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A Review on Slow-Release Coated Urea Synthesis, Coating Materials and Methods

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Abstract

The rapid growth of the Earth's population is forcing agricultural sector to use greater amounts of fertilizers to fulfil requirement of food, which results in increasing production costs. When urea is applied to crops it is more receptive to losses due to leaching and volatilization. The use of traditional urea often decreases Nitrogen Use Efficiency (NUE), therefore lowering crop's yield and conferring to environmental challenges which include water eutrophication and air pollution. Urea efficiency can be enhanced by encasing it with slow-release coatings that reduces urea volatilization. This review explains the research on urea coatings including mechanisms such as sulfur-based coatings, zinc-based coatings, polymer-based coatings, bio-composite coatings, and superabsorbent coating materials, in addition to coating methods, this article also addresses nutrient release mechanisms, along with an analysis of future prospects. It further presents an overview of the limitations of conventional urea and the requirements for coated urea. This work concludes that slow-release fertilizers increase nitrogen use efficiency (NUE), reduce nutrient loss, and control environmental pollution by limiting volatilization and leaching, maintaining crop productivity with reduced fertilizer application rates and improving agronomic safety. Future research will improve nitrogen use efficiency via slow- or controlled-release coating technologies. Because current coating materials harm the environment and economy, biodegradable polymers like starch are good alternatives. More research on new coatings, field evaluations, standardized procedures, and scale-up methodologies is needed for the practical and commercial implementation of slow-release fertilizers.

Keywords: slow-release urea, Urea Coating, urea release mechanism, coating methods, nitrogen use efficiency

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1. Introduction

1.1. Background

The increasing rate of Earth's population is causing a serious commination to food security [1]. The need for food is constantly increasing Earth's population which is expected to reach 9.5 billion by 2050 [2]. This speedy growth is placing a major stress on agricultural sectors to increase their crops yield. At the same time fertile land is contracting due to urbanization, industrial development, soil degradation and desertification due to extreme floods [3]. To solve these problems and enhance crop yield many steps are taken. The most common method involves the use of fertilizers, which enhances nutrient content in soil and increase crop yield. Consequently, fertilization utilization has increased sharply across the world [4]. However, conventional fertilizer effectiveness has decreased with time because large portion of its nutrients have lost [5]. So, developing new steps to increase crop productivity and decrease environmental pollution has become very important. Consequently, there is a strong need to formulate new fertilizers that have ability to reduce nutrient loss. One of the most important developments in this field is the innovation of slow-release fertilizers (SRFs). These fertilizers supply nutrients slowly over an extended period unlike conventional fertilizers, therefore sustaining nutrient availability in soil for longer durations and enhancing plant uptake efficiency [6].

1.2. Conventional Urea Limitation

The primary target of fertilizer application is to supply essential nutrients to crops and to enhance or maintain optimal crop yield levels. In order to maximize effectiveness and availability of nitrogen based fertilizers, their careful regulation and controlled delivery process is very important [7]. Out of three main macronutrients used by plants_ phosphorus, potassium and nitrogen, nitrogen plays the most important role in plant development. Because of high nitrogen concentration (46wt %) urea is most commonly used nitrogen fertilizer and it is also relatively inexpensive [8]. However, the field performance of conventional urea is often inefficient, leading to substantial nitrogen losses from the soil. These losses contribute to environmental pollution and associated risks, which have placed increasing constraints on the use of urea as a nutrient source for crops [9]. Previous studies have estimated that nearly 20–70% of conventionally applied urea is lost to the environment through processes such as nitrification, leaching, and volatilization. These losses not only intensify environmental contamination but also lower urea use efficiency, ultimately reducing biomass yield and the economic viability of crop production (Figure 1) [10].

1.3. Requirement for slow-release Coated Urea

The amount of nitrogen absorbed by the crop determines the effectiveness of urea fertilizer over a given period. In recent years, the research is permanently based on improving efficiency of urea during its application to crops and soil [11]. Slow-release mechanisms are used to address rapid release and associated nutrient loss of conventional urea fertilizer. Most effective strategy for supplying continuous nitrogen source, thereby enhance fertilizer efficiency while increasing crop growth is sustained-release fertilizers [12]. Coated urea with appropriate material control nutrient release in soil by lowering its water solubility. When urea is supplied, these physical barriers regulate its dissolution rate (Table 1) [13]. Thind et al. reported that nitrogen release and environmental loss can be reduced by applying coatings to urea pills [14]. The advantages and limitations of several commonly used coating materials are summarized in Table 1. The nutrient release patterns of slow-release fertilizers can vary considerably depending on the type of coating material and the proportion of fertilizer with damaged coating. Severe damage to the coating layer can lead to immediate nutrient release upon contact with soil moisture When cracks or holes form in the coated film, the fertilizer loses all or part of its controlled-release capability. Therefore, physico-chemical properties of the coating materials play a critical role in determining the nutrient release behavior [15].

