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# A review of minimizing fertilizer losses through controlled-release technology, with a focus on urea and leaching prevention

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**Abstract**
The increasing global population and the demand for food production have led to higher usage of fertilizers in the agricultural sector. This, in turn, has raised the cost of food production. Urea, commonly used in crop fertilization, is prone to losses through volatilization and leaching, and current methods reduce the efficiency of nitrogen use by plants, leading to limited crop yields and environmental pollution. A potential solution to this problem is the use of controlled release urea (CRU), achieved through various methods and materials. One such method is the physical conversion of urea granules with an appropriate coating material, which produces controlled-release coated urea (CRCU). The development of CRCU, a green technology, not only reduces nitrogen loss caused by volatilization and leaching, but also adjusts the rate of nitrogen release, providing nutrients to plants in a manner more aligned with their metabolic needs. This mini review discusses the physical coating of original urea granules, emphasizing the latest coating methods, release experiments, and mechanisms, and provides critical analysis and suggestions for future research.

**Keywords:** Urea, leaching, controlled release urea, control release coated urea and green technology

## Introduction
Controlled release fertilizer (CRF) is a specially designed fertilizer that releases nutrients slowly and in sync with the plant's needs, improving nutrient use efficiency and yields (Shaviv, 2005) [23]. An ideal CRF is coated with an environmentally friendly material that slows down the release of fertilizers, ensuring that a single application can meet the nutrient requirements for the entire crop growth cycle (Blouin, G.M. 1967) [2]. While the terms "controlled release fertilizer" and "slow release fertilizer" are often used interchangeably, there are differences. Slow release fertilizers have unpredictable release patterns influenced by soil and climate, while controlled release fertilizers allow for more predictable nutrient release. The development of CRFs can be traced back to the early 1960s, initially using sulfur and polyethylene as coating materials (G.M. Blouin., 1971) [8]. Over time, there have been advancements in materials such as polymers, natural coating agents, and super-absorbent materials, with many CRFs being produced on a commercial scale.

## Various Classification of Controlled Release Fertilizer Grades
The CRFs have been classified in a diverse manner according to the literature. A comprehensive classification has been based on the opinions of (Shaviv, 2005) [23], (Trenkel, 2010) [14] and (Liu *et al*., 2008) [13] diversifying on the basis of various coating materials as portrayed in Fig. 1. Comprehensively, CRFs were classified into three major categories:
1. Organic compounds can be further divided into natural organic compounds (such as animal manure and sewage sludge) and synthetically produced organic-nitrogen, low-solubility compounds. The latter group generally includes condensation products from urea and acetaldehyde. These compounds can be further subdivided into biologically decomposing compounds, such as urea formaldehyde (UF), and chemically decomposing compounds, such as iso butylidene-diurea (IBDU) or urea acetaldehyde/cyclo diurea (CDU).

The second major category includes renowned water-soluble fertilizers with physical barriers that control nutrient release. These appear either as granules/cores coated with a hydrophobic polymer or as a matrix of active fertilizer nutrients dispersed on a continuum via hydrophobic material that encumbers fertilizer dissolution. However, controlled-release matrices are less common compared to coated CRFs, which is why this paper is focused on controlled-release coated fertilizers that contain only urea. Coated granular CRFs are subcategorized into those coated with organic polymer materials (e.g., thermoplastics, resins, etc.) and those coated with inorganic materials (including sulfur and other minerals). The controlled-release matrix material can be either hydrophobic (e.g., polyolefin, rubber, etc.) or gel-forming polymers, sometimes referred to as a hydrogel. A hydrogel is hydrophilic, and the dissolution of fertilizer dispersed through hydrogel material is impeded by its ability to retain high amounts of water (swelling).
The last category consists of inorganic compounds with low solubility, such as metal ammonium phosphates (e.g., $KNH_4PO_4$ and $MgNH_4PO_4$) and partially acidulated phosphate rock (PAPR). Controlled-release fertilizers (CRFs) can be classified based on the mechanism of release control, including diffusion, erosion, chemical reaction, swelling, and osmosis. While Blaylock *et al*., 2005) [1] classified CRFs into two major types: those coated with low solubility compounds and those coated with water-soluble materials.

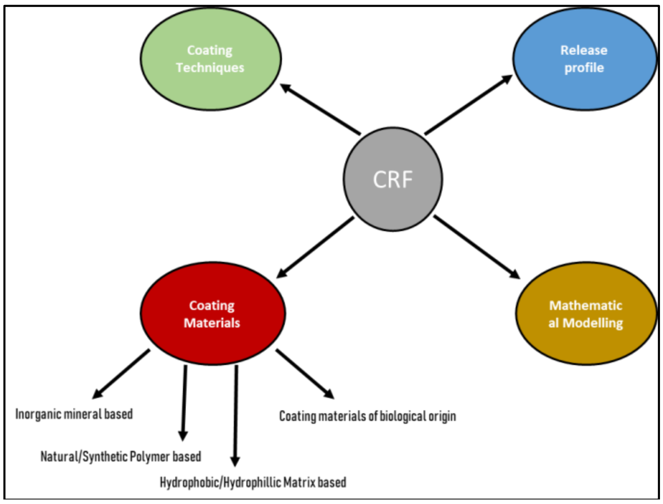


**Fig 1:** Classification of Controlled Release Fertilizers (CRF) on the basis of various coating materials.

## Mechanism of Controlled Release

Understanding the controlled release mechanism is essential as it directly measures the effectiveness of a CRF. This mechanism is complex and depends on factors such as the type of coating material, the CRF type, and agronomic conditions. There are various mechanisms mentioned in literature, still under development. Liu *et al*., 2008 [13] and Shaviv 2005 [23] proposed the multi-stage diffusion model as a release mechanism for coated fertilizers. According to this model, after applying the coated fertilizer, irrigation water penetrates the coating to condense on the solid fertilizer core, leading to partial nutrient dissolution (Fig. 2). Subsequently, as osmotic pressure builds within the containment, the granule swells, causing two potential processes. Firstly, when osmotic pressure exceeds the threshold membrane resistance, the coating bursts and the entire core is rapidly released, known as the "failure mechanism" or "catastrophic release". Secondly, if the membrane withstands the developing pressure, core fertilizer is released slowly via diffusion, driven by concentration or pressure gradient or a combination of both, known as the "diffusion mechanism". The failure mechanism is generally observed in fragile coatings (e.g., sulfur or modified sulfur), while polymer coatings (e.g., polyolefin) are expected to show the diffusion release mechanism. The coated fertilizer release mechanism entails nutrient transfer from the fertilizer–polymer interface to the polymer–soil interface, driven by water. The governing parameters for the release mechanism are: (i) diffusion/swelling, (ii) degradation of the polymer coating, and (iii) fracture or dissolution. Guo *et al*., 2005 [9], Liang *et al*., 2007 [19], Liu *et al*., 2007 [19], and Wu and Liu 2008 [13] have also presented similar release mechanisms.

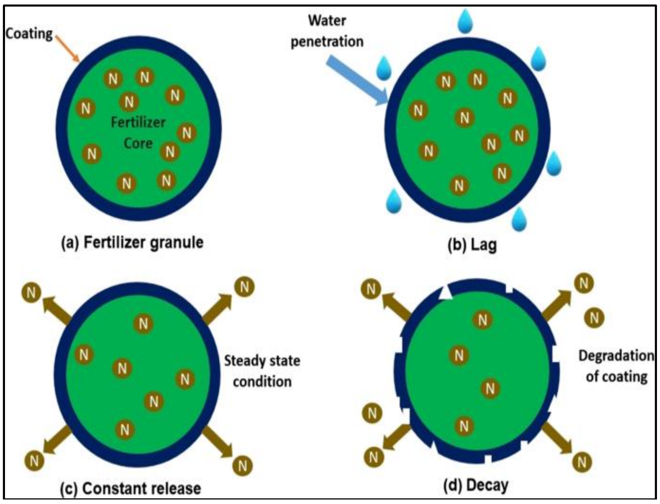


**Fig 2:** Mechanism for Controlled Release of Fertilizers using Coating Technique

Although the domain of controlled release fertilizer is huge but here in this mini review we will focus on urea and where literature stands on Controlled Release of Coated Urea (CRCU).
Urea is the most widely used fertilizer globally because of its high nitrogen content (46%), low cost, and ease of application. Therefore, the development of CRCU has been a subject of interest for decades. When applied to the soil, urea undergoes a series of biological, chemical and physical transformations to produce plant available nutrients as follows (G.M. Blouin *et al*., 1971) [8].

$$(NH_2)_2CO + 2H_2O \xrightarrow{\text{Urease}} (NH_4)_2CO_3 \quad (1)$$

$$(NH_4)_2CO_3 + 2H^+ \xrightarrow{\text{Ammonification}} 2NH_4^+ + CO_2 + H_2O \quad (2)$$

$$2NH_4^+ + 3O_2 \xrightarrow{\text{Nitrosomonas/nitrosococus bacteria}} 2NO_2^- + 2H_2O + 4H^+ + \text{Energy} \quad (3)$$

$$2NO_2^- + O_2 \xrightarrow{\text{Nitrobacter bacterium/nitrification}} 2NO_3^- + \text{Energy} \quad (4)$$

$$NO_3^- \xrightarrow{\text{Microorganisms}/O_2\text{deficient soil}} N_2 + N_2O \quad (5)$$

$$NH_4^+ \xrightarrow{\text{Urease enzyme/Basic soil pH}} NH_3(g) + H^+ \quad (6)$$

The 2nd and 4th reactions produce necessary nutrients for plants. Since plants need only a small quantity of food during early growth, excess nutrients are lost in the leaching process. In the 5th and 6th reactions, the nitrogen is lost through hazardous gaseous emissions in the form of nitrous oxide and ammonia. Therefore, there is a need to produce a more suitable CRCU to solve these problems. A visual representation of these transformations is provided. Various perspectives on slow/controlled release fertilizers have been discussed in different reviews and book chapters. Ussiri, R and Lal (2013) [5] presented fertilizer management strategies to boost plant nutrient-use efficiency and reduce nitrous oxide emissions. D. Davidson and F.X. Gu (2012) [4] wrote on the controlled release details of nutrients N, P, K, Mg, Zn, and the commercial availability of CRFs, along with some descriptions of crops that use CRFs for nutrition. Trenkel published a review on different options to enhance the nutrient use efficiency of plants, including the use of CRFs, urease inhibitors, nitrification inhibitors, as well as economic and legislative aspects concerning these materials. A similar review on the improvement of nutrient-use efficiency with an additional segment for the controlled release of phosphorus fertilizers was presented by Chien *et al*., 2009 [21]. The use of controlled release nitrogenous fertilizers, specifically for vegetable crops, was discussed by Guertal, 2009 [6]. Akiyama *et al*., (2010) [10] used beta analysis to evaluate how successfully modified fertilizers alleviated nitrous oxide emissions. Similarly, Xiang *et al*., 2008 [28]: Puoci *et al*., 2008 [16], Liu *et al*., 2008 [13], Blaylock *et al*., 2005 [1]; Shavi, 2005 [23]; Sartain *et al*., 2004 [22] and Tharanathan, 2003 [20] shed light on different aspects of coated urea and other controlled-release fertilizers.

Despite the significant amount of research on CRFs, there is still a lot of scope to further expand the research frontiers for controlled-release coated urea (CRCU) products. This review aims to provide a detailed overview of the knowledge base related to CRCU. We primarily focus on the coating materials, coating methods, and release experiments of the controlled release mechanism for CRCU. Our review is focused on contemporary research from the 21st century, but we have also included some papers from the past to offer an overview of the historical evolution of CRCU. We have divided this review into sections to categorize the prototype of coating materials used in the production of controlled release coated urea (CRCU) to help readers better understand the subject.

## Classification of coating materials for making CRCU fertilizers

### Sulfur based coating material

Sulfur was initially considered a good option for coating urea due to its many benefits. Major work on urea coating was carried out by Blouin, 1967 [2] for the Tennessee Valley Authority (TVA), USA. Their aim was to encapsulate granular urea and provide controlled release characteristics. They developed a cost-effective production process for sulfur coating urea. Initially, urea granules were coated with a petroleum by-product to act as a sealant and then immersed in a vacuum to penetrate the granules. The sealed urea was then sprayed with molten sulfur. Plasticizers were added to the sulfur-coated urea to aid spreading and fusion of the sulfur layer and decrease cracking. They also tested urea coated with only petrolatum or only sulfur and found that a combination of both gave effective controlled release results. However, challenges remained, such as the need for a uniform sulfur coating, and so microcrystalline wax and microbicides were implemented to improve the coated urea granules. Lastly, a conditioner was added to prevent tackiness from the wax, and dissolution tests revealed different rates based on particle size and duration.

### Polymer based coating material for production of CRCU

Various aqueous polymeric solutions were used to reduce cost, increase viability, and decrease environmental hazards. One such solution is the Methacrylic acid copolymers + Talc + Magnesium triethylcitrate + Polyethylene Glycol formulation, known as Eudragit LD30-D55 coating material given by M.W. Donida and S.C. Rocha, 2002) [15].

Furthermore, three different controlled release fertilizers were proposed by Han *et al.* (2008) [26] to enhance nitrogen uptake efficiency of tea plants. These fertilizers involved coating urea granules with Ca–Mg phosphate, polyolefin, and polyolefin plus dicyandiamide (DCD).

In addition, a study documented the feasibility of using poly (lactic acid-co-ethylene terephthalate) as a coating material. Urea granules were coated with commercial PolyLactic acid (PLA) and PLA plus Poly (lactic acid-co-ethylene terephthalate). The controlled release properties were evaluated using various methods and was done by Jintakanon *et al*., (2008) [11].

Lastly, a study by Qiu *et al.* (2013) [17] reported the preparation of a coating material called PBMHs-NAA, which was used for controlled release and plant growth regulation of urea granules.

Additionally, Costa *et al.* (2013) [3] synthesized a coating of urea granules with polyhydroxybutyrate (PHB) and ethyl cellulose (EC) using simple immersion and manual spraying with a pulverizer and trigger.

### Superabsorbent or highly retention coating materials for CRCU

Superabsorbent polymer materials (SPMs) have recently caught the attention of research circles because of interesting properties that favour CRCU production. These SPMs are 3-dimensional cross-linked hydrophilic polymers with an ability to imbibe water that is hundreds of times higher than their own weight and which cannot easily be removed even under extended pressure Yong *et al*., 2005) [27]. They find attractive use in agricultural and horticultural applications due to reduced water consumption and irrigation frequency, especially in drought prone areas and are thus considered economical. The advantages of SPM produced CRCUs include soil improvement through aeration, abatement of soil degradation, alleviation of water evaporation losses, reduction of environmental pollution through volatilization and leaching, and a decrease in crop morbidity due to increased nutrition through enhanced nutrient retention periods Yong *et al*., 2005 [27]. Yong's study (2005) [27] triggered new vistas of research for the production of multifunctional controlled release coated urea fertilizers with attributes of controlled release and improved water retention properties that are very beneficial, especially in regions with limited water supply. The most frequently used SPMs are classed as cross-linked polyacrylates/polyacrylamides, hydrolysed cellulose-polyacrylonitriles/ starch polyacrylonitriles graft copolymers, and cross-linked copolymers of maleic anhydride. The general methods employed in most studies for SPMs as a coating material are based on either solution polymerization or inverse-suspension polymerization. The solution polymerization involves the blending of $NH_3$-neutralized acrylic acid (AA) or acrylamide (AM) based monomers in aqueous solution, followed by the addition of a water-soluble cross-linking N,N′-methylenebisacrylamide (MBA) and potassium/ammonium persulfate as initiators. The blending is continued at increased temperature until a rubbery product is obtained which is then dried, ground and sieved for coating purposes. For inverse suspension polymerization, the surfactant and dispersant are mixed to form a water-in-oil phase in which AA/AM monomers are blended with a cross-linker and initiator as described above. The resultant micro-spherical product is dried to form a free flowing powder that requires no grinding or sieving.

**Bio-composite natural coating materials used for making CRCU**

The use of bio-composites as coating material has gained attention as a potential solution to manage non-biodegradability and high cost. In this context, several coating materials and methodologies are being discussed.

One example is the preparation of CRCU using a coating solution made by mixing starch, acrylic acid, and polyethylene glycol with slow additions of water, and continuous stirring until a homogeneous mixture is obtained. The methodology was demonstrated by Suherman (2011) [24]. The urea coating was carried out in a fluidized bed with a top spray of the starch-based coating solution. Water dissolution experiments showed reduced release rates with increased starch content of the coating. Higher temperatures enhanced the release rate due to premature drying of the coating droplets. Additionally, elevated temperatures reduced the proportion of liquid bridges on the urea granules, leaving uncoated spots that permitted higher release rates later on.

Finally, there is a focus on lignin as a coating material. Lignin is a cheap and natural macromolecular compound abundantly available as a waste material from pulp and paper industries Fernández-Pérez *et al*., (2008) [7]. Moreover, lignin is renewable, biodegradable, amorphous, and relatively hydrophobic compared to other polymers (Mulder, 2011) [25]. Perez prepared a lignin-based controlled release urea formulation by mixing urea and lignin in a glass reactor immersed in a thermostatic silicon oil bath. The mixture was heated, and the resultant urea-lignin matrix was cooled to give a glass-like structure, which was later milled in a crusher to obtain the desired size range of controlled release particles.

**Conclusions**

The urea coating is necessary to prevent nitrogen loss through leaching, volatilization, and denitrification. Controlled-Release Coated Ureas (CRCUs) inhibit this loss and release nitrogen in a manner that suits the metabolic needs of plants. Despite significant research efforts and expenditures to develop various coating materials and techniques, the industrial-scale production of CRCU has not yet been achieved.

Sulfur alone cannot effectively be used as a coating material for CRCU production due to its amorphous nature. Several sealants, binders, plasticizers, and protective agents have been utilized to counter the immediate burst effect. However, these additives increase process complexity and costs, leading to the near abandonment of sulfur-coated urea production.

CRCUs based on polymer/superabsorbent materials show potential for extended controlled release and water retention. However, the complexity of processing, high costs, and non-environmentally friendly side effects of some materials hinder industrial-scale production. Relatively little research has been conducted on the production of CRCUs with coating materials based on starch, lignin, and cellulose, which are comparatively cheaper, biodegradable, and renewable. Nonetheless, their increased hydrophilicity and limited controlled release characteristics are areas of concern.

This mini-review emphasizes the need for improvisation and the efficient development or implementation of a coating material that considers all intrinsic and extrinsic factors, compatibility, stability, and its potential to reduce fertilizer wastage, specifically urea, through slow and controlled release.

**To successfully commercialize CRCF/CRCU, the following points should be considered**

- Start production with original industrial-grade urea granules, avoiding procedures like melting, transforming, dissolving, or polymerization to fabricate controlled-release matrices with other materials.
- Select a coating material based on its affinity with urea, its ability to permeate water and urea solution, its capability to impede immediate urea escape from the coating surface without delay, and its ability to release urea in a manner that meets a crop's metabolic requirements over a specified period in a slow and controlled fashion. The material should also be biodegradable and cost-effective. While the ideal material with all of these traits may not currently exist, bio-composites based on starch, lignin, and cellulose can be modified to achieve such properties and are promising due to their biodegradability.

Ensure that the coating process allows for industrial-scale production of CRCU without altering the spherical geometry of urea granules. The use of a fluidized bed coater, pan coater, or rotary drum coater is recommended. The fluidized bed coating is a good candidate for industrial scale production due to its excellent heat and mass transfer characteristics and ease of operation. However, it's important to ensure that coating materials are compatible with the effortless spraying of the fluidized bed of urea granules.

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