ADVANCES IN CHITOSAN-UREA NANOHYBRIDS: TOWARD SUSTAINABLE NITROGEN MANAGEMENT IN CROP SYSTEMS

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ABSTRACT

A major challenge to sustainable agriculture is the inefficiency of conventional urea fertilizers—marked by nitrogen losses exceeding 60% through volatilization, leaching, and denitrification. Encapsulating urea in biodegradable polymer matrices such as chitosan, alginate, and gelatin aim to mitigate these drawbacks with the recent advances in controlled- and slow-release fertilizers (CRFs and SRFs) by. This review explores the development and application of chitosan-based urea nanohybrids, formulated to modulate nitrogen release profiles and enhance nutrient-use efficiency. Techniques such as in situ copolymerization, emulsion cross-linking, and ionotropic gelation have enabled the encapsulation of urea into biodegradable matrices for controlled N_2 release. Advanced material characterization—via FTIR, SEM, XRD, and EDX—confirms the formation of multifunctional networks with tunable porosity, swelling capacity, and crystallinity. These smart formulations exhibit release patterns influenced by pH, particle size, polymer composition. Integration of co-factors like magnesium sulfate, rice husk ash, and nano-silica further elevate the nutrient-release kinetics. Experimental trials in diverse crops, from potatoes and rice to leafy greens, show enhanced root development, chlorophyll content, soil enzyme activity, and yield performance, all while reducing Nitrogen leaching and environmental burden. The potential of these "Next-generation fertilizers" to deliver nitrogen in a controlled, crop-responsive manner signals a paradigm shift in nutrient management. This review emphasizes deeper research into nanostructure–function relationships, field-level scalability, and eco-toxicological impact to drive next-generation fertilizer systems for sustainable agriculture.

Keywords: Controlled-release fertilizer, Chitosan nanohybrid, Nitrogen-use efficiency, Urea encapsulation, Sustainable agriculture

1. INTRODUCTION

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The rapid growth of the global population has intensified the demand for food, making developing nations depend on Agriculture for their livelihood where a significant portion of the population relies on crop production. As Nitrogen (N) is an essential macronutrient that significantly influences plant growth, yield, and biomass accumulation, it has been extensively supplied through fertilizers to meet the nutritional demands of high-yielding crop varieties and to mitigate associated productivity concerns [1-3]. Among nitrogen fertilizers, urea $[CO(NH_2)_2]$ is popular due to its high nitrogen content (46%), low cost, and ease of handling [4-11].

However, contrary to expectations, urea's effectiveness is unexpectedly suppressed by its rapid degradation in the soil–plant system, leading to substantial nitrogen losses through volatilization, leaching, and denitrification. These losses leads to low nitrogen use efficiency (30% - 50%) which pose significant environmental challenges, including eutrophication of aquatic systems, soil acidification, and greenhouse gas emissions (specially N_2O and NH_3). Furthermore the urea hydrolysis by urease enzymes in soil, escalates volatilization, especially under high pH and temperature conditions particularly in tropical and subtropical regions .

$$(NH_2)_2CO + 2H_2O \xrightarrow{\text{Urease}} (NH_4)2CO_3 \qquad (1)$$

$$(NH_4)_2CO_3 + 2H^+ \longrightarrow 2NH_4^+ + CO_2 + H_2O \qquad (2)$$

$$2NH_4^+ + 3O_2 \xrightarrow{\textit{Nitrosomonas,Nitrococcus}} NO_2^- + 2H_2O + 4H^+ + \text{energy} \qquad (3)$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^- + \text{energy} \qquad (4)$$

Another immediate and simultaneous natural reaction, takes place in the soil that converts nitrite to nitrate nitrogen [12-15].

Nonetheless, uncontrolled use of urea alters soil microbial dynamics, disrupts nutrient cycling, and results in accumulation of toxic nitrate residues in food crops, particularly in mono-cropping systems, raising concerns about long-term soil health, soil structural degradation ,food safety, environmental sustainability [16-17].

To address these limitations and disadvantages, Controlled Release Fertilizers (CRFs) have emerged as a promising alternative to integrate nutrient release with crop uptake demand, mitigating environmental degradation, and supporting sustainable crop production, with the modulation of the nutrient release kinetics . Both the chemical modification and encapsulation techniques have been used to develop CRFs. Modification of urea into urea-aldehyde condensation products like urea-formaldehyde , urea triazone , crotonylidene diurea, and isobutylidene diurea and physical encapsulation techniques involving coatings with hydrophobic polymers, sulphur, polyolefins, or hydrogels are some popular approaches. Although the large-scale implementation of CRFs faces challenges due to complex manufacturing processes, high production costs, and non-biodegradability of some synthetic coatings [18-22].

Recent technologies have delve the potential of synthetic (e.g. acrylamide, urethane, epoxy, melamine, and phenol resins) as well as biodegradable polymers (e.g. chitosan, alginate, cellulose, and starch) to serve as carriers for controlled release formulations. These systems offer sustainable alternatives to conventional CRFs due to their biodegradability, non-toxicity, and soil-conditioning properties [23-25]. At present nanofertilizers are emerging as an alternative approach in sustainable agriculture practices. Nano scale encapsulation of nutrients allows controlled and sustained nutrient delivery, induced plant uptake, and reduced frequent application. Studies with the use of nano-nitrogen formulations have shown notable improvements in crop yield, nutrient content, and food quality assessments. These approaches further improve the responsiveness of nutrients, representing a merging of materials science, agriculture, and environmental engineering [26-32].

Natural biopolymers like *Chitosan* have emerged as a potential substitute due to its unique functional and physicochemical properties. It is a biodegradable, and bio-resorbable polysaccharide extracted from the deacetylation of chitin, a structural polymer found in the exoskeletons of crustaceans and fungal cell walls. It comprises β-(1,4)-linked D-glucosamine and N-acetyl-D-glucosamine units, which offers integral antimicrobial activity, film-forming ability, non-toxicity, and high water-retention capacity. As a conveniently available and low-cost material, chitosan presents a sustainable alternative to synthetic polymers and inorganic coatings, which makes chitosan an economic and ecological fertilization strategy. These features make chitosan suitable for both biomedical based pharmaceutical applications and agricultural renovation, particularly in the fertilizer delivery [33-35]. Furthermore, Chitosan's high swelling capacity, chemical modifiability, and stable cross-linked matrix support the development of nanostructured carriers with uniform, spherical morphology, making it an exceptional option for encapsulating chemicals like urea, enabling controlled and sustained nitrogen release over time [36-37].

According to researchers chitosan-based nanohybrids, combined with urea and other bioactive compounds or biodegradable and soil-conditioning polymers (e.g., gelatin, alginate, polyacrylamide), can significantly improve the release kinetics , reduce nutrient loss and soil erosion. Chitosan composites with inorganic components such as magnesium compounds or montmorillonite clays have been analyzed to further enrich the mechanical stability and nutrient retention of the formulations [38-40].

Additionally, the uniqueness of chitosan in forming microspheres and nanocarriers via different cross-linking techniques (e.g., glutaraldehyde, genipin, or ionic gelation) provides a broad spectrum for strategy specialized fertilizer delivery systems [41].

In light of the growing importance of sustainable agricultural practices, this review aims to critically evaluate the present development in the formulation design, modification, and application of chitosan-based materials, particularly in the composition of Urea-incorporated microspheres and nanohybrids. Furthermore it facilitates an extensive and relative analysis of the formulation, characterization, and agricultural effectiveness of urea-based controlled-release fertilizers (CRFs) incorporated with biopolymers such as chitosan, acrylamide, alginate, gelatin, and supplemented with additives like silicone, magnesium, and glutaraldehyde. It analyzes the interaction mechanisms, agro economic execution, and environmental impact, with the alignment of the principles of green chemistry for improved crop productivity and soil health.

2. CHITOSAN AS A RENEWABLE BIOMATERIAL

2.1 Historical background and discovery of Chitin and Chitosan

Chitin is a naturally occurring polysaccharide and the second most abundant biopolymer after cellulose. It is predominantly found in the exoskeletons of arthropods(crustaceans and insects), in the cell walls of fungi and certain bacteria. Deacetylation of chitin produces Chitosan which is considered one of the most accomplished natural polymers [42-45].

The discovery of chitin and its derivative, chitosan, marks a pivotal development in the study of natural polysaccharides. In 1811, French Professor Henri Braconnot first isolated an insoluble material from mushrooms, which he named “fungine.” This substance was later identified as chitin. In 1823, Auguste Odier extracted a related compound from beetle cuticles and coined the term “chitin,” deduced from the Greek word *chitōn*, meaning tunic or covering. In 1843 Lassaigne demonstrated the presence of nitrogen in chitin, establishing its distinction from other polysaccharides. In 1859, Professor Charles Rouget discovered that chitin could be transformed into a water-soluble form through alkaline treatment. This marked the first step toward the production of chitosan, which was later formally named by Hoppe-Seiler in 1870 [46].

2.2 Structure–Function Interrelationships in Chitosan: Biomolecular Origins and Physicochemical Characteristics

Chitosan is widely appraised for its combination of physicochemical and biological properties. Its biodegradable, biocompatible, and non-toxic properties make it suitable for the diverse range of applications in agriculture, medicine, pharmaceuticals, cosmetics, and food industries. Chitosan is a linear, cationic polysaccharide consist of repetitive units of β-(1→4)-linked D-glucosamine (deacetylated units) and N-acetyl-D-glucosamine (acetylated units) (Figure 1). It is the partial deacetylation of chitin. Table 1 describes the various natural sources of Chitosan [47-48].

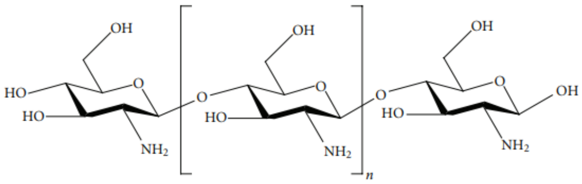

Figure 1 : Structure of Chitosan

Chitosan closely resembles the structure of cellulose, the key difference being the presence of an amino group at the C-2 position of the glucose ring in chitosan, replacing the hydroxyl group found in cellulose. (Figure 2)

The high degree of uniqueness in chitosan is exhibited due to its functional groups—primary amine, and both primary and secondary hydroxyl groups. These groups influence the polymer’s solubility, especially in acidic environments where the protonation of the amine group converts it into a polyelectrolyte, providing a positive charge to chitosan which supports the binding with negatively charged surfaces or polyanions.The presence of reactive amino and hydroxyl functional groups defines the chitosan's antimicrobial and antifungal activity [49-55].

