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Biopolymer-Coated Urea as a Sustainable Controlled-Release Nitrogen Fertilizer: Design, Characterization, and Environmental Performance

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KEYWORDS

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ABSTRACT:

Nitrogen use efficiency (NUE) of conventional urea rarely exceeds 50% under field conditions because rapid urease-catalysed hydrolysis liberates reactive nitrogen faster than crops can assimilate it, driving losses through ammonia volatilisation, nitrate leaching, and denitrification. This investigation describes the development and laboratory-scale evaluation of a fully biodegradable, dual-layer encapsulated urea product intended to extend nitrogen availability and reduce these losses. A five-constituent biopolymer blend comprising polyvinyl alcohol (PVA), corn starch, pharmaceutical-grade gelatin, gum arabic, and glycerol was deposited onto granular urea in five sequential spray-coating and thermal-curing cycles on a rotating pan coater, then sealed with an outer neem oil (Azadirachta indica) hydrophobic layer cured at 40°C. The finished product was characterised by scanning electron microscopy (SEM), gravimetric moisture-uptake measurement, aqueous dissolution testing over 20 days, and continuous pH monitoring. SEM examination confirmed a structurally intact, fibrous, defect-free biopolymer membrane with intimate adhesion to the granule substrate; coating weight gain measured $8.2 \pm 0.4\%$ and mean membrane thickness was approximately 85 µm by cross-sectional analysis. Bare urea dissolved entirely within 5 min, whereas the coated product released nitrogen progressively over 15–20 days; Moisture absorption at 75% relative humidity was reduced by approximately 50% compared with uncoated controls. pH medium during coated-granule dissolution remained at 7.2–7.4, substantially below the 7.8 recorded for conventional urea, suppressing the ammonium–ammonia shift responsible for atmospheric nitrogen losses. The neem-oil-sealed biopolymer system is an effective, microplastic-free, scalable platform for precision nitrogen management compatible with sustainable agricultural practice.

1. Introduction

Global food security increasingly depends on the efficient use of nitrogen fertilizers, yet conventional urea is the world's most widely applied nitrogen source (~46% N) that delivers its nutrient payload with striking inefficiency. Under field conditions, rapid urease-catalysed hydrolysis converts urea to ammonium carbonate within hours of soil application, liberating reactive nitrogen far faster than crops can assimilate it. The result is a nitrogen use efficiency (NUE) of only 30–50% [1–4], with the remainder lost as ammonia to the atmosphere, nitrate to groundwater, or nitrous oxide (N_2O) which acts a potent greenhouse gas through denitrification [5,6]. Beyond these direct losses, chronic over-application promotes soil acidification, depletion of organic carbon, suppression of beneficial microbial communities, and downstream eutrophication of aquatic ecosystems, while the energy-intensive Haber–Bosch production route heightens economic vulnerability for smallholder farmers [7,8].

Controlled-release fertilizers (CRFs) address these limitations by interposing a physical barrier between the soluble nutrient core and the soil solution, modulating nitrogen flux to better match plant uptake demand [9]. However, first-generation CRFs is based on sulfur shells or synthetic polymers (polyurethane, polyethylene) generate persistent microplastic residues upon coating rupture [10]. This environmental issues have driven interest in fully biodegradable alternatives derived from renewable macromolecules such as starch, gelatin, chitosan, gum arabic, and polyvinyl alcohol (PVA) [11]. Single-component biopolymer coatings, however, are prone to rapid swelling and premature release [12]; multi-constituent blends overcome this by combining the structural rigidity of PVA, the adhesive viscosity of starch, the amphiphilic film-forming character of gelatin, and the void-filling stabilisation of gum arabic, with glycerol plasticisation reducing film brittleness. Neem oil (Azadirachta indica), rich in triterpenoid limonoids, adds pronounced surface hydrophobicity and secondary nitrification-inhibition activity [13,14].

Despite these promising component properties, the systematic integration of all five biopolymers with a neem oil overlay via a multi-step layer-by-layer (LbL) spray protocol has received limited attention. The present study therefore fabricated and characterised a five-component biopolymer/neem-oil dual-layer coated urea, evaluating it for coating morphology, hygroscopic moisture uptake, aqueous nitrogen release kinetics, and medium pH dynamics. Release data were modelled with the Higuchi and Korsmeyer–Peppas equations to elucidate the dominant transport mechanism. By integrating biodegradable materials with green chemistry principles, this work aims to deliver a scalable nitrogen management platform that advances NUE while safeguarding soil and water quality [15].

2. Materials And Methods

2.1 Materials

Spherical granular urea with a declared nitrogen content of 46% (w/w) was procured commercially and used without further purification as the fertilizer core. The biopolymer coating matrix was assembled from four macromolecular constituents: partially hydrolysed polyvinyl alcohol (PVA, degree of hydrolysis ~88%), food-grade corn starch, pharmaceutical-grade gelatin (Type B, bloom strength ~200 g), and spray-dried gum arabic (acacia gum). Glycerol of reagent grade (≥99.5% purity) was incorporated as a chain-mobility-enhancing plasticiser. Technical-grade cold-pressed neem oil (Azadirachta indica), characterised by its high azadirachtin content and pronounced hydrophobicity, was selected for the secondary outer coating. Absolute ethanol (99.9% v/v) served as the volatile co-solvent for dispersing neem oil. All polymer solutions and dilutions were formulated using freshly prepared deionised water (conductivity <1 µS cm^{-1}) to exclude ionic interference during dissolution experiments.

Figure 1. Raw materials used in the preparation of biopolymer-coated urea

Preparation of Biopolymer Coating mix design for urea coating.

Table 1. Materials and their functional roles in the preparation of coated urea

S. No	Material	Quantity Used	Functional Role
1	Urea Granules	100g	Core nitrogen fertilizer (46% n)
2	Starch	5g	Natural binder and viscosity enhancer
3	Gelatin	4g	Film- forming agent
4	Polyvinyl Alcohol (PVA)	5g	Structural backbone polymer
5	Gum Arabic	4g	Adhesion promoter and stabilizer
6	Glycerol	4ml	Plasticizer to improve coating flexibility
7	Deionized Water	100ml	Solvent for polymer dissolution
8	Neem oil	3ml	Hydrophobic outer seal and natural nitrification inhibitor
9	Ethanol(99.9%)	5ml	Volatile carrier solvent for neem oil

2.2 Preparation of Biopolymer Coating Solution

The quaternary biopolymer coating solution was formulated by a stepwise hot-dissolution procedure. Deionised water (100 mL) was charged into a 250-mL glass beaker and heated to 75 ± 2°C on a temperature-controlled magnetic hot plate while maintaining continuous agitation at 500 rpm. PVA (5 g) was introduced first and allowed to dissolve completely, yielding a clear viscous base solution; corn starch (5 g) was then added incrementally to avoid lump formation. Once a uniform PVA–starch matrix was established, gelatin (4 g) and gum arabic (4 g) were added sequentially with continued stirring to integrate their respective film-forming and adhesive functionalities. Glycerol (4 mL) was introduced last to act as a chain-flexibility modifier. The combined mixture was stirred continuously for 60 minutes at process temperature until a fully homogeneous, translucent, high-viscosity solution free of undissolved particulates was obtained. The solution was cooled to 55°C prior to spraying to prevent premature drying in the nozzle.

2.3 Spray Coating of Urea Granules

Encapsulation of urea granules was carried out on a laboratory-scale rotating pan coater fitted with a variable-flow peristaltic pump connected to an air-atomizing spray nozzle (orifice diameter 0.8 mm). The pan geometry and rotational dynamics promoted continual tumbling of the granule bed, ensuring all granule surfaces were exposed to the spray plume during each application cycle.

A weighed 100 g charge of urea granules was loaded into the rotating pan set to 40–50 rpm. The warm biopolymer solution was delivered at a controlled spray rate while heated inlet air (45 ± 2°C) was directed continuously over the tumbling bed to remove solvent moisture and consolidate each deposited film before the next spray application commenced. The moderate pan speed was selected to balance centrifugal dispersion of the spray against granule–granule collision intensity, minimizing both agglomeration and impact-induced coating abrasion.

2.3.1 Multi-Layer Spray Deposition (5-Layer Process)

The coating was applied in five sequential spray-coating and curing cycles:

Layers 1 and 2 (priming cycles): The initial two spray passes deposited thin primer coats to establish adhesion to the urea crystal surface, each followed by a 30-minute forced-air drying period at 45°C to consolidate the film before the subsequent layer was applied.

Layers 3 and 4 (consolidation cycles): Two further spray passes incrementally increased membrane thickness; an intermediate thermal curing step between these layers promoted inter-layer polymer entanglement and enhanced overall mechanical resistance to compressive and hydrostaticstress.

Layer 5 (finish coat): The terminal biopolymer layer was applied at a reduced spray rate to achieve a smooth, tack-free surface, then cured at 50°C for 45 minutes to drive off residual moisture and complete film coalescence.

This sequential spray–cure protocol afforded independent control over the thickness of each individual stratum and effectively precluded the burst-release artefact that typically accompanies the application of a single thick coat.

2.3.2 Secondary Hydrophobic Spray Coating (Neem Layer)

Following completion of the five-layer biopolymer coating, a secondary hydrophobic seal was applied. Neem oil (3 mL) was dissolved in absolute ethanol (5 mL) under mild agitation at ambient temperature to yield a homogeneous low-viscosity spray solution. This formulation was then atomised uniformly onto the polymer-coated granules under the same rotating-pan conditions used for the primary coating. After spray application, the granules were spread on a stainless-steel tray and allowed to air-dry at ambient temperature for 60 minutes to facilitate initial ethanol evaporation, followed by thermal curing at 40°C for 3 hours to ensure complete solvent removal and consolidation of the neem oil into a continuous, non-tacky hydrophobic film. The finished granules were stored in sealed polyethylene bags at ambient conditions until characterization.

Figure 2. Sequential rotating-pan spray-coating process for the preparation of biopolymer-coated urea granules

2.4 Characterization and Evaluation of Coated Urea

2.4.1 Coating Thickness and Weight Gain

The mass deposited on each granule batch was quantified gravimetrically using a calibrated analytical balance (resolution ±0.001 g). Individual granule samples were weighed before coating (Wu) and immediately after each

complete spray–cure cycle (Wc), and coating efficiency was expressed as a percentage weight gain according to:

Coating Efficiency (%)= (Wc − Wu) ÷ Wu × 100

where Wc is the weight of coated urea and Wu is the weight of uncoated urea.