1.4. Working Mechanism of coated Urea

Application of urea fertilizer to soil initiates a series of biochemical processes, leading to its transformation and gradual release of nitrogen essential for plant growth. [16].

$$NH_2COONH_4 \longrightarrow (NH_2)CO + H_2O$$

$$NH_2CO + 2H_2O + \text{Enzyme Urease} \longrightarrow (NH_4)_2CO_3$$

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

$$2NO_2^- + O_2 + \text{Nitrification Bacteria Nitrobacter} \longrightarrow 2NO_3^-$$

$$NO_3^- + \text{Microorganisms} \longrightarrow N_2 + N_2O$$

$$NH_4^+ + \text{Enzyme Urease} \longrightarrow NH_3 + H^+$$

In reactions 1 and 2 urea is synthesized under elevated temperature and pressure conditions. Within fertilizers, nitrogen is present in form of nitrite (NO_2^-), ammonium (NH_4^+), nitrate (NO_3^-), as well as inorganic gaseous nitrogen species. When urea is applied to soil, 40-70% of it is absorbed by the crops while the left is transformed into gaseous state. While the remaining nitrogen is lost by releasing harmful gases into the atmosphere or through leaching into the soil. In reaction 4 ammonium ions are produced and subsequently converted into nitrate ions known as mineralization. In reaction 6 due to the negative charge of soil clay particles, nitrate ions are particularly susceptible to leaching. Reactions 7 and 8 release hazardous ammonia and nitrous oxide contributing to gaseous pollution. Hence, in order to fulfill nutrient release of crops, slow-release fertilizers are used which delivers nitrogen in regulated manner [17].

2. Review of coating material for coated urea production

2.1. Sulfur based coatings

Despite several advantages of sulfur as a coating material for urea, several challenges still remain. These challenges include complex processing requirements, insufficient abrasion and impact resistance, unpredictable slow-release behavior due to surface cracks, and difficulties in achieving a compact and uniform coating. Sulfur forms thin, uneven, fragile, and discontinuous layers on urea granules because of its crystallinity and brittleness [18]. Advance approaches include coating urea granules with petroleum by-products such as soft wax, petrolatum, or motor oil to create a sealant and sub coating. The sealant is allowed to enter the granules, penetrating fine holes through capillary action and reducing urea dissolution by applying a vacuum. After that in a second drum the granules were tumble-coated with molten sulfur, followed by applying plasticizers, such as polyvinyl acetate or polyethylene to the sulfur layer in third compartment to reduce crack formation, improve fusion and spreading [19]. Sulfur was modified with dicyclopentadiene (DCPD) to improve coating performance by enhancing abrasion resistance, mechanical growth and moisture resistance. Instead of pure sulfur, increasing DCPD content strengthened the sulfur coating which produces thick layers with less cavities. As compared to unmodified sulfur-coated urea, the DCPD-sulfur coating was free of crack and more uniform due to smaller cavities [20].

2.2. Zinc based coatings

Zinc plays an important role in various metabolic processes and is a vital micronutrient needed for optimal plant growth. It supports many physiological functions like growth regulation, photosynthesis and seed development, sugar production and disease resistance [21]. Zinc help plants in surviving under-low temperature stress by aiding carbohydrate production, starch to sugar conversion and chlorophyll formation and also activates enzymes involved in synthesis of specific proteins [22]. Zinc-coated urea fulfills the early nutritional needs of crops by providing an efficient source if both zinc and nitrogen [23]. It contributes to maintain improvements in crop quality and productivity by enhancing physiological processes and plant metabolism. Furthermore, it improves overall crop quality by increasing zinc content in wheat grains and rice [24].