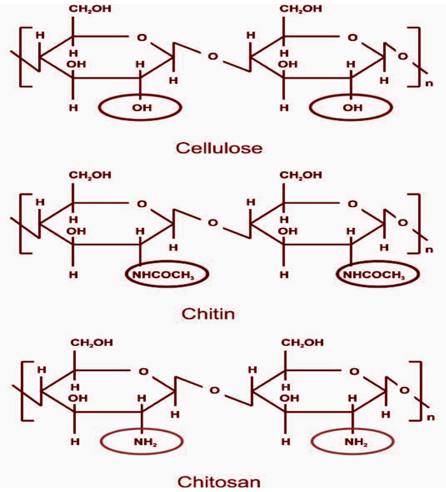

Figure 2 : Structural similarity between Cellulose, Chitin and Chitosan

Table 1: Natural sources of Chitin and chitosan

Source	Chitin percentage
Podophthalmus vigil	
Paralithodes camtschaticus	
Carcinus mediterraneus	
Water lobster	17
Crawfish (*Palinurus vulgaris)*	
Shrimp	22
Aristens antennatus	
Krill	2.4 to 2.7%
Daphnia longispina	
Anax imperator	
Hyrophilus piceus	
Notonecta glauca	
Agabus bipustulatus	
Asellus aquaticus	
Molluscs	10%
Squid pens	
Loligo sp	
Todarodes pacificus	
Arthropods	10-15%
Spiders	
Geolycosa vultuosa	
Nephila edulis	
Cockroaches	
Scorpions	30%
Mesobuthus gibbosus	
Beetles	5%
Bombyx mori	
Holotrichia parallela [34]	
Leptinotarsa decemlineata	
Brachiopods	26%
Lingula seta	
Fungus (cell walls)	15%
Ascomydes	
Mucor rouxii	
Blastomycota	
Blastocladiaceae Chytridiomycota	
Chytridiaceae	
Aspergillus niger	
Aspergillus phoenicis	

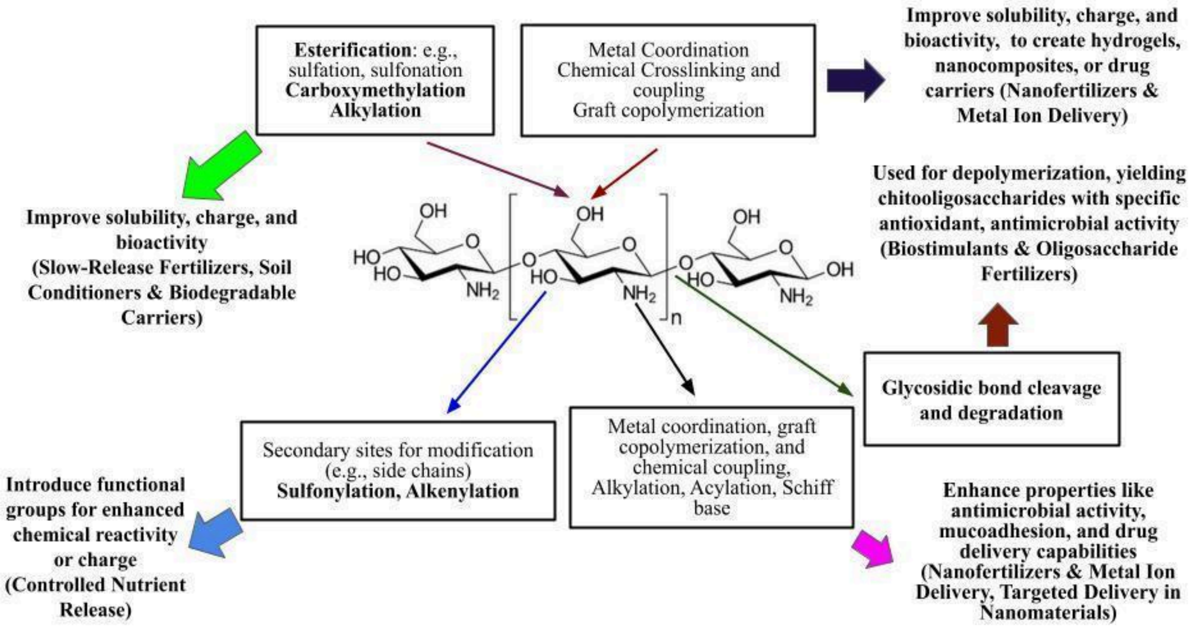

Figure 3: Chemical modifications of chitosan, linked to specific applications in fertilizers and nanomaterials

These groups also promote cross-linking and chemical modifications, enhancing its utility in the formation of composites and delivery systems with the encapsulation property and controlled-release applications, such as in the formulation of slow-release fertilizers. Chitosan demonstrates a high swelling ratio, strong water retention capacity, and film-forming ability, while its nanoparticles typically exhibit spherical morphology and uniform size distribution [56-57].

