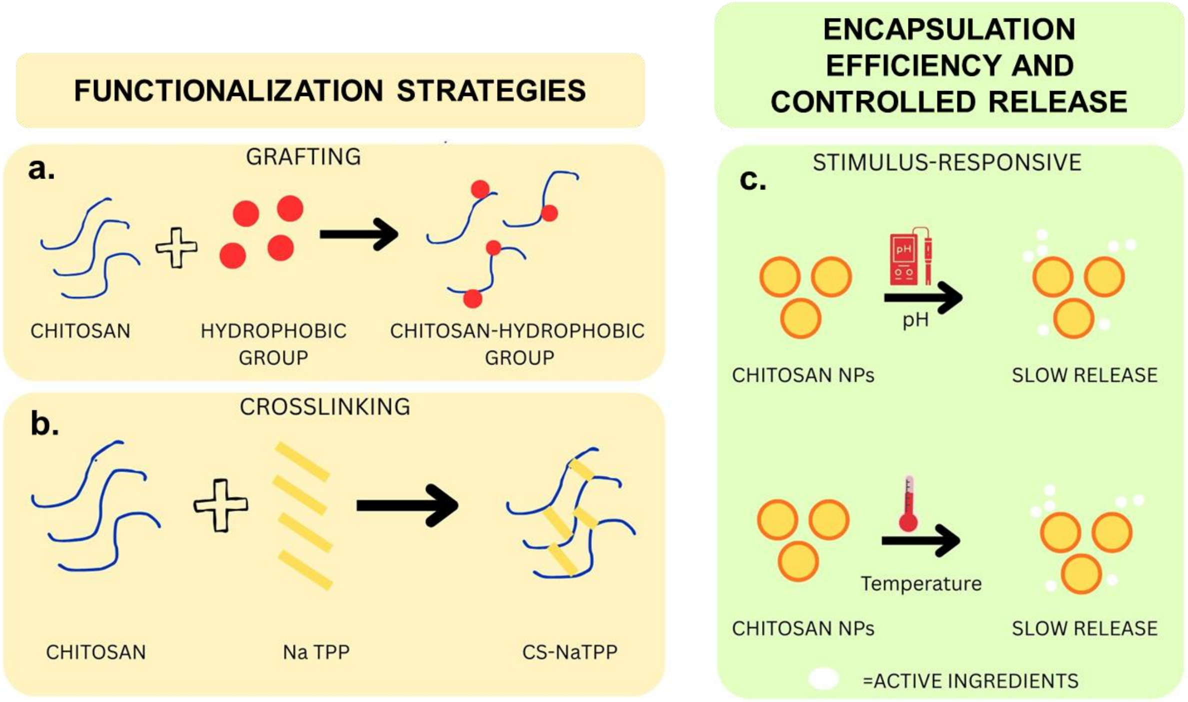

Figure 3. Functionalization strategies of chitosan nanoparticles for pesticide delivery, including (a) grafting with hydrophobic groups, (b) ionic crosslinking with sodium tripolyphosphate (NaTPP), and (c) stimuli-responsive controlled release of encapsulated pesticides in response to pH and temperature variations/

Chitosan-based pesticide carriers offer multiple advantages over traditional pesticide formulations. One major benefit is controlled and sustained release, which reduces the frequency of pesticide application and minimizes runoff into water bodies [22]. Its bioadhesive nature enhances pesticide retention on plant surfaces and pest cuticles, reducing losses from environmental factors like wind and rain [17]. Due to its biodegradable nature, chitosan minimizes soil and water contamination, making it a sustainable option for modern agriculture [23]. Furthermore, chitosan-based formulations improve the solubility of hydrophobic pesticides, ensuring even distribution and uptake in crops [24]. Compared to conventional chemical carriers, chitosan also has a lower toxicity to non-target organisms, such as beneficial insects and soil microbiota, thereby promoting ecological balance [25]. In addition to acting as a pesticide carrier, chitosan possesses antimicrobial and plant growth-promoting properties, which further enhance crop protection and yield [14].

Mechanisms of Antimicrobial Action

Many pests, including insects, mites, and nematodes, serve as vectors for plant diseases caused by bacteria, fungi, and viruses. Controlling these pests is essential not only to prevent direct crop damage but also to limit the spread of plant pathogens. Chitosan-based nanopesticides offer a dual function by directly targeting pests while also exhibiting antimicrobial properties that help control plant diseases [26]. Figure **4** shows the antimicrobial effects through multiple mechanisms, including disruption of microbial cell membranes, inhibition of essential enzymatic pathways, chelation of vital metal ions, and interference with genetic material synthesis.

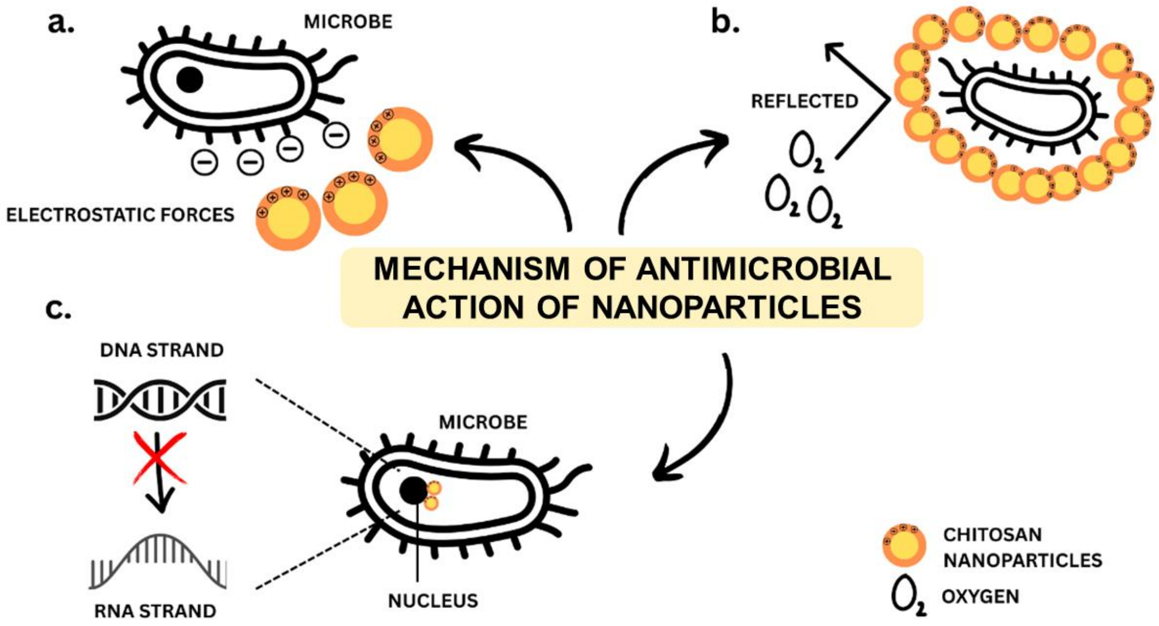

Figure 4. Schematic illustration of the antimicrobial mechanisms of chitosan-based nanoparticles, including (a) membrane disruption via electrostatic interactions, (b) ROS-mediated oxidative stress, and (c) intracellular DNA/RNA damage.

One of the primary mechanisms underlying the antimicrobial activity of chitosan is its interaction with microbial cell membranes. The positively charged amino groups of chitosan interact electrostatically with negatively charged components of bacterial and fungal cell surfaces, resulting in increased membrane permeability and leakage of intracellular constituents (Figure 4a) [15]. This membrane destabilization compromises cellular integrity and can ultimately lead to cell lysis. Chitosan nanoparticles further enhance this effect due to their high surface-area-to-volume ratio, which promotes stronger and more extensive contact with microbial membranes, leading to rapid antimicrobial action [26, 27].

In addition to membrane disruption, chitosan induces oxidative stress within microbial cells. Chitosan-based nanoparticles can promote the generation of reactive oxygen species (ROS), which damage membrane lipids, proteins, and other essential cellular components (Figure 4b) [28, 29]. The accumulation of ROS interferes with normal metabolic processes, including cellular respiration and nutrient transport, thereby reducing microbial viability. This ROS-mediated mechanism contributes significantly to the broad-spectrum antimicrobial efficacy of chitosan nanostructures.

Chitosan also exerts antimicrobial effects through intracellular interactions. Once internalized, chitosan can bind to microbial DNA and RNA, disrupting transcription and replication processes and inhibiting the synthesis of essential proteins (Figure 4c) [30]. Such interference with genetic material prevents normal cell division and ultimately leads to microbial cell death [29]. The ability of chitosan to penetrate microbial cells and impair critical intracellular functions highlights its potential as an effective biocontrol agent for the management of plant pathogens.

Uptake and Bioavailability

Bioavailability refers to the extent and rate at which a pesticide becomes available for plant uptake after application, influencing its effectiveness and environmental impact. Figure 5 shows nanoparticles can enter plants through multiple pathways, including root absorption, foliar uptake, and internal transport via vascular tissues, ensuring efficient delivery of active ingredients. In root absorption, nanoparticles penetrate the root epidermal cell walls and travel through the apoplast, eventually reaching the endoderm before being absorbed into the plant's vascular system (Figure 5 (a)) [31]. Once inside, they are translocated to different tissues, including stems, leaves, and seeds, enhancing the systemic action of pesticides [32, 33]. In foliar uptake, nanoparticles first pass through the protective epidermal layer of leaves before entering mesophyll cells through endocytic or non-endocytic mechanisms (Figure 5 (b)) [33, 34]. Their small size and surface properties facilitate easy penetration and controlled release of active ingredients within plant cells [33]. Once inside, nanoparticles move through the phloem, distributing the pesticide throughout the plant and ensuring prolonged protection against pests and diseases [35].

This enhanced bioavailability not only increases the pesticide's efficiency but also minimizes environmental contamination by reducing excessive leaching into soil and water systems, ultimately mitigating pesticide residues and improving sustainability in agricultural practices.

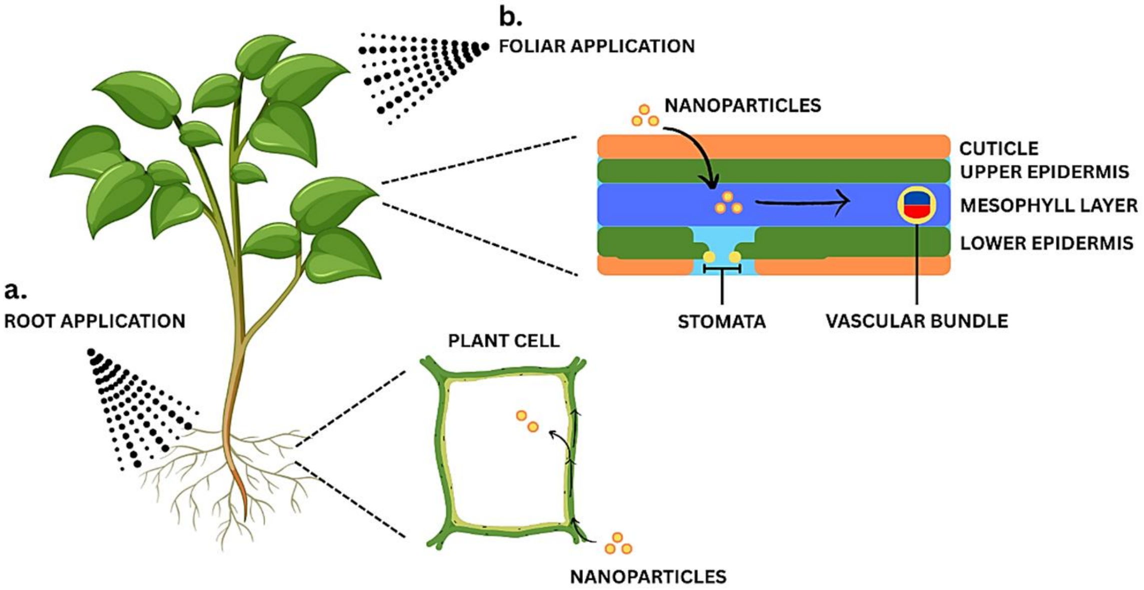

Figure 5. Uptake pathways of nanopesticides in plants via (a) root application and (b) foliar application, illustrating nanoparticle penetration into plant tissues and translocation through vascular systems.

Table 1. Recent studies on functionalized chitosan-based pesticide carriers for enhanced bioavailability in crops.

Nanopesticide	Crop/ plant	Bioavailability and half-life ($t_{1/2}$)	Reference
Chitosan-hexaconazole nanoparticles	Oil palm	$t_{1/2}$ in stem up to 383 days; $t_{1/2}$ in tissue up to 515 days	[20]
Chitosan-imazapic-imazapyr nanoparticles	Maize, soybean and peanut	$t_{1/2}$ in soil up to 30 days	[36]
Chitosan-chlorantraniliprole nanoparticles	Mealy bugs	$t_{1/2}$ up to 14 days	[37]
Chitosan-chlorfenapyr nanoparticles	Cucumber fruits	$t_{1/2}$ up to 0.9 days	[38]
Chitosan-emamectin benzoate nanoparticles	Cucumber fruits	$t_{1/2}$ up to 0.4 days	[38]
Chlorfenapyr-chitosan nanopesticide	Maize	$t_{1/2}$ in soil up to 15.3 days (black), 18.8 days (red) and 28.11 days (sandy)	[39]
Imidacloprid-chitosan nanoparticles	Guava, thyme	$t_{1/2}$ in leaves up to 7.6 days (thyme); $t_{1/2}$ in leaves up to 9.7 days (guava)	[40]
Deltamethrin-chitosan nanoparticles	Guava, thyme	$t_{1/2}$ in leaves up to 10.3 days (thyme); $t_{1/2}$ in leaves up to 12.1 days (guava)	[40]
Chitosan-coated zinc oxide nanoparticles	Vegetable crops	$t_{1/2}$ in soil up to 20.5 hrs (sandy loam); $t_{1/2}$ in soil up to 22.3 hrs (sandy clay)	[41]
Chitosan-dazomet nanoparticles	Oil Palm	Prolonged release up to 24 hours	[21]
Chitosan-dazomet-hexaconazole nanoparticles	Oil palm	Prolonged released for up to 130 hours (hexaconazole); 50 hours (dazomet)	[26]
Chitosan-guargum-chlorpyrifos nanoparticles	Vegetables crops	Prolonged released for up to 15 days	[42]

In agricultural pest management, ensuring high bioavailability is crucial for effective pest control while minimizing environmental losses. Conventional pesticides often suffer from poor bioavailability due to their limited solubility, rapid degradation, and inefficient absorption by plant tissues [43]. These limitations lead to excessive application rates, increased environmental contamination, and higher pesticide residues in food crops [8]. Table 1 summarizes the bioavailability and the half-lives of chitosan nanopesticide formulations which indicate that chitosan-based nanopesticides offer a promising solution by enhancing pesticide uptake, retention, and controlled release, ultimately reducing the need for frequent application.

Several factors influence pesticide bioavailability in plants, including particle size, solubility, and formulation stability. Nanoparticles, typically ranging from 10 to 200 nm, can penetrate plant cuticles and cell walls more effectively than larger particles, leading to better absorption and systemic distribution [33]. Studies have demonstrated that chitosan nanoparticles with sizes below 50 nm enhance pesticide uptake compared to conventional formulations as they fit the cell wall pores [14]. Upon encapsulation in a chitosan matrix, hexaconazole demonstrated high uptake, with residues persisting in plant tissue and stems for up to 515 and 383 days, respectively [20]. Notably, no detectable residue was found in palm oil matrices, indicating that the fungicide did not accumulate in the soil itself, thereby ensuring its safety for consumer use. In a previous study, chitosan acted as a nanocarrier for chlorfenapyr (CF) and emamectin benzoate (EB) by forming nanoformulations CFNPs and EBNPs that were used against spider mites. Their residues in cucumber fruits were found to have $t_{1/2}$ values of 0.9 and 0.4 days, respectively [38]. Another paper reported on a chlorfenapyr chitosan nanopesticide applied to maize plants, in which they compared the half-life of degradation in 3 different soils (black, red and sandy). Black soil had the highest degradation rates due to its high content of soil organic matter which contributed to higher microbial activity in the soil [39].

Research has been done on imidacloprid-chitosan nanoparticles residues in thyme and guava leaves, which followed pseudo-first order and their half-life values in leaves were up to 7.6 days for thyme leaves and 9.7 days for guava leaves [40]. Other researchers also did a similar study on deltamethrin-chitosan nanoparticles which had half-lives of 10.3 days and 12.1 days in thyme and guava, respectively [40]. Another study used chitosan-coated zinc oxide nanoparticles to degrade thifluzamide and difenoconazole in 2 different soils (sandy loam and sandy clay) through photocatalytic degradation, in which the nanoparticles had a lower half-life with difenoconazole compared to thifluzamide [41].

Chitosan-based nanoparticles are also good in sustaining or controlling the release of the active ingredients. For instance, chitosan-dazomet nanoparticles used to counter the pathogens in a oil palm plantation managed to have a sustained release for up to 24 hours [21]. Chitosan-dazomet-hexaconazole nanoparticles, which had a relatively small size range of 5.3 to 57.9 nm resulting in a large surface area for increased antifungal activity against *Ganoderma boninense*, had a good dual controlled release of up to 130 hours for hexaconazole and 50 hours for dazomet [26]. A recent study on a chitosan-guar gum based nanoformulation containing chlorpyrifos that was synthesized using a glyoxial crosslinker that was slightly large in size (200 nm), had better encapsulation efficiency at 85 % while showing sustained release for up to 15 days. The soil mobility study indicated that chlorpyrifos was detected up to the depth of 15-20 cm with the nanoformulation, compared to 20-25 cm with the conventional form [42]. Enhanced bioavailability not only improved pest control but also minimized the accumulation of harmful residues in soil and water, contributing to more sustainable agricultural practices.

Controlled and Sustained Release Mechanisms

Chitosan-based nanocarriers provide a controlled and sustained release of pesticides, ensuring prolonged pest control while minimizing environmental contamination. As illustrated in Figure 6 the release of active ingredients from chitosan nanoparticles is governed by multiple mechanisms, including electrostatic interactions, enzymatic degradation, hydration, swelling, and pore enlargement. These mechanisms collectively enhance bioavailability, reduce pesticide loss, and improve field efficiency. The release kinetics of chitosan-based nanopesticides depend on environmental conditions and formulation design. Factors such as pH, temperature, humidity, soil composition, and microbial activity influence the rate at which the pesticide is released [22]. For instance, enzymatic degradation of chitosan nanoparticles occurs more rapidly in the presence of microbial chitinases in the soil, leading to faster pesticide release in biologically active environments [27, 44]. Similarly, higher humidity levels promote hydration-induced swelling, increasing the diffusion of active ingredients [14]. Formulation parameters such as nanoparticle size, crosslinking density, and surface functionalization also play a crucial role in modulating release rates [45]. Smaller nanoparticles with a high surface areas provide faster diffusion, while cross-linked chitosan matrices offer prolonged pesticide retention by controlling pore enlargement [45].

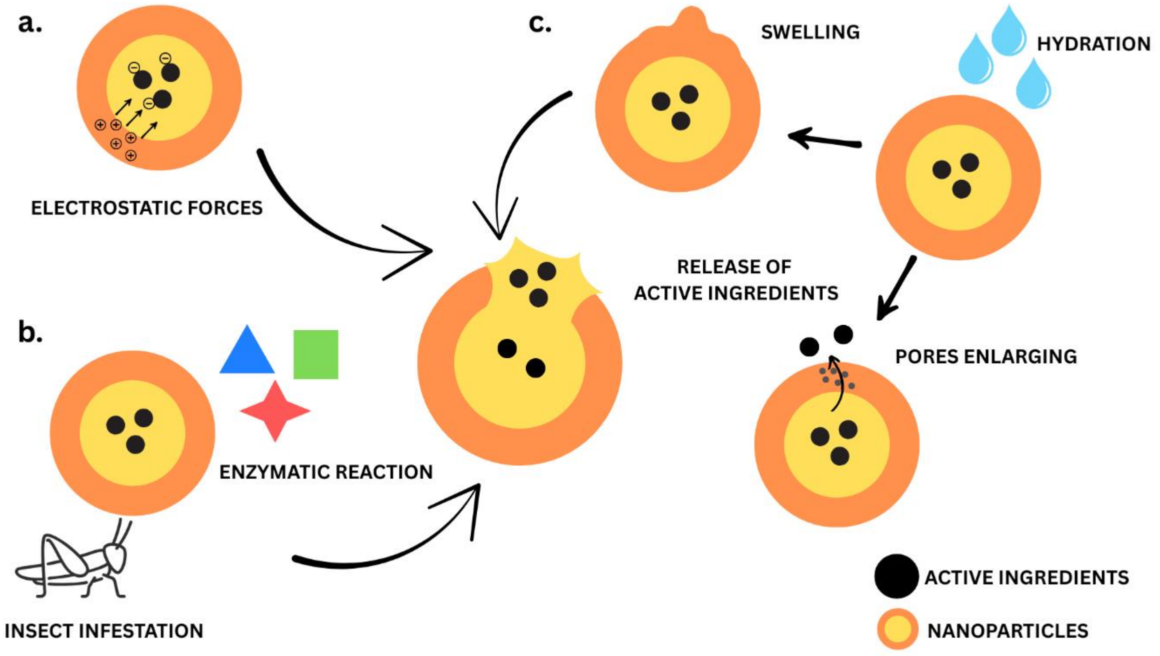

Figure 6. Controlled and sustained release mechanisms of chitosan-based nanopesticides involving (a) electrostatic interactions, (b) enzymatic degradation, and (c) hydration-induced swelling that facilitates gradual release of active ingredients.

One of the primary release mechanisms is electrostatic interactions, where the positively charged chitosan nanoparticles bind to negatively charged surfaces of insect exoskeletons, microbial cells, or plant tissues (Figure 6 (a)) [27]. This interaction destabilizes the nanoparticle structure, facilitating pesticide diffusion upon contact with the pest or pathogen [27]. Enzymatic degradation further accelerates release, as soil and plant enzymes such as chitinases and proteases break down the chitosan matrix, progressively freeing the active ingredient (Figure 6 (b)) [27, 44]. Hydration and swelling-induced release are another key mechanism, where the nanoparticles absorb water, expand, and trigger pore enlargement, allowing the pesticide to diffuse gradually (Figure 6 (c)) [14]. The gradual and sustained release profile is crucial in maintaining effective pesticide concentrations over extended periods, thereby minimizing the need for repeated application and lowering overall chemical input.

Compared to conventional pesticides, chitosan-based nanopesticides exhibit a more controlled and prolonged release, with studies demonstrating sustained pesticide availability for up to months in certain formulations [20, 26]. Conventional bulk pesticide formulations often lead to inefficient pest control due to their tendency to dissipate quickly, requiring frequent reapplication and increasing the risk of environmental contamination [7]. In contrast, chitosan-based nanopesticides enhance pesticide retention within plant tissues and soil, ensuring prolonged bioavailability and improved efficacy [7, 8]. The rapid release of active ingredients from conventional pesticides often results in high volatilization and leaching, contributing to groundwater contamination and pesticide residues in agricultural environments [4, 8, 46]. However, chitosan-based nanoformulations regulate pesticide diffusion through multiple mechanisms, including hydration, swelling, enzymatic degradation, and electrostatic interactions, allowing for a gradual and sustained release. This controlled release mechanism ensures that pesticides remain effective over extended periods, reducing application frequency and lowering the overall chemical load in the ecosystem [47].

Several studies have highlighted the superior performance of chitosan-based controlled-release nanopesticides in improving pest management efficiency. A study on chitosan as a nanocarrier for encapsulating the combined herbicides imazapic and imazapyr, aimed at controlling weeds in major crops such as maize and soybean, demonstrated promising results. Although the nanoparticles were relatively large in size (under 400 nm), the formulation remained stable for up to 30 days. In terms of release behaviour, only about 35 % of the herbicides were released after 300 minutes, indicating a controlled and sustained release profile [36]. A chitosan-based nanocarrier that delivered chlorantraniliprole, an insecticide against mealybugs on the *Hippeastrum reticulatum* plant, had a good encapsulation efficiency of 75.71 % and good stability for up to 14 days [37]. In another study, chitosan-based chlorantraniliprole nanoparticlesin *Chilo suppressalis* with an average particle size of

39.67 nm managed to release only 64.4 % of the pesticides within 5 days at pH 8.5 [48]. In maize, chitosan-pectin-paraquat nanoparticles had a high encapsulation efficiency of 89.41 % but the release of paraquat from the nanocarriers was faster at only 360 min for 74.36 % [49]. Zheng et al. used chitosan as nanocarriers to encapsulate rotenone to counter red fire ants with a good slow release for not more than 12 days [50]. These findings emphasize the role of nanotechnology in optimizing pesticide bioavailability, thereby reducing the overall chemical load on the environment.

ENVIRONMENTAL FATE OF CHITOSAN-BASED NANOPESTICIDES

Unlike conventional pesticides that persist in the environment due to their chemical stability and slow degradation, chitosan-based formulations offer an eco-friendly alternative due to their biodegradability, strong soil adsorption, and controlled release mechanisms. One of the key advantages of chitosan-based nanopesticides is their enzymatic degradation in soil, facilitated by microorganisms such as *Bacillus*, *Pseudomonas*, and *Trichoderma* species, which produce chitinases and glucosaminidases that break chitosan down into non-toxic byproducts like glucosamine [51, 52]. Studies have reported that chitosan-based formulations degrade within weeks to months, depending on soil conditions and microbial diversity, significantly reducing the risk of long-term chemical accumulation in agricultural ecosystems [52, 53]. When buried in soil, chitosan nanofilm fully degraded after 2 months, allowing the nutrients to be recycled back into the soil [54].

The mobility and sorption behaviour of chitosan-based nanopesticides in soil play a critical role in determining their environmental impact. Due to their cationic nature, chitosan nanoparticles exhibit strong electrostatic interactions with negatively charged soil particles and organic matter, resulting in high sorption capacity and limited mobility. This reduces leaching risks and prevents the contamination of groundwater, compared to conventional water-soluble pesticides which often percolate through soil layers [15]. A high concentration of the conventional fungicide hexaconazole (64 %) was shown to persist in the soil surface at a maximum depth of 10 cm after 7 days of application [55]. Other findings indicate that nanoencapsulated pesticides are more likely to be found at low concentrations in the stems and leaves of the plant, ensuring their bioavailability to crops while minimizing environmental contamination [7]. A study has confirmed that chitosan nanoparticles loaded with zinc oxide (CS-ZnO NPs) were a promising catalyst to remove pesticide residues in soil [41]. However, factors such as excessive rainfall, soil texture, and pH variations may still influence the leaching potential of chitosan-based nanopesticides, necessitating site-specific evaluations to optimize environmental safety [14].

The interactions of chitosan-based nanopesticides with soil microbiota and non-target organisms are a crucial aspect of their environmental fate. Unlike conventional pesticides that often disrupt microbial diversity, one study showed that chitosan could stimulate beneficial bacteria like *Baccillus sp*., a nitrogen fixer, and *Burkholderia gladioli*, a phosphate solubilizer. These resulted in the formation of nitrogen and phosphorus, which are nutrients required for plant growth that also help suppress leaf blotch disease caused by the *Taphrina maculans* fungus [56]. However, the antimicrobial properties of chitosan could potentially suppress certain soil bacteria at high concentrations, altering microbial community structures [57]. Therefore, long-term investigations into the ecological impacts of repeated applications are necessary to determine optimal dosages that balance pest control efficacy with soil microbial sustainability.

Runoffs from agricultural fields are a major pathway for pesticide contamination in rivers, lakes, and aquatic ecosystems, affecting biodiversity and ecosystem stability [46, 58]. Due to their high-water solubility and poor soil adhesion, conventional pesticides often enter aquatic environments where they can bioaccumulate in fish, disrupt amphibian endocrine systems, and exert toxic effects on aquatic invertebrates [2, 58]. In contrast, chitosan-based nanopesticides demonstrated reduced runoff potential due to their enhanced retention in soil and controlled release mechanisms [14]. A study found that calcium-alginate-chitosan nanoparticles enhanced pesticide retention in the soil by improving interactions between water and soil particles, effectively reducing pesticide concentrations in runoff [59, 60].

Hexaconazole-loaded chitosan nanoparticles exhibited enhanced soil retention and reduced leaching, ensuring prolonged bioavailability in plants for up to 60 days [20]. Similarly, nanoencapsulated imidacloprid formulations demonstrated higher photostability and lower volatilization losses, reducing airborne pesticide contamination [61]. Chitosan-silver nanoparticles (CSAg NPs) showed great inhibitory effects at lower concentrations indicating a lower likelihood of reapplication, thus reducing toxic effects to non-target organisms [62, 63]. A study on chitosan-copper nanoflowers used against *R. Solani* showed that they had an inhibitory effect six times greater than normal copper oxides nanoparticles (CuO NPs), with only 45 % of the copper (Cu) content of CuO NPs [64].

A study showed that chitosan and carboxymethyl chitosan encapsulating cyantraniliprole forming nanopesticides CS/CMCS/Cya promoted the spore wettability of *S. frugiperda* and the stability of sedimentation of the spore suspension. It also showed strong adhesion with an adsorption rate of over 150 % [65]. Similarly, a study on chitosan and carboxymethyl chitosan nanoparticles loaded with penconazole which was pH-stimulated showed great controlled release at different pH levels and presented good resistance to washout, preventing loss of active ingredients to the environment [66]. Wettability is the ability of a liquid to remain in contact with a solid surface, thus higher wettability leads to longer retention in the solid surface, reducing runoff risks. Another study of chitosan and carboxymethyl chitosan nanoparticles loading rotanone also demonstrated a pH-responsive release while showing better insecticidal effects compared to its counter form, proving that chitosan was a good UV protector for the active ingredients [50].