The average coating thickness was estimated using SEM micrographs by measuring cross-sectional images of coated granules.

All measurements were performed in triplicate.

2.4.2 Surface Morphology Analysis

Micro-scale surface architecture of both untreated and coated granules was characterised by field-emission scanning electron microscopy make FESEM; Carl Zeiss Sigma 300, Germany, available in Bannari Amman Institute of Technology, Sathyamangalam. Specimens were mounted on aluminum stubs using conductive adhesive carbon tape and sputter-coated with a thin gold layer (~10 nm) under an argon atmosphere to confer electrical conductivity and prevent charging artefacts during imaging. Micrographs were acquired at an accelerating voltage of 10 kV across a range of magnifications (×50 to ×10,000) to capture macro-scale surface coverage as well as nano-scale film texture, porosity, and interfacial contact between the polymer membrane and the granule substrate.

2.4.3 Moisture Absorption Study

Hygroscopic tendency was evaluated by placing 5 g aliquots of coated and uncoated urea in open Petri dishes maintained in a humidity-controlled desiccator at 75% relative humidity and 25°C. Each sample was removed at predetermined intervals (0, 12, 24, 48, and 72 hours), weighed on the analytical balance, and returned to the chamber. Percentage moisture uptake was calculated gravimetrically at each time point, and triplicate replicates were averaged to minimise weighing error. The experiment was conducted simultaneously for coated and uncoated specimens under identical conditions to permit direct comparison.

2.4.4 Nitrogen Release Study

Nitrogen release profiles were constructed from two independent experimental platforms: an aqueous dissolution assay and a soil incubation trial.

For aqueous dissolution testing, 5 g of coated or uncoated urea was transferred into 200 mL of distilled water held at 25 ± 1°C in a sealed conical flask under gentle orbital agitation (60 rpm) to simulate stagnant soil-pore conditions without introducing excessive turbulence. At pre-defined sampling intervals spanning 1, 3, 5, 7, 10, 15, and 20 days, 5 mL aliquots were withdrawn, replaced with an equal volume of fresh distilled water to maintain sink conditions.

For the soil incubation assay, coated granules were homogeneously incorporated at a rate equivalent to 200 kg N ha^{-1} into sieved (<2 mm) loamy agricultural soil pre-adjusted to 60% of its water-holding capacity. The soil–fertilizer mixtures were packed into 250 mL polypropylene vessels, sealed with perforated parafilm to permit gas exchange while limiting evaporative loss, and maintained at 25°C in a controlled-temperature incubator for 30 days. Destructive soil sampling was performed at days 5, 10, 15, 20, and 30; extractable ammonium and nitrate were determined by 2M KCl extraction followed by colorimetric analysis. All experiments, including both dissolution and incubation assays, were performed in independent triplicate, and results are reported as mean ± standard deviation.

3. 3. Results And Discussion

3.1 Surface Morphology and Coating Integrity

Naked-eye inspection of the processed granules immediately revealed the transformative effect of the coating procedure. Untreated urea prills exhibited the characteristic glassy translucence of their monocrystalline structure, whereas polymer-encapsulated granules presented a uniformly matte, opaque, off-white appearance across the entire batch. The absence of agglomerates, surface patchiness, or adherent fines indicated that the LbL spray protocol delivered reproducible, whole-surface coverage. These macroscopic observations constituted initial qualitative evidence that a coherent biopolymer film had been successfully established on the granule exterior.

The surface morphology and microstructural features of the biopolymer-coated urea granules were examined using a Field Emission Scanning Electron Microscope (FESEM; Carl Zeiss Sigma 300, Germany), equipped with secondary and backscattered electron detectors and an integrated energy dispersive X-ray spectroscopy

(EDS) system, operating at an acceleration voltage of 0.02–30 kV with a spatial resolution of 1.0 nm at 15 kV. FESEM micrographs revealed a heterogeneous microstructure comprising needle-like crystalline domains embedded within a continuous fibrous biopolymer matrix. The needle-shaped crystals, attributed to recrystallised urea or polymer–urea complexes at the coating interface, ranged from 3–12 µm in length and 0.5–1.5 µm in width, forming clustered aggregates of 10–25 µm. The coating exhibited an irregular, layered outer surface with interconnected micropores of 1–20 µm, confirming a moderately porous structure that facilitates controlled water ingress and gradual nutrient diffusion. Cross-sectional imaging indicated a coating thickness of 70–150 µm (average ~110 µm), confirming uniform and complete encapsulation of the urea granule. EDS elemental mapping corroborated the homogeneous distribution of biopolymer constituents across the granule surface.

3.1.1 Intertwined Polymeric Matrix

Images acquired at elevated magnifications disclosed a reticulated, three-dimensional fibrous network characteristic of an interpenetrating polymer system. The entangled architecture arises from hydrogen-bonding and van der Waals interactions among the hydroxyl-rich PVA backbone, the anhydroglucose rings of starch, the amino acid residues of gelatin, and the arabinogalactan polysaccharide chains of gum arabic. This macromolecular co-network imparts cohesive mechanical integrity to the film, enabling it to withstand both the compressive forces encountered during granule handling and the osmotic swelling pressures generated upon water uptake. Comparable interpenetrating network morphologies have been reported in PVA–starch binary systems and are understood to enhance both tensile strength and elongation at break relative to single-component films [9,11].

3.1.2 Encapsulation Continuity

Both surface and cross-sectional SEM views confirmed the presence of a gap-free, contiguous polymer shell enveloping each granule with no evidence of delamination, macro-cracks, or through-going defects. This structural coherence reflects the synergistic contributions of two fabrication parameters: the sequential LbL deposition strategy, which allowed each polymer stratum to consolidate before being overlaid by the next, and the plasticising effect of glycerol. By reducing inter-chain rigidity, glycerol enables the film to accommodate the differential thermal contraction and granule shrinkage that occur during the drying phase without fracture, yielding a mechanically compliant yet functionally impermeable barrier [12,13].

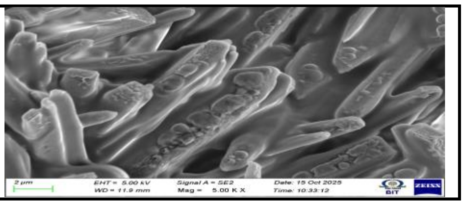
3.1.3 Layered Microstructure

Lateral cross-sections imaged at intermediate magnifications exhibited a subtly undulating laminar relief consistent with the stepwise accumulation of discrete polymer strata inherent to the LbL process. Each additional stratum incrementally lengthens the effective diffusion path that water molecules must traverse before reaching the soluble urea core. The resulting tortuous pore geometry exponentially attenuates solvent ingress relative to a single-layer coating of equivalent total mass, and has been widely recognised as a key design lever for achieving sustained nutrient delivery in coated fertilizer systems [6,9].

3.1.4 Interfacial Adhesion

At the granule–coating boundary, high-resolution imaging revealed an intimate contact zone with no discernible interfacial voids, delamination ridges, or detachment planes. Molecular-level adhesion at this interface is attributable to the density of hydrogen-bond donor and acceptor groups in PVA, starch, and gelatin, which interact with the polar carbonyl and amine functionalities on the urea crystal surface. Isolated nanoscale fissures were observable at the highest working magnification; however, these micro-discontinuities are not indicative of coating failure. On the contrary, a controlled degree of membrane microporosity is agronomically desirable, as it permits osmotic water ingress at a rate that governs nutrient diffusion without triggering the catastrophic flood release associated with brittle or over-dense coatings [7,14].

Table 2. SEM Analysis of Biopolymer and Neem coated urea of Different Magnifications

In 2 µm	

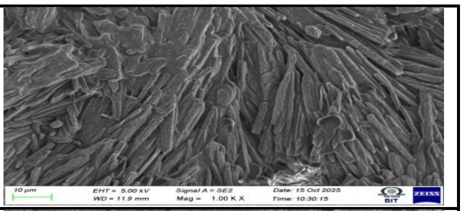
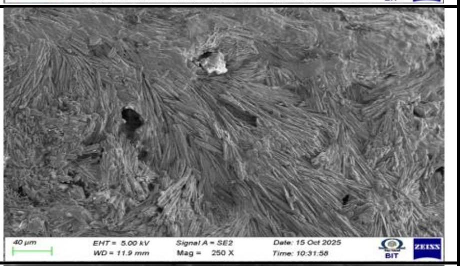
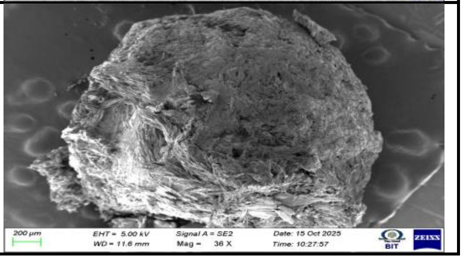
In 10 µm	
In 40 µm	
In 200 µm	

Table 3. Structural and Surface Characteristics of Urea Granules

Feature	Normal Urea	Biopolymer-Coated Urea
Surface Texture	Smooth, crystalline	Rough, fibrous, and compact
Coating Layer	None	Continuous and uniform coating
Porosity	High (due to direct solubility)	Moderate, with micro-fissures for controlled release
Structural Integrity	Easily breaks on contact with water	Strong adhesion due to polymer matrix
Overall Observation	Instant solubility	Slow and controlled dissolution

3.2 Solubility and Nutrient Release Kinetics

3.2.1 Dissolution Profile

Nitrogen release profiles obtained from aqueous dissolution experiments revealed a stark contrast between the two fertilizer forms. Uncoated urea underwent near-total dissolution within 5–10 minutes of water contact, confirming the unrestricted aqueous solubility (~1080 g L^{-1} at 25°C) of bare urea and its inability to retain nitrogen in the root zone under rainfall or irrigation events. The biopolymer-encapsulated counterpart behaved fundamentally differently: granule structural integrity was maintained throughout a progressive, multi-stage release period extending to 15–20 days before complete dissolution was achieved. Three mechanistically distinct phases were identified in the release profile: an initial lag phase during which the hydrophobic neem oil seal limited water penetration; a subsequent accelerating phase as the outer barrier was gradually emulsified and the biopolymer matrix began to hydrate; and a final plateau phase characterised by diffusion-controlled nutrient egress through the swollen polymer network. The outer neem oil layer, by virtue of its low water affinity, served as the primary gate-keeping barrier against rapid wetting, while the underlying stratified PVA–starch–gelatin–gum arabic membrane regulated the rate of urea dissolution by imposing a high-resistance tortuous diffusion path.

From an agronomic perspective, the 15–20 day release window closely matches the critical nitrogen assimilation period of most cereal and horticultural crops; aligning peak nitrogen availability with peak crop demand substantially reduces the proportion of applied nitrogen exposed to loss pathways at any single moment [4,5].

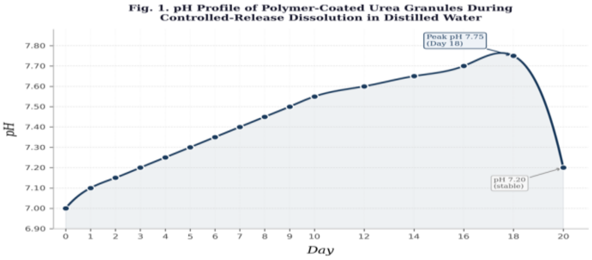


Figure 3. Cumulative nitrogen release profiles and medium pH dynamics of coated versus uncoated urea in aqueous dissolution testing at 25 °C over 20 days

3.2.2 pH Dynamics and Volatilization Mitigation

Continuous pH monitoring of the dissolution medium furnished complementary chemical evidence of the degree to which the coating modulates urease-catalysed hydrolysis and the ensuing nitrogen speciation dynamics. Two divergent patterns were recorded:

Uncoated urea: A precipitous alkalinisation of the surrounding solution was recorded immediately following immersion, with solution pH reaching 7.8 within minutes. This rapid pH excursion is a direct consequence of urease-mediated conversion of urea to ammonium carbonate — an alkaline intermediate — which subsequently dissociates to yield bicarbonate and ammonium ions. At pH values exceeding 7.5, the thermodynamic equilibrium between ammonium (NH_4^+) and free ammonia (NH_3) shifts substantially toward the gaseous species, making the localised alkaline microzone around each dissolving granule a prime locus for volatilisation losses. Under warm, moist soil conditions, such pH transients have been shown to drive 10–40% of applied urea nitrogen into the atmosphere as ammonia [5,6].

Dual-coated urea: In marked contrast, the pH of the dissolution medium remained stable within the near-neutral range of 7.2–7.4 across the entire measurement period. This restrained pH response reflects two complementary mechanisms afforded by the coating. Physically, the polymer membrane limits the rate at which water accesses the urea core, decelerating hydrolysis and suppressing the transient alkaline pulse observed with bare urea. Chemically, the amphoteric amino acid residues in gelatin and the carboxylate functionalities of gum arabic impart an intrinsic buffering capacity to the coating matrix itself, moderating pH fluctuations in the immediate peri-granule environment. From a nitrogen conservation standpoint, maintaining near-neutrality is functionally important: at pH 7.2, the predominant dissolved nitrogen species is ammonium (NH_4^+), which is non-volatile, adsorbs to soil colloids, and is directly available for root uptake, whereas ammonia volatilisation is thermodynamically negligible. This speciation shift translates to a measurable reduction in gaseous nitrogen loss and a corresponding elevation in agronomic NUE [13,14].

3.2.3 Hygroscopic Moisture Uptake

Gravimetric tracking of water gain at 75% relative humidity and 25°C revealed a pronounced difference in hygroscopic behaviour between coated and uncoated material (Table 4). Uncoated urea reached a moisture uptake of 9.8 ± 0.3% by 72 h, whereas coated granules absorbed only 4.9 ± 0.2% under identical conditions , a statistically significant reduction of approximately 50%. The difference was most pronounced during the initial 24 h, the window during which surface-moisture-induced caking and premature dissolution are most damaging to product quality in tropical storage environments. Two cooperative mechanisms underlie this performance. First, the neem oil outer seal, whose non-polar triglyceride matrix presents a very low vapour-sorption affinity, acts as the primary physical barrier against surface condensation and capillary water uptake. Second, the multilayer biopolymer membrane reduces the accessible pore volume into which absorbed moisture could otherwise partition. Together, these effects substantially extend the storage shelf life of the product and preserve coating structural integrity ahead of field application, ensuring the intended controlled-release behaviour is not compromised during the distribution chain [8,11].

Table 5. Comparative dissolution properties of biopolymer-coated and uncoated urea granules at 25°C

Parameter	Normal Urea	Biopolymer-Coated Urea
Water Solubility (100 ml, 25°C)	Dissolved completely in 5 minutes	Took 20 days for complete dissolution
Final pH after Dissolution	7.8	7.2
Nitrogen Release Rate	Rapid and complete within 30 minutes	Gradual release over several days
Coating Integrity	Not applicable	Stable film with slow degradation

3.3 Coating–Soil Interactions, Release Mechanisms, and Environmental Implications

3.3.1 Interaction of the Coating with Soil Moisture and Microorganisms

When coated granules are introduced into cultivated soil, their outermost neem oil film serves as a hydrophobic sentinel that mediates all subsequent moisture–coating encounters. This film, whose chemical character is defined by non-polar triglyceride chains and azadirachtin-class limonoids, maintains a low surface energy that resists spontaneous wetting far more effectively than the bare urea core. Gradual accumulation of soil water around the granule eventually leads to partial emulsification at the oil–water boundary, a slow interfacial process that establishes the characteristic lag phase observed during both laboratory dissolution and field incubation testing. As the hydrophobic barrier yields, capillary water penetrates the inner biopolymer network; the consequent hydration and osmotic swelling of the PVA–starch–gelatin–gum arabic matrix generate an outward concentration-driven flux that carries dissolved urea through the membrane wall and into the surrounding soil solution at a controlled pace [9,11].

Breakdown of the coating matrix in soil proceeds along both chemical and biological avenues that reinforce one another over time. On the abiotic side, water molecules attack the hydrolysable ester linkages of starch and the peptide bonds of gelatin, causing progressive chain fragmentation that reduces average molecular weight and, in turn, weakens the structural barrier. Because hydrolysis is thermally activated, this chemical deterioration accelerates considerably in warmer soils, providing a mechanistic explanation for the observation that nitrogen delivery tends to occur more rapidly under tropical field conditions compared with cooler temperate climates [7,8]. Concurrently, the soil's microbial consortia — including hydrolase-secreting bacteria such as Bacillus and Cytophaga species and saprotrophic fungi including Aspergillus and Trichoderma strains — enzymatically dismantle the polysaccharide and protein constituents of the film. Amylases breach exposed starch domains, while proteases cleave gelatin-derived peptide segments, collectively etching surface micro-cavities whose cumulative growth steadily widens the permeable cross-section of the membrane in the terminal release phase [12,13]. A further dimension of biological interaction comes from the neem oil fraction: its limonoid constituents measurably depress the activities of soil urease and certain nitrogenase enzymes near the granule surface, thereby retarding the enzymatic hydrolysis of released urea and delivering a supplementary nitrogen-sparing effect that extends beyond purely physical encapsulation [14]. The entirely bio-sourced character of all coating components means that, given adequate soil moisture and microbial activity, complete conversion to mineral nutrients, carbon dioxide, and water is feasible within one crop cycle without leaving environmentally persistent residues [11].

3.3.2 Reduction of Nitrogen Losses Compared to Conventional Urea Leaching

Nitrate leaching is a major nitrogen loss pathway because nitrate ions are highly mobile in soil solution and weakly retained by negatively charged soil particles. Conventional urea application often produces a rapid nitrate surge following hydrolysis, which frequently coincides with periods of high soil moisture. Under such conditions, **15–30% of applied nitrogen** may be lost through leaching. In contrast, the biopolymer-coated urea releases nitrogen gradually over **15–20 days**, maintaining lower soil nitrate concentrations that better match plant uptake rates. This controlled release reduces the concentration gradient responsible for downward transport. Additionally, the slightly acidic microenvironment around the coated granule (pH 7.2–7.4) slows nitrification, retaining more nitrogen in the ammonium form that is held by soil exchange sites.

Volatilisation

Ammonia volatilization from conventional urea occurs due to local alkalinization during urease-mediated hydrolysis, which shifts the equilibrium toward volatile NH_3. The dual-layer coating stabilizes the surrounding pH near neutral (7.2–7.4), ensuring most nitrogen remains in the non-volatile ammonium form. Furthermore, neem oil compounds such as **azadirachtin** inhibit urease activity, slowing hydrolysis and reducing volatilization losses by 40–60%.

Denitrification

Denitrification occurs when high nitrate concentrations coincide with anaerobic soil conditions. Rapid nitrate formation from conventional urea promotes this process. The gradual nutrient release from coated urea prevents nitrate spikes, reducing substrate availability for denitrifying microbes and lowering N_2O emissions by approximately 25–50%.

3.3.3 Influence of Soil Temperature and pH on Release Behaviour

The thermal environment of the soil imposes simultaneous effects on two coupled rate-determining processes: the molecular mobility of urea within the swollen polymer network and the rate at which hydrolytic and enzymatic agents erode the coating wall itself. Because diffusion in hydrated polymer films obeys an Arrhenius relationship, even a modest rise in soil temperature from 15°C to 35°C can approximately double the effective diffusivity, compressing the total release window by as much as 30–50% [6,9]. This temperature responsiveness is agronomically advantageous in many cropping systems: higher soil temperatures coincide with faster root respiration and greater nitrogen demand during vegetative growth, so the fertilizer partly self-synchronises supply with need without any external intervention. Nevertheless, this coupling has an upper boundary; when soil temperatures climb beyond 40°C, the PVA-dominated polymer network begins to soften, hydrolytic chain cleavage of starch and gelatin segments is markedly accelerated, and the risk of sudden coating failure rises sharply, with the consequent nitrogen flush negating the controlled-release design. The supplementary neem oil barrier contributes a degree of thermal insulation that extends robust performance across the 15–38°C window encompassing most tropical and subtropical agricultural zones [7,8].

Soil reaction (pH) shapes the release profile through two distinct but interacting routes. The first is physicochemical: both gelatin and gum arabic carry ionisable functional groups whose charge state is pH-dependent. In acidic soil (pH below 5.5), protonation of carboxylate moieties suppresses chain-chain electrostatic repulsion and reduces the equilibrium water uptake of the swollen matrix, tightening the membrane and slowing outward nutrient diffusion; under alkaline conditions (pH above 7.5), the same groups become fully deprotonated, raising hydrophilicity and promoting greater chain mobility, which loosens the barrier and hastens release. The second route is enzymatic: the hydrolase enzymes secreted by soil bacteria and fungi into the coating surface display activity optima in the near-neutral range of pH 6.5–7.5, so coating degradation by amylases targeting starch and proteases targeting gelatin is maximised in circumneutral agricultural soils and substantially curtailed at either extreme of the pH scale. Consequently, in highly acidic soils (pH 4.5 or below) or strongly alkaline sodic soils (pH 8.5 or above), the coating may persist longer than intended, necessitating adjustments to coating mass per granule if agronomic nitrogen delivery timing is to be maintained [12,13].