3.COMPARATIVE EVALUATION OF SYNTHETIC METHODOLOGIES FOR CHITOSAN-BASED CONTROLLED RELEASE FERTILIZERS

3.1 Refluxed In Situ Copolymerization Technique

Among the widely adopted methods is refluxed *in situ* copolymerization technique, which involves cross-linking urea with chitosan and acrylamide, with further modification through silicone doping and N,N′-methylenebisacrylamide cross-linking (Figure : 4A). The resulting microstructures produce chemically crosslinked hydrogels with improved mechanical stability, hydrophobicity and controlled nutrient release capacity. However, questions regarding characterizing the thermal stability and degradation kinetics of the Controlled Release Fertilizers formulations, determining accurate release profiles under real-world soil conditions, considering variations in pH and microbial activity, and investigating the precise role of silicone doping in inducing the linear and deformed sigmoid release patterns remain underscoring the need for further investigation before large-scale application [58]. Moreover, the requirement of organic solvents and increased temperatures in this technique, may limit its environmental friendliness and scalability for green agriculture.

3.2 Ionic Gelation and Nanoencapsulation Approach

In contrast, ionic gelation, using sodium Tripolyphosphate (TPP) is a widely used, and non-toxic method for creating hydrogels, microparticles, and nanoparticles. This technique relies on the electrostatic interaction between a positively charged polymer and the negatively charged TPP, which acts as a crosslinking agent. In a mildly acidic environment, such as acetic acid, chitosan’s amino groups become protonated, imparting a positive charge to the polymer chains. The negatively charged oxygen molecules in the phosphate groups of the TPP are electrostatically attracted to the positive amino groups on the chitosan. This causes intermolecular and intramolecular ionic cross-linking, which instantly forms a three-dimensional gel matrix that precipitates into spherical chitosan–urea nanoparticles (Figure: 4B). Chitosan–urea nanohybrids made via TPP-facilitated ionic gelation yield a colloidal dispersion with high surface area and optimized release profile. A distinct concentration-dependent behavior, wherein increasing urea loading (%w/v) resulted in a proportional rise in available urea concentration , confirming the role of chitosan as an effective matrix for controlled nutrient release. Notably, the nanoparticle size decreased with higher urea content, likely due to the increased positive charge density of urea molecules. This method offers flexible delivery systems, appropriate for foliar or drip irrigation systems, with promising nutrient release kinetics. Despite these advantages, nanoparticles may be less mechanically stable compared to acrylamide-cross linked systems for which the resulting materials may exhibit lower structural integrity and faster degradation rates compared to covalently crosslinked systems. Moreover their colloidal stability during storage and handling remains a primary concern [59-70]

3.3 Tablet Formulation and Chitosan Coating Methods

Magnesium and chitosan provides a synergistic effect in regulating nutrient release from urea–magnesium fertilizer tablets prepared from rice husk ash, urea, magnesium sulfate and natural rubber where Magnesium acted as a matrix stabilizer and nutrient regulator, while chitosan functioned as a diffusion-controlling polymer (Figure: 4C). Chitosan coating forms a semi-permeable film around the tablets, controlling the release of urea, ammonia, and nitrate while maintaining optimal dissolution for plant uptake, and intriguingly, it accelerates magnesium-ion release, possibly through ionic interactions between the amino groups of chitosan and magnesium ions. This dual behavior highlights the delicate balance between nutrient retention and availability in the coated system. This solid form is user friendly with promising results in water retention and nutrient release properties. But at the same time, coating uniformity and mechanical integrity may be variable [71].

3.4 Biopolymer Bead Formation via Ionotropic Gelation

Another innovative technique is the formation of Chitosan-alginate and gelatin-alginate beads created by ionic interaction with calcium ions, producing biodegradable, porous beads suitable for moderate urea entrapment and slow release. These beads are easy to prepare under mild conditions and advantageous for encapsulating urea or other nutrients, facilitating gradual release while maintaining biodegradability and making it environmentally friendly. The combination of biopolymers allows for controllable pore structure and swelling behavior, although encapsulation efficiency and nutrient retention remain points for enhancement [72].

3.5 Emulsion Cross-Linking and Aldehyde-Based Systems

The application of formaldehyde and glutaraldehyde in emulsion-based crosslinking offers strong mechanical stability and controlled degradation (Figure: 4D). In this method chitosan dispersed in the aqueous phase of a water-in-oil emulsion is crosslinked using glutaraldehyde. It enables the fabrication of rigid and uniform microspheres with a controlled nutrient release profile. However, the dependency on toxic crosslinkers and organic solvents present environmental and regulatory challenges, especially in food-related crop applications [73].Comparative analysis of selected methodologies are given in **Table : 2**.

4. CHITOSAN-UREA NANOHYBRIDS: MODULATION OF SOIL ENZYMATIC ACTIVITY AND ENHANCEMENT OF GROWTH TRAIT

4.1 Influence of Chitosan–Urea Nanohybrids on Soil Enzymatic Activities and Plant Growth Dynamic

Soil microbial function and nutrient cycling efficiency is enhanced through indicators such as Soil enzymatic activities such as dehydrogenase and urease which displayed distinct trends in response to different nitrogen formulations and application levels. Dehydrogenase activity, a key indicator of overall microbial oxidative metabolism, varied among treatments during the cultivation of nitrogen-responsive crops potato cultivar ‘Kufri Pukhraj’. The chitosan-urea nanoparticle formulation consistently stimulated dehydrogenase activity, often performing on par with or better than conventional urea. The chitosan-urea nanoparticle treatments maintain a steady enhancement of microbial metabolism, suggesting their strong ability to support soil biological processes. This sustained enhancement suggests that the chitosan-urea nanoparticle system provides a favorable microenvironment for microbial proliferation and activity.In contrast, urease activity, which plays a central role in urea hydrolysis and subsequent nitrogen mineralization, exhibited a different response pattern. Both chitosan-urea nanoparticle and conventional urea treatments supported similar urease activity across fertilizer levels, reflecting comparable nitrogen-release capacities. However, the chitosan nanoparticle formulation alone consistently exhibited lower urease activity irrespective of application rate, likely due to the regulatory influence of the chitosan matrix in modulating urea diffusion and enzymatic hydrolysis, thereby reducing potential nitrogen losses.At early crop growth stages, chitosan-urea nanoparticles induced a significant increase in dehydrogenase activity,attributable to the biodegradable chitosan matrix serving as an additional carbon substrate that enhances microbial respiration.This elevated activity gradually stabilized as the crop matured. As the crop progressed, this activity stabilized, reflecting the establishment of a balanced microbial community. Conversely, urease activity peaked under conventional urea at later growth stages, whereas chitosan-urea nanoparticle treatments maintained moderated enzymatic activity, consistent with a controlled-release mechanism. These findings corroborate earlier studies reporting delayed urea hydrolysis and improved microbial respiratory activity under biodegradable or polymer-coated nitrogen fertilizers.The application of chitosan–urea nanohybrids has shown considerable potential in enhancing the growth performance of potato cultivar ‘Kufri Pukhraj’ wherein the stimulation of soil enzymatic activities—particularly those linked to nutrient mineralization and microbial metabolism—correlates with marked improvements in primary root development, shoot biomass accumulation, and overall tuber productivity. Notably, these nanohybrids coupled with improved rhizospheric microbial activity stimulate early root growth,

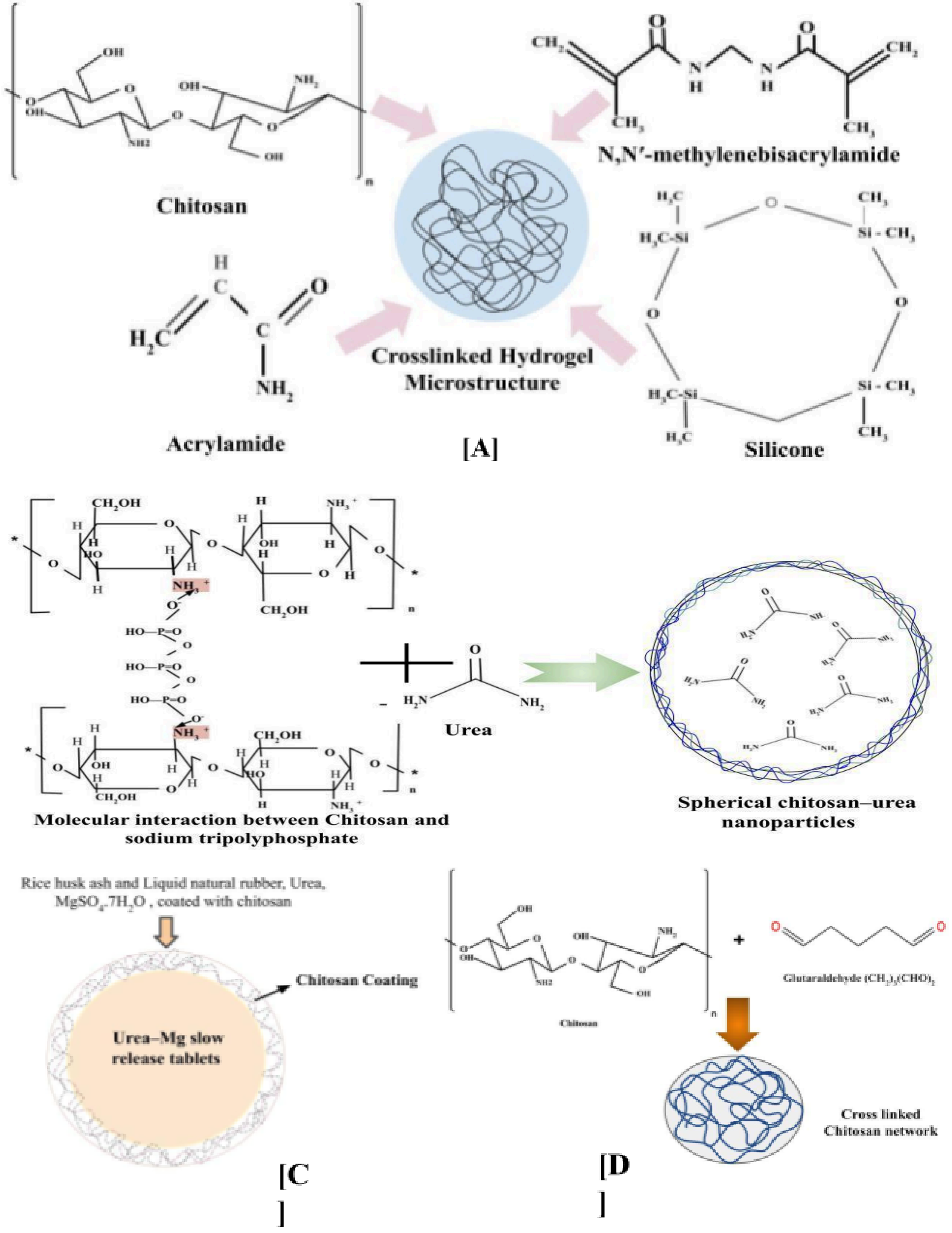

Figure 4: Comparative overview of major synthesis routes—[A]: Refluxed In Situ Copolymerization, [B]: Ionic Gelation and Nanoencapsulation, [C]:Chitosan Coated Tablet Formulation, [D]: Emulsion Cross-Linked Aldehyde-Based Systems —used in producing chitosan-based controlled-release fertilizers.

Table 2: Comparative Overview of Chitosan-Based Fertilizer Preparation Methods

Methodology	Crosslinking Agent	Form	Advantages	Disadvantages	References
Chitosan-Acrylamide	AIBN + MBA	Granules	Covalent crosslinking leads to a stable 3D network. High nutrient entrapment efficiency and controlled release.	Use of organic solvents and synthetic initiators raises environmental concerns.	[58]
Ionic Gelation	Tripolyphosphate	Nanoparticles	Simple, green method suitable for nanoparticle formation. Does not require high energy input or toxic reagents. Biocompatible, easy to scale up.	Limited mechanical strength and faster degradation.	[59-70]
Chitosan-Coated Tablets (Surface Application)	None (coating only)	Tablets	Chitosan acts as a semi-permeable barrier for nutrient release Simple, does not require complex synthesis.	Coating may be uneven; less efficient in regulating long-term nutrient release.	[71]
Ionotropic Gelation Beads	$CaCl_2$ (ionic)	Beads	Combines multiple natural polymers to tune swelling and release behavior. Eco-friendly, low-cost, customizable porosity.	Lower encapsulation efficiency compared to synthetic routes.	[72]
Emulsion Cross-Linking	Glutaraldehyde/Formaldehyde	Microspheres	Allows formation of microspheres with controlled size distribution. Excellent control over morphology and release kinetics.	Toxic crosslinkers and organic solvents may limit use in food-related agriculture	[73]

highlighting the importance of sustained nutrient availability achieved through nano-enabled delivery systems. In contrast, urease activity, which plays a central role in urea hydrolysis and subsequent nitrogen mineralization, exhibited a different response pattern. Both chitosan-urea nanoparticle and conventional urea treatments supported similar urease activity across fertilizer levels, reflecting comparable nitrogen-release capacities. However, the chitosan nanoparticle formulation alone consistently exhibited lower urease activity irrespective of application rate, likely due to the regulatory influence of the chitosan matrix in modulating urea diffusion and enzymatic hydrolysis, thereby reducing potential nitrogen losses.At early crop growth stages, chitosan-urea nanoparticles induced a significant increase in dehydrogenase activity,attributable to the biodegradable chitosan matrix serving as an additional carbon substrate that enhances microbial respiration.This elevated activity gradually stabilized as the crop matured. As the crop progressed, this activity stabilized, reflecting the establishment of a balanced microbial community. Conversely, urease activity peaked under conventional urea at later growth stages, whereas chitosan-urea nanoparticle treatments maintained moderated enzymatic activity, consistent with a controlled-release mechanism. These findings corroborate earlier studies reporting delayed urea hydrolysis and improved microbial respiratory activity under biodegradable or polymer-coated nitrogen fertilizers.The application of chitosan–urea nanohybrids has shown considerable potential in enhancing the growth performance of potato cultivar ‘Kufri Pukhraj’ wherein the stimulation of soil enzymatic activities—particularly those linked to nutrient mineralization and microbial metabolism—correlates with marked improvements in primary root development, shoot biomass accumulation, and overall tuber productivity. Notably, these nanohybrids coupled with improved rhizospheric microbial activity stimulate early root growth, highlighting the importance of sustained nutrient availability achieved through nano-enabled delivery systems.

Moreover, CS–urea NPs at reduced nitrogen application rates exhibit a more favorable response pattern by optimized tuber yield, highlighting their value in improving productivity under lower fertilizer inputs. Beyond root and tuber traits, nano-chitosan–urea composites remarkably enhance shoot growth metrics, including fresh and dry biomass, compared with equivalent doses of conventional urea. While the conventional urea shows inconsistent effects on root growth and a

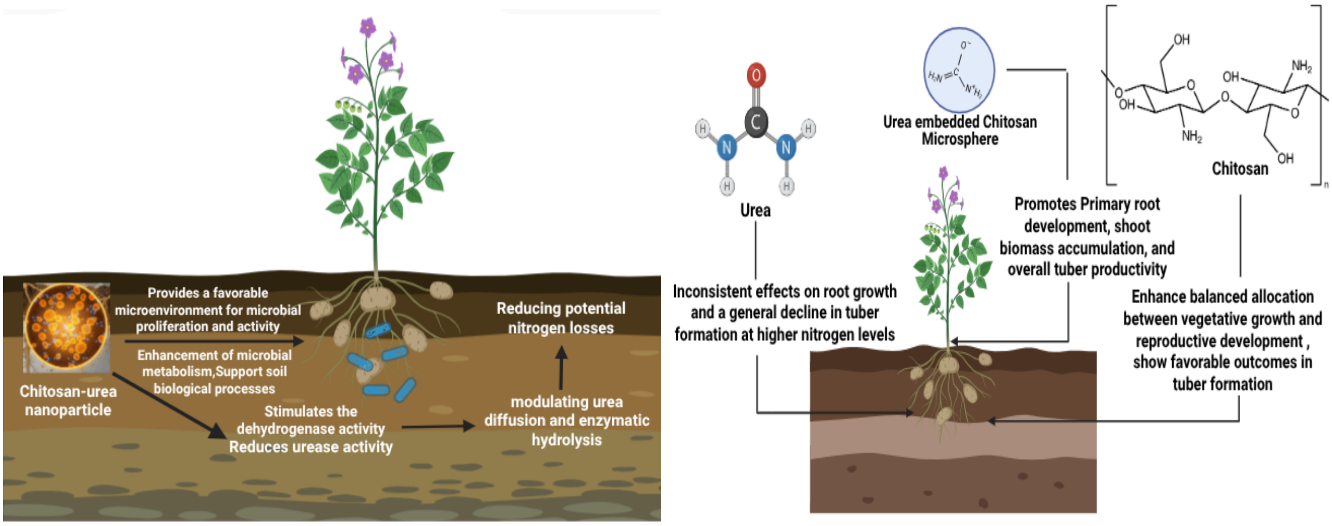

Figure 5: Interaction pathway illustrating how chitosan–urea nanohybrids modulate soil biochemical enzyme activities, leading to enhanced plant growth dynamics.

general decline in tuber formation at higher nitrogen levels ,Chitosan nanoparticles enhance balanced allocation between vegetative growth and reproductive development when applied at moderate nitrogen levels, and show favorable outcomes in tuber formation (Figure :5). These improvements reinforce the premise that slow-release nitrogen systems not only enhance nutrient use efficiency but also contribute to greater vegetative vigor. Multi-year field evaluations of controlled-release fertilizers show similar patterns in improvements of potato yield performance across cultivars [59,63].

Chitosan microsphere-based controlled-release nitrogen fertilizers have demonstrated remarkable superiority over conventional urea reflecting improvements in both physiological and biochemical functions in Chinese cabbage (Figure: 6). While the equivalent urea doses shows limited or adverse effects, especially on root development,chitosan based formulations enhance chlorophyll fluorescence efficiency,chlorophyll content, photosynthetic rate, transpiration rate, correlating improved physiological efficiency and biochemical traits of the plant such as improved plant height, leaf growth, biomass and increased sugar, protein,polyphenols,flavonoids contents respectively [73].

Chitosan–urea nanohybrids have also demonstrated clear advantages in rice cultivation, outperforming conventional urea across both vegetative and reproductive growth parameters. Its applications are associated with notable enhancements in key physiological processes, including chlorophyll biosynthesis, canopy development, and overall nutrient assimilation, reflecting more sustained and efficient nitrogen delivery (Figure: 7). Reduced conventional urea inputs supplemented with CS–urea NH have been shown to promote greater leaf expansion and improved light

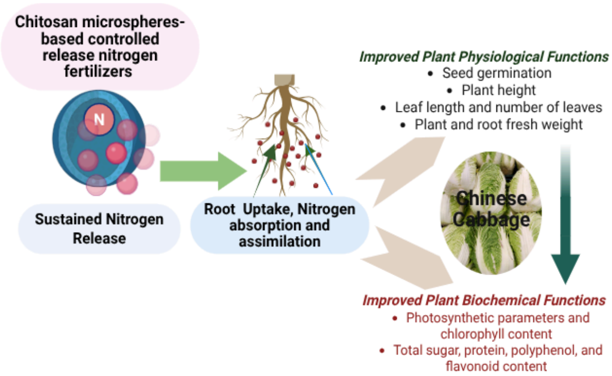

Figure 6: Chitosan microsphere–based controlled-release nitrogen fertilizers improve Chinese cabbage growth by boosting nutrient uptake, antioxidant activity, and metabolite accumulation

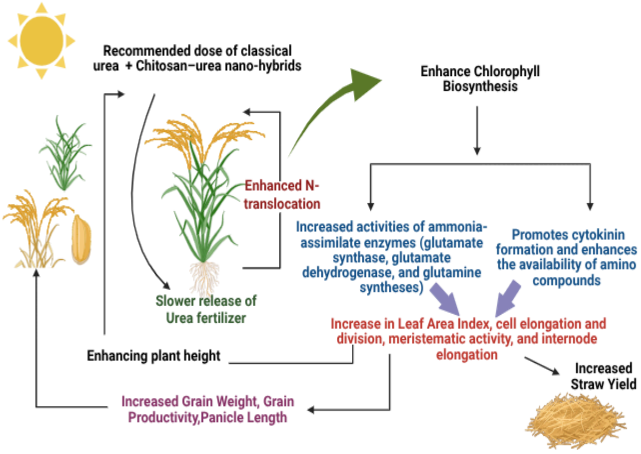

Figure 7: Illustration showing how urea–chitosan nanohybrids improve nitrogen uptake and grain yield in *Oryza sativa* L., enabling reduced dependence on synthetic urea.

interception, contributing to a more productive canopy structure. Yield evaluations similarly indicate that these treatments support more vigorous plant growth, improved panicle development, and increased biomass accumulation when compared with traditional fertilization practices. Importantly, combinations of lowered urea rates with CS–urea NH are capable of maintaining performance comparable to full-dose urea, underscoring their potential to reduce nitrogen dependency without compromising crop productivity.By facilitating nitrogen release in coordination with plant demand, CS–urea NH improves both assimilation efficiency and nutrient utilization. Parallel studies confirm comparable higher utilization efficiency with nano-urea composites such as urea-hydroxyapatite nanohybrids, achieving reductions in urea usage in rice while simultaneously enhancing yield performance. These responses highlight the translational potential of nano-fertilizer technologies across diverse agro-ecosystems [74-76].

These applications collectively strengthen the synergistic impact of sustained nutrient release and biopolymer-mediated delivery, establishing the formula as a highly efficient, low-toxicity strategy for optimized nitrogen use and improved crop performance. It suggests that nano-chitosan–urea composites can reduce nitrogen requirements while maintaining or improving crop productivity, representing an important advancement toward more sustainable and resource-efficient agricultural practices. The improved nitrogen uptake efficiency is presumed to result from the integration of several coordinated mechanisms which facilitate robust physiological responses including:

- Enhanced foliar uptake via phloem transport.
- Activation of ammonia-assimilation enzymes (e.g., glutamate synthase).
- Improved cytokinin production and amino acid availability.
- cell division, meristematic activity, and internode elongation.
- CS–urea NH serve as a controlled-release system, aligning Nitrogen availability with crop demand phases (e.g., tillering and panicle initiation).
- Improve photosynthesis, transpiration, and gas exchange due to better N metabolism.
- Enhance the synthesis of carbohydrate and protein, aiding grain filling and increasing grain mass.
- Reduce tiller abortion and enhance reproductive tillering through better early vegetative Nitrogen uptake [77-85]

4. CONCLUSIONS

The development of chitosan-based controlled-release urea fertilizers ranging from chitosan-acrylamide copolymers to chitosan-alginate, gelatin-based beads, and silicone-doped microspheres—presents a promising innovation demonstrating improved nitrogen use efficiency, prolonged nutrient release, and enhanced crop performance.These bio-based CRFs significantly reduce nutrient losses, minimize environmental pollution, and improve soil enzymatic and microbial dynamics when compared to conventional chemical fertilizers.

These formulations have demonstrated effective nitrogen encapsulation, extended release kinetics regulated by diffusion and swelling mechanisms, and significant decline in urease activity and microbial populations associated with nitrogen loss pathways. The integration of chitosan with different cross-linkers and encapsulating agents enables optimization of release profiles according to crop needs, environmental conditions, and application methods. The noted alteration of soil biochemical properties (pH, EC, OC) and suppression of nitrification rates supports their environmental compatibility by reducing nitrate leaching and greenhouse gas emissions. Most notably, the interaction of CRFs with nitrifying and denitrifying microflora showed a significant downregulation in ammonia-oxidizing and nitrate-reducing bacteria, aligning with the reduced nitrate leaching and supporting the controlled nutrient release hypothesis. These findings indicate the divergent functional roles of dehydrogenase and urease in soil microbial dynamics and nutrient cycling. Time-course evaluations further supports the potential of chitosan-based formulations to accelerate biodegradation through microbial activity while modulating nitrogen dynamics to reduce environmental degradation.

Despite the refinement, several critical research questions remain unresolved and unanswered. These include the thermokinetics of nitrogen release patterns under heterogeneous environmental scenarios, the precise behavior of doped CRFs in varied soil pH, and the long-term effects on microbial diversity and soil health.

In conclusion, the transition from the conventional urea to urea encapsulated in biopolymers such as chitosan is feasible and highly desirable from both agronomic and environmental aspects. The collective findings demonstrate that chitosan-based CRFs can drastically reduce nitrogen loss and mitigate adverse ecological impacts without compromising the yield. The pragmatic adaptability of these systems in formulation design allows them to be specific for crops, climates, and soil conditions, facilitating progress in broader commercialization and application in sustainable agriculture. All together, the synthesis, characterization, and application of chitosan-based urea nanofertilizers represent a significant advancement in resource-efficient agriculture. Future research should focus on expanding to large-scale field implementation and evaluating their influence on soil microbial diversity, long-term soil health, and multi-season crop productivity to further support their practical implementation into mainstream agricultural practices.

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