2.3. Polymer based coating

To address the challenges associated with sulfur coating, polymeric materials due to their less susceptibility to microbial degradation have become widely adopted for urea coating. To overcome rapid nitrogen release from traditional urea researchers have focused on synthesizing polymer blends. For instance, Ni et al. [25] reported the production of double-polymeric coated control-released urea fertilizer. The primary coating was of ethyl cellulose on which second layer of poly (acrylic acid-co-acrylamide) was added. It resulted in the final coated fertilizer which consisted of three layers, exhibiting an inner core of urea with N-vinylpyrrolidone hydrogel, second layer is of ethyl cellulose and an outer layer of super absorbent poly (acrylic acid-co-acrylamide) film. Analysis and results indicated that the water holding capacity of the coating increased up to 70 times its actual weight and a nitrogen content was 21.1%. Crop yield in regions facing severe water scarcity can be enhanced by using polymer-coated urea. Nitrogen release patterns affected by coating thickness, which grew with higher suspension rates and increased atomizing air pressure, but diminished as fluidizing air velocity and temperature rose [26]. Unlike inorganic coatings, nitrogen leaching through polymer membranes is largely determined by the physical properties and moisture permeability of the coating rather than by soil characteristics. By optimizing polymer composition, the moisture permeability can be precisely controlled [27], making it possible to predict nitrogen release from polymer-coated urea over a specified period with greater reliability than fertilizers coated with inorganic materials [28].

2.4. Bio-composite coatings

To address the challenges of non-biodegradable polymer coatings and their high production costs, recent studies have concentrated on developing bio composite coatings for controlled-release urea, with starch identified as a promising material [29]. Starch is a naturally occurring polysaccharide polymer easily derived from sustainable plant materials. However, due to its hydrophilic nature, starch cannot be used alone as a coating material for controlled-release urea and must be combined with other materials to be effective [30]. Ito, Boris, and Shinohara developed slow-release urea fertilizer granules using a two-layer coating system. Using a high-shear granulation system, a low-solubility isobutylidene diurea (IBDU) layer was applied as the inner coating, while a starch–wax blend was used to form the outer coating. Nutrient release behavior was evaluated through high-performance liquid chromatography by varying the quantity of dispersion medium and modifying the thickness of both the internal and external coating layers. Granules with a single coating layer released nutrients through a diffusion-controlled process, whereas those with dual-layer coatings exhibited a sigmoidal release profile when applied to soil. This sigmoidal mechanism involves gradual increase in nitrogen which was initially released slowly. Slow nitrogen dissolution into the soil was due to outer starch-wax layer which acted as a barrier. Dual-path process was followed by release mechanism: when core nutrient was dissolved in water it shrank gradually, and the nutrient concentration was decreased in the solution until equilibrium was maintained within the reservoir. In contrast to single-layer coated granules which showed diffusion-controlled release of nutrients, the dual-layer formulation, due to less permeable layer impeded nutrient diffusion, follow sigmoidal release pattern [31].

2.5. Superabsorbent coating materials

The unique properties of superabsorbent polymer materials (SPMs) have recently attracted considerable attention for the synthesis of slow-release urea (SRU). These cross linked hydrophilic polymers are three-dimensional and can absorb large amount of water, retaining it even under prolonged pressure [32]. Improvement of soil aeration, minimized water evaporation, decreased environmental pollution due to leaching and volatilization, reduced soil degradation and enhanced crop productivity due to prolonged availability of nutrients are some benefits of SPM-based urea applications [33]. Liang reported in his work that an inner polystyrene layer and an outer cross-linked poly (acrylic acid) containing urea can be prepared by double coating method. Shaviv describe the three-stage mechanism for nitrogen release from polystyrene coating [34]: the first phase is the lag phase where urea retained and water penetrated the coating, second is the constant release phase known as burst phase where urea dissolved and diffused through the coating, and the last phase is a decline phase which continued till complete release. The introduction of the second layer prevented the fast release of almost 70% urea by reducing burst effect, while the outer layer supported effective irrigation through increased water retention and improved slow release [32]. The combination of superabsorbent polymers with slow-release urea has many advantages due to water absorption capacity associated with regulated nutrient release. Nonetheless, the preparation process has high production costs that hinder large scale commercialization because the process is complicated and required raw materials are inexpensive. Additionally, the new form of soil pollution occurs due to the use of non-biodegradable coatings which further limