



## Review

## Chitosan nanoparticle based delivery systems for sustainable agriculture

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## ABSTRACT

Development of technologies that improve food productivity without any adverse impact on the ecosystem is the need of hour. In this context, development of controlled delivery systems for slow and sustained release of agrochemicals or genetic materials is crucial. Chitosan has emerged as a valuable carrier for controlled delivery of agrochemicals and genetic materials because of its proven biocompatibility, biodegradability, non-toxicity, and adsorption abilities. The major advantages of encapsulating agrochemicals and genetic material in a chitosan matrix include its ability to function as a protective reservoir for the active ingredients, protecting the ingredients from the surrounding environment while they are in the chitosan domain, and then controlling their release, allowing them to serve as efficient gene delivery systems for plant transformation or controlled release of pesticides. Despite the great progress in the use of chitosan in the area of medical and pharmaceutical sciences, there is still a wide knowledge gap regarding the potential application of chitosan for encapsulation of active ingredients in agriculture. Hence, the present article describes the current status of chitosan nanoparticle-based delivery systems in agriculture, and to highlight challenges that need to be overcome.

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## 1. Introduction

The biggest challenge faced by agricultural researchers is to produce sufficient quantity and quality of food to feed the ever increasing global population without degrading the soil health and agro-ecosystem. It has been estimated that global food production must increase by 70–100% by 2050 to meet the demand of the growing population explosion [1]. Agricultural production continues to be challenged by a large number of insect pests, diseases, and weeds accounting for 40% losses to the tune of US \$2000 billion per year [2]. To manage these losses and enhance productivity, farmers are making excessive and indiscriminate use of agrochemicals which leads to deterioration of soil health, degradation of agro-ecosystems, residue problems, environmental pollution and pesticide resistance in insects and pathogens. Hence, there is an urgent need to change the manner in which we use agrochemicals. Changes can include (i) judicious deployment of pesticide and fertilizer, (ii) rapid and precise detection of pathogens and pests, as well as pesticides and nutrient levels, and (iii) promoting soil health by agrochemical degradation. In this context, nanotechnology has emerged as a technological advancement that can transform agriculture and allied sectors by providing with novel tools for the molecular management of biotic and abiotic stresses, rapid disease detection and enhancing the ability of plants to absorb nutrients or pesticides [3–5]. Besides this, nanobiotechnology can also improve our understanding of crop biology and thus can potentially enhance crop yields or their nutritional values. Nanosensors and nano-based smart delivery systems are some of the nanotechnology applications that are currently employed in the agricultural industry to aid with combating crop pathogens, minimizing nutrient losses in fertilization, improving crop productivity through optimized water and nutrient management as well as to enhance the efficiency of pesticides at lower dosage rates [6,7]. Nanotechnology derived devices are also being explored in the field of plant breeding and genetic transformation [8,9]. Table 1 describes some of the advancements made in the field of agricultural nanotechnology. Among all these advancements, encapsulating active ingredients, such as fertilizers, herbicides, fungicides, insecticides, and micronutrients in controlled release matrices is one of the most promising and viable options for tackling current challenges in the area of agricultural sustainability and food security in the face of climate change. It has been shown that encapsulation of active ingredients in nanoparticles enhances the efficacy of chemical ingredients, reducing their volatilization, and decreasing toxicity and environmental contamination [40].

Chitosan has emerged as one of the most promising polymers for the efficient delivery of agrochemicals and micronutrients in nanoparticles (Fig. 1; Table 2). The enhanced efficiency and efficacy of nanoformulations are due to higher surface area, induction of systemic activity due to smaller particle size and higher mobility, and lower toxicity due to elimination of organic solvents in comparison to conventionally used pesticides and their formulations [62,63]. Chitosan nanoparticles have been investigated as a carrier for active ingredient delivery for various applications (Fig. 1) owing to their biocompatibility, biodegradability, high permeability, cost-effectiveness, non-toxicity and excellent film forming ability [64]. Over the past three decades, various procedures like cross-linking, emulsion formation, coacervation, precipitation and self-assembly, etc. have been employed to synthesize chitosan

nanoparticles [65,66]. Chitosan has also known for its broad spectrum antimicrobial and insecticidal activities [67,68]. Further, it is biodegradable giving non-toxic residues with its rate of degradation corresponding to molecular mass and degree of deacetylation [69,70]. However, the low solubility of bulk chitosan in aqueous media limits its wide spectrum activity as an antimicrobial agent. Therefore, various strategies have been employed to enhance its antifungal potential [41]. Chitosan is able to chelate various organic and inorganic compounds, making it well-suited for improving the stability, solubility and biocidal activity of chelated fungicides or other pesticides [64]. For example, copper (Cu) compounds are well known for their antifungal nature and have been used with chitosan for antibacterial and antifungal activities. The majority of the research on chitosan nanoparticles in agricultural research studied their biocidal and antagonistic effects on bacteria and fungi, and gave encouraging results [71–73]. Chitosan-based nanocomposite films, especially silver-containing ones, showed antimicrobial activity against several pathogens [74], but some effect was also observed with chitosan films alone [75]. Other studies investigated the use of chitosan–PVA hydrogels for antimicrobial and food packaging applications [76–78]. The combination of silver nanoparticles within a chitosan–PVA polymeric material also emerged as one of the most promising candidates for new antimicrobial materials [44]. Recently, application of chitosan particles loaded with copper has been reported in waste water treatment [79,80]. Considering the growing interest, and recent advances, in chitosan-based nanomaterials in medical and pharmacological applications, the purpose of this article is to review the current and ongoing research and developmental efforts into chitosan nanoparticles as a delivery system, with particular focus on describing methods that would be suitable for promoting crop productivity.

### 1.1. Chitosan in crop production and protection

There have been several reports describing the use of chitosan for biotic and abiotic stress management in agriculture [73,81–85]. Table 3 lists some of the applications of chitosan in crop production and protection. For the first time, Allan and Hadwiger [130] described the application of chitosan as an antimicrobial agent. This has led to the exploitation of its antimicrobial potential in various sectors of agriculture. Since the 1980s, the study of chitosan has been shift from a general sewage treatment agent to plant growth regulator, soil conditioner, vegetables and fruits antistaling agent, and seed coating agent, especially in the crop disease management. Several studies showed that chitosan is not only an antimicrobial agent but also an effective elicitor of plant systemic acquired resistance to pathogens [73,82,84,131]. This polymer has been reported to be the enhancer and regulator of plant growth, development and yield [85,132,133]. Chitosan has been demonstrated to induce plant defences in tomato [87,89], cucumber [97], chilli seeds [102], strawberry fruits [88] and rose shrubs [99]. Chitosan can activate innate immunity by stimulating hydrogen peroxide ( $H_2O_2$ ) production in rice [134,135], induce a defense response by nitric oxide (NO) pathways in tobacco [136,137], promote the development and drought resistance of coffee [138], support the synthesis of phytoalexin [139], impact the jasmonic acid–ethylene (JA/ET) signaling marker in oilseed rape [140], cause changes in protein phosphorylation [141], activate mitogen-activated protein kinases (MAPKs) [142] and trigger

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