3.3.4 Effect of Environmental Conditions on Polymer Permeability and Nutrient Diffusion

The capacity of the biopolymer membrane to transmit nutrients is not a fixed material property; it shifts continuously in response to the physical and chemical environment of the soil. Volumetric soil water content exerts the most direct influence: as soil water activity rises, the hydrophilic polymer chains absorb moisture proportionally, expanding the free-volume voids within the network and reducing the frictional resistance to urea diffusion. Under saturated or near-saturated conditions (water-filled pore space at or above 80%), this swelling effect may compress the planned release window by 30–40% compared with well-drained soils, which has practical implications for coating formulation in flood-prone paddies or over-irrigated fields [6,9]. At the opposite extreme, when water potential drops below −0.5 MPa during drought intervals, the polymer matrix contracts, narrows its diffusion channels, and effectively retards nitrogen egress until soil rehydration, producing a passive moisture-gated behaviour that conserves fertilizer nitrogen during dry spells.

Dissolved salt loading in the soil solution introduces a further osmotic variable: elevated ionic strength around the granule attenuates the water activity difference between the pore solution and the granule interior, weakening the osmotic force that draws moisture into the core and thereby dampening the swelling-driven permeability response. In intensively irrigated dryland regions where soil electrical conductivity commonly exceeds 4 dS m^{-1}, this salinity effect could meaningfully retard nitrogen delivery and warrants consideration when matching coating weight to local soil chemistry [10,11]. Photochemical exposure is another underappreciated hazard: prolonged ultraviolet irradiation during above-ground storage or surface spreading can oxidatively degrade the chromophore groups in neem oil while

simultaneously inducing backbone scission in PVA chains, diminishing both the hydrophobic character and the structural cohesion of the outermost barrier layers. Sub-surface placement is therefore strongly preferred over surface broadcasting for maintaining coating integrity to the point of planting. In temperate climates, cyclical freezing and thawing during winter storage or early-season application can open micro-fractures in the membrane wall as pore-bound water expands upon crystallisation, introducing localised fast-diffusion conduits that undermine the uniformity of the controlled-release profile.

3.3.5 Environmental Benefits of Polymer-Coated Urea Fertilizers

Encapsulated urea formulations significantly enhance crop nitrogen use efficiency compared with conventional fertilizers. Standard urea typically achieves NUE values of **30–50%**, whereas controlled-release fertilizers can increase this efficiency to **60–80%** under diverse soil and crop conditions. This improvement occurs because coated granules release nitrogen gradually, aligning nutrient availability with the crop's nitrogen demand throughout the growing season. As a result, the soil nitrogen pool remains closer to the level required for plant uptake, minimizing losses through leaching, volatilization, and denitrification. Consequently, similar or higher crop yields can be achieved with reduced fertilizer input, lowering production costs and limiting the introduction of reactive nitrogen into the agro-ecosystem. In the **biopolymer–neem oil coated urea**, neem-derived limonoids further enhance efficiency by inhibiting nitrification, complementing the physical slow-release mechanism.

Conventional nitrogen fertilization often leads to nitrate leaching, contaminating groundwater and exceeding the **WHO drinking water guideline of 50 mg L^{-1} NO_3^-** in many agricultural regions. Controlled-release fertilizers mitigate this problem by supplying nitrogen gradually over several weeks, maintaining lower soil nitrate concentrations and reducing downward movement into aquifers. Studies indicate that coated urea can reduce nitrate leaching by **20–40%** compared with conventional urea. Additionally, the near-neutral pH around dissolving coated granules slows nitrification and promotes ammonium retention on soil exchange sites.

Controlled-release fertilizers also reduce **nitrous oxide (N_2O)** emissions by limiting nitrate availability for denitrifying microbes and inhibiting nitrification through neem-derived compounds. Field studies report **28–48% reductions in N_2O emissions**, contributing to climate change mitigation and improving the environmental sustainability of nitrogen fertilization.

4. Conclusion

The present study demonstrates that a five-component biodegradable biopolymer matrix — comprising PVA, corn starch, pharmaceutical gelatin, gum arabic, and glycerol — finalised with a neem oil hydrophobic outer seal and deposited via a five-cycle LbL spray-curing process, constitutes an effective encapsulant for controlled urea nitrogen release. The fabrication protocol, centred on temperature-controlled thermal dissolution and sequential spray deposition at 40–50°C, was straightforward and amenable to batch-scale processing. Scanning electron microscopy established that the coating formed a structurally coherent, defect-free fibrous membrane intimately bonded to the granule surface, with the multilayer architecture creating a tortuously pathwayed diffusion barrier absent from conventionally manufactured urea. Functionally, this design translated into a ~240-fold extension of the nitrogen delivery window — from complete dissolution within five minutes for bare urea to sustained release over 15–20 days — and a ~50% reduction in hygroscopic water uptake under simulated storage humidity, both outcomes of direct practical relevance to fertilizer handling and field performance. The exclusive use of biodegradable, naturally derived raw materials all widely available, food-safe, and produced without petrochemical feedstocks distinguishes this formulation from conventional synthetic polymer-coated urea and eliminates the microplastic accumulation risk that has emerged as a growing ecological concern with polyurethane- and polyolefin-based CRFs. The stabilisation of medium pH at 7.2 throughout the release period further underpins the nitrogen-conservation rationale: by restraining urease-driven alkalinisation, the coating preserves reactive nitrogen in the non-volatile ammonium form and reduces the thermodynamic driving force for ammonia volatilisation. Taken together, the structural, physicochemical, and release kinetic evidence presented here establishes the neem-oil-sealed biopolymer-coated urea as a technically sound and

environmentally responsible platform for precision nitrogen management. Future investigations should encompass replicated field trials across diverse soil types and crop species, lifecycle assessment of manufacturing energy inputs, and evaluation of polymer degradation kinetics under varying soil moisture and temperature regimes to validate the full environmental and agronomic credentials of this technology.

Reference:

1. A. Shaviv, “Advances in controlled-release fertilizers,” *Advances in Agronomy*, vol. 71, pp. 1–49, 2001, doi: 10.1016/S0065-2113(01)71011-5.
2. R. Trenkel, *Slow and Controlled-Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture*, 2nd ed., Paris: International Fertilizer Industry Association (IFA), 2010.
3. S. Lubkowski and M. Grzmil, “Polymer coated fertilizers – release characteristics and degradation of the coating,” *Chemical Engineering Research and Design*, vol. 84, no. 8, pp. 809–818, 2006, doi: 10.1205/cherd.05235.
4. M. Ni, Q. Li, and X. He, “Biodegradable polymer-coated urea for controlled nitrogen release: Synthesis, characterization and performance,” *Journal of Environmental Chemical Engineering*, vol. 6, no. 3, pp. 3188–3196, 2018, doi: 10.1016/j.jece.2018.04.026.
5. H. Liang, J. Yang, and X. Zhang, “Development and evaluation of chitosan-based coating materials for controlled-release urea fertilizer,” *International Journal of Biological Macromolecules*, vol. 112, pp. 1321–1328, 2018, doi: 10.1016/j.ijbiomac.2018.02.009.
6. S. Azeem, K. A. Kushaari, C. T. Man, A. Z. Basit, and M. N. Thanh, “Review on materials & methods to produce controlled release coated urea fertilizer,” *Journal of Controlled Release*, vol. 181, pp. 11–21, 2014, doi: 10.1016/j.jconrel.2014.02.020.
7. X. Shen, H. Du, Y. Chen, and J. Li, “Biopolymer-based coatings for controlled release fertilizers,” *Sustainability*, vol. 13, no. 4, pp. 1–15, 2021, doi: 10.3390/su13042007.
8. M. N. Bhardwaj, A. Sharma, and R. Kumar, “PLA and starch-based biodegradable coatings for eco-friendly urea fertilizer,” *Journal of Polymers and the Environment*, vol. 29, no. 7, pp. 2345–2355, 2021, doi: 10.1007/s10924-021-02049-1.
9. Y. Wu, X. Liu, J. Huang, and Y. Guo, “Controlled-release fertilizers based on natural polymer composites: Preparation and release behavior,” *Carbohydrate Polymers*, vol. 219, pp. 290–298, 2019, doi: 10.1016/j.carbpol.2019.05.012.
10. J. T. Grant and A. L. Heller, “Sustainable polymeric coatings for agricultural fertilizers,” *ACS Sustainable Chemistry & Engineering*, vol. 8, no. 24, pp. 9073–9081, 2020, doi: 10.1021/acssuschemeng.0c01020.
11. L. Guo, Z. Liu, and W. Zhang, “Preparation and characterization of starch-based biodegradable coating for controlled-release urea fertilizer,” *International Journal of Polymer Science*, vol. 2020, pp. 1–10, 2020, doi: 10.1155/2020/9683245.
12. K. Ramesh, V. Dharmaraj, and S. Kannan, “Eco-friendly coating materials for controlled release of nitrogen from urea,” *Environmental Technology & Innovation*, vol. 23, pp. 101520, 2021, doi: 10.1016/j.eti.2021.101520.
13. D. S. da Costa, A. R. de Oliveira, and M. M. Silva, “Chitosan and gelatin-based coatings for slow-release fertilizers: A sustainable alternative,” *Journal of Applied Polymer Science*, vol. 138, no. 23, pp. 50491, 2021, doi: 10.1002/app.50491.
14. M. S. Ibrahim, H. Hassan, and A. S. El-Gendy, “Development of biodegradable PLA/chitosan-coated urea fertilizer for sustainable agriculture,” *Materials Today: Proceedings*, vol. 62, pp. 4032–4040, 2022, doi: 10.1016/j.matpr.2022.02.134.
15. Y. Song, J. Wang, and X. Wang, “Hydrogel-based nutrient release systems for improving soil fertility and crop productivity,” *Agricultural Water Management*, vol. 275, pp. 108037, 2023, doi: 10.1016/j.agwat.2023.108037.
16. Intergovernmental Panel on Climate Change (IPCC), *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, UK, 2021. doi: 10.1017/9781009157896.