The environmental fate of chitosan-based nanopesticides is generally favourable. Figure 7, shows the comparison between conventional pesticides and chitosan-based nanopesticides. Unlike conventional pesticides, which often persist in soil and water due to their chemical stability, chitosan-based formulations degrade naturally into harmless by-products through microbial action, reducing long-term environmental accumulation. Their strong affinity for soil particles minimizes leaching and runoff, while their protective encapsulation limits volatilization and enhances photostability. These features contribute to reduced contamination of water bodies and lower exposure risks for non-target organisms. Furthermore, their ability to support beneficial soil microbiota, improve pesticide retention at the target site, and reduce application frequency highlights their potential to replace conventional formulations in more sustainable pest management systems. However, as promising as these results are, field-scale studies across various agroecological zones are still needed to fully understand their long-term interactions with soil, water, and biological communities. Continued research is essential to optimize formulation parameters, assess cumulative effects, and establish comprehensive environmental safety profiles before large-scale adoption.

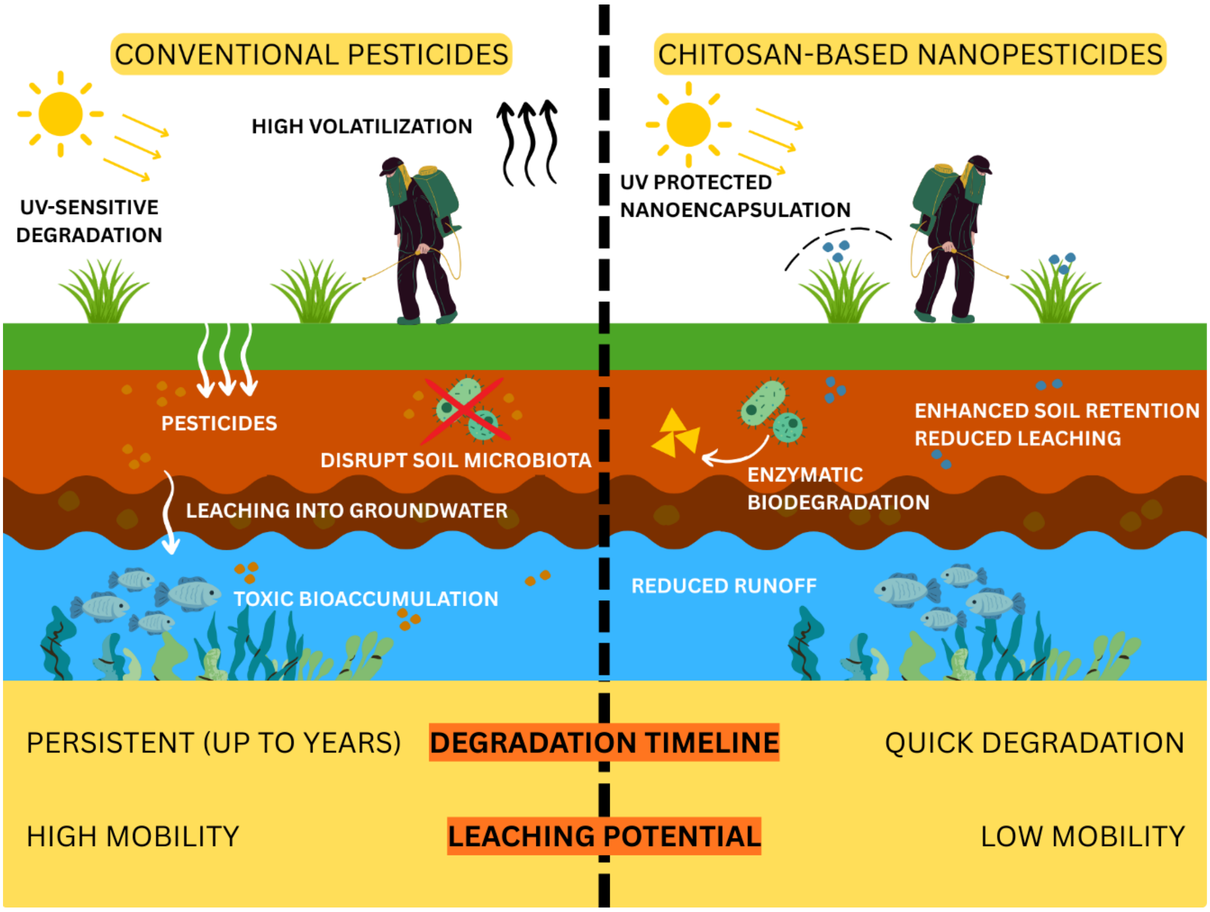

Figure 7. Comparative environmental fate and transport of chitosan-based nanopesticides and conventional pesticides after field application.

REDUCED TOXICITY AND ECOLOGICAL IMPLICATIONS

The prolonged bioavailability of chitosan-based nanopesticides in plant matrices raises concerns regarding food safety. To ensure consumer protection, pesticide residues must remain below the acceptable daily intake (ADI) levels established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). One of the key advantages of chitosan encapsulation is its controlled release capability, which helps prevent sudden spikes in pesticide concentration and supports residue levels that remain within the acceptable safety range. Studies have shown that nanoencapsulated pesticides release their active ingredients more gradually and in a controlled manner compared to conventional formulations. This ensures sustained efficacy while significantly reducing the risk of acute toxicity.

As summarized in Table 2, several pesticides including mancozeb, hexaconazole, dazomet, imazapic and imazapyr exhibit improved release profiles when encapsulated in chitosan nanoparticles. For example, while conventional mancozeb and dazomet release nearly all their active ingredients within a few hours, their chitosan-based formulations extend the release period to between 10 and 80 hours, depending on the pesticide [20, 36, 67]. This slower, controlled release helps prevent sudden spikes in pesticide concentration that could harm non-target organisms. In line with this, in vitro cytotoxicity tests show a marked reduction in toxicity for chitosan-formulated pesticides when compared to their pure counterparts. For instance, hexaconazole and dazomet in their unencapsulated forms reduced cell viability significantly at concentrations as low as 0.03 mg/mL [68]. In contrast, their chitosan-based formulations maintained high cell viability, ranging from 65 % to 85 %, even at concentrations up to 1 mg/mL [68]. Similar results were observed for imazapic and imazapyr, where encapsulation not only improved sustained release but also lowered cytotoxic and genotoxic effects in mammalian cells [36]. These findings support the use of chitosan nanoparticles as a safer delivery system for pesticides, offering effective pest control while reducing risks to human health, beneficial organisms, and the environment.

The chitosan nanoparticles act as a protective shell, significantly reducing the toxicity of the encapsulated pesticide by controlling the release of active ingredients and minimizing direct exposure to non-target organisms [47]. Conventional pesticides, when applied in bulk formulations, often disperse uncontrollably in the environment, leading to acute toxicity risks for humans, beneficial insects, soil microbes, and aquatic organisms [8]. The chitosan shell functions as a barrier, shielding both the pesticide from premature degradation and the surrounding ecosystem from unintended exposure, thereby mitigating the harmful effects commonly associated with conventional pesticide applications [69]. Additionally, the chitosan shell reduces pesticide volatilization and prevents toxic airborne exposure. Many conventional pesticides, especially organophosphates and pyrethroids, evaporate rapidly upon application, leading to inhalation risks and atmospheric pollution [70]. This not only enhances pesticide retention on plant surfaces, but also minimizes respiratory toxicity for farm workers and surrounding communities.

Chitosan encapsulation plays a crucial role in protecting non-target organisms, including pollinators and natural pest predators. Conventional pesticides often exhibit broad-spectrum toxicity, harming beneficial insects such as bees, butterflies, and predatory arthropods [71]. The protective chitosan shell prevents uncontrolled pesticide dispersal, ensuring that the active ingredient is released primarily at the target site rather than indiscriminately affecting beneficial species [47]. A study on chitosan-based nanopesticides found a reduction in their toxicity to honeybees compared to conventional formulations, highlighting the potential of this technology in promoting ecological balance while maintaining pest control efficiency [72].

Table 2. Comparison of controlled release properties and toxicities of pure/conventional pesticides versus chitosan-based nanopesticides (NP).

Pesticide (Active ingredient)	Controlled release properties (Pure/conventional vs. chitosan NP)	Toxicity assessment		References
		Pure/conventional pesticides	Chitosan-based nanopesticides	
Mancozeb (fungicide)	*Conventional:* 98 % of active released within 2 h. *Chitosan NP:* Only 42 % released in 2 h (76% in 6 h), with complete release by 10 h (sustained release).	Marked toxicity even at low doses – e.g. only 12 % cell viability at 2.0 mg/mL in Vero kidney cells. Significant cytotoxic effects observed with the conventional formulation.	Greatly reduced toxicity at equivalent doses – e.g. 77–84 % cell viability at 0.25 mg/mL (near untreated control 90 %). High doses eventually induced similar toxicity (12–15 % viability at 2.0 mg/mL), but at low/moderate concentrations the chitosan-encapsulated form was far less cytotoxic.	[67]

Hexaconazole (fungicide)	*Pure:* Essentially no controlled release (free hexaconazole is immediately bioavailable; no sustained-release matrix). *Chitosan NP:* Strongly controlled release – 99.9 % of payload released over 86 h (half-release $t_{1/2}$ is 42 h). Encapsulation greatly prolonged release duration.	Very high cytotoxicity – viability of mammalian cells dropped below 50 % at 0.03 mg/mL (V79 lung cells), indicating a low IC_{50}.	Significantly lower cytotoxicity – cell viability remained at 83 % at 1 mg/mL in V79 lung cells and 73 % at 1 mg/mL in 3T3 fibroblasts (no significant toxicity up to 1,000 μg/mL). Encapsulation in chitosan thus mitigated the direct cytotoxic effects of hexaconazole.	[20, 68]
Dazomet (fungicide)	*Pure:* Rapid decomposition to MITC gas upon contact with water – essentially an immediate release of the active fumigant (no sustained release, leading to a burst of toxic MITC). *Chitosan NP:* Controlled release with diffusion limits – e.g. half-release time 11 h in chitosan–TPP nanoparticles, greatly slowing and prolonging MITC generation.	Very high cytotoxicity – viability <50 % at 0.03 mg/mL in 3T3 fibroblast cells, reflecting strong cell killing at low concentrations. Pure dazomet/MITC was acutely toxic to cultured cells.	Greatly reduced toxicity – 85 % viability at 1 mg/mL in lung cells and 70 % at 1 mg/mL in fibroblasts, with no significant cell death observed up to high doses. The chitosan-encapsulated dazomet showed much higher biocompatibility compared to the free fungicide.	[21, 68]
Imazapic (herbicide)	*Pure:* 55 % of active released within 5 h (in aqueous diffusion setup). *Chitosan NP:* Only ~30 % released in 5 h under the same conditions – significantly slower release than the free herbicide (nano-carrier provides sustained release).	Pure herbicide caused considerable cytotoxic and genotoxic effects in vitro. For example, the mixture of free imazapic + imazapyr led to significantly higher DNA damage in cells (*Allium cepa* root assay) and higher toxicity in CHO mammalian cells, compared to the encapsulated form.	Encapsulation markedly reduced toxicity. Chitosan-based NP formulation showed low cytotoxicity in CHO cells and ~50 % less DNA damage in the *Allium cepa* assay relative to the free herbicide. Overall, the nano-imazapic demonstrated substantially improved cell compatibility, with encapsulation lowering both cytotoxicity and genotoxicity versus the conventional form.	[36]
Imazapyr (herbicide)	*Pure:* 97 % of active released in 5 h (almost complete release in hours). *Chitosan NP:* Only 20 % released in 5 h – encapsulation dramatically slowed down the release (imazapyr's quick leaching was curtailed by the chitosan matrix).		Encapsulated imazapyr (in chitosan NP) showed minimal cytotoxic and genotoxic impact on non-target cells. Cytotoxicity assays confirmed the chitosan-carrier herbicide had very low toxicity (comparable to controls), and genotoxicity (DNA damage) was significantly lower than with the free herbicide. This indicates a much safer profile compared to its conventional counterpart.	[36]

FUTURE PERSPECTIVES AND CHALLENGES

Despite the promising advantages of chitosan-based nanopesticides in enhancing controlled-release behaviour and reducing environmental contamination, their successful application remains limited in practical agricultural deployment. Many reported benefits such as improved encapsulation efficiency, reduced toxicity, and targeted delivery were obtained from controlled greenhouse or laboratory experiments, which do not fully capture the complexity of real agricultural environments. Therefore, much of the current research tends to highlight practical effectiveness and does not completely address issues related to long-term environmental impact, cost-effectiveness, or regulatory approval processes.

To study the potential of chitosan, it is important to compare it with other polymers used in pesticide nanoencapsulation. Synthetic polymers such as poly(lactic-co-glycolic acid) (PLGA) or petroleum-derived polyacrylates offer good mechanical strength and controlled-release potential, but each comes with major drawbacks. PLGA often has low drug loading, suffers from a high initial burst release and unstable release kinetics, and its degradation can produce acidic by-products which trigger unwanted pH changes [73]. Meanwhile, polyacrylates are persistent in the environment and poorly biodegradable, which raises ecological and long-term sustainability concerns. Biopolymers such as starch or alginate avoid some of these issues but suffer their own limitations which include weak mechanical strength, high water sensitivity, poor moisture properties, and inconsistent stability or release behaviour [74]. In contrast, chitosan is biodegradable, biocompatible, and has properties that can be modified. This results in good mechanical strength, controlled degradation, the ability to form films, and stable water resistance. Chitosan is broken down by enzymes into non-toxic residues and does not create acidic by-products which alter soil pH, while also offering antimicrobial and adhesive properties [75]. However, it has some drawbacks: it is sensitive to changes in pH, prone to UV degradation, and its quality can change from batch to batch. So, even though it has potential, chitosan is not always better than other polymers and needs to be modified to work well.

A major technical challenge lies in formulation inconsistency. Variations in molecular weight, degree of deacetylation, crosslinking efficiency, and synthesis method contribute to the wide variability in nanoparticle stability and release kinetics. These inconsistencies make it hard to achieve reproducibility across studies, and requires more effort to obtain a reliable relationship between the formulation's structure and function. Stimuli-responsive systems use changes in pH, enzymes, or temperature to control pesticide release which could improve how pesticides are delivered, but it is not yet clear if these systems work well in real agricultural conditions. Field soils contain unknown chemicals and biological environments, and many proposed smart-release mechanisms have not been applied outside laboratory conditions. Multi-season field studies are needed to confirm if these systems work well and can be used in real farming. Without this evidence, their useful application is uncertain.

Scaling up production and making it cost-effective are also major challenges. Lab methods like ionic gelation and polyelectrolyte complexation need precise controls and are hard to scale. Industry-level production needs consistent polymer quality, good mixing equipment, and energy-efficient processes, all of which increase costs. Using chitosan from seafood or farm waste may lower material costs, but introduces more variability in its properties.

Nanotoxicity is an important issue that needs more study. Although chitosan is usually considered safe, its nanoparticle form can behave differently due to changes in surface charge, reactivity, and movement. These changes may affect soil structure, how plants absorb nutrients, and how substances move through the food chain, but these effects are not yet fully understood. Most current research looks at short-term impacts in controlled settings. There is still little information about what happens after long-term exposure, how nanoparticles build up in soil, how they interact with helpful soil microbes, and their effects on pollinators and water life. The speed at which chitosan nanoparticles break down also changes depending on soil pH, moisture, microbes, and how the particles are synthesised. This makes it hard to predict their long-term effects on the environment. These unknowns show that there is a need for clear standards for testing the toxicity of nanoparticles, and for ongoing checks on their impact over time.

Regulatory challenges make it harder to bring these products to market. Most countries have pesticide rules that do not clearly separate standard pesticides from those made with nanotechnology, so it is unclear what information is needed for approval. There are no shared international rules on how to test and describe these nanoparticles, e.g., what counts as a nanoparticle, how they clump together, or how long they last in the environment. This makes risk assessments and obtaining approval take longer. Also, regulators now ask for details specific to nanoparticles, such as how they dissolve, how they change in soil, and if there are breathing risks during use, but most studies do not cover these points [76]. To make approval faster and safer, clear and consistent rules across countries are needed for nano-based pesticides.

Moving forward, incorporating chitosan-based nanopesticides into precision agriculture systems such as AI-assisted pest detection, drone-based targeted spraying, and automated delivery technologies may significantly enhance efficiency and reduce pesticide overuse. However, integrating nanotechnology with precision agriculture requires not only technical optimization but also evaluation of socioeconomic feasibility, including farmer training, technology affordability, and infrastructure readiness. Without addressing these factors, even the most advanced nanoformulations may experience limited adoption.

CONCLUSION

Chitosan-based controlled-release nanopesticides represent a promising advancement in modern pest management, offering a sustainable alternative to conventional pesticides by reducing pesticide residues, toxicity, and environmental contamination. Their biodegradable and biocompatible nature, coupled with controlled and targeted release mechanisms, enhances pesticide efficiency while minimizing off-target effects on non-target organisms, soil, and water systems. By reducing leaching, volatilization, and bioaccumulation, these formulations help mitigate the long-term ecological and health risks associated with synthetic pesticides. While challenges remain in optimizing formulation stability, scalability, and regulatory approval, continued research, policy support, and industry investment will be crucial to unlocking their full potential. The integration of chitosan-based nanopesticides with precision agriculture and smart-release systems could further enhance their effectiveness and promote environmentally responsible pest control, and contribute to global efforts toward sustainable agriculture and food safety.

ACKNOWLEDGEMENTS

This work was supported by a Universiti Sains Malaysia Short-Term Grant, with Project No: 304/PKIMIA/6315732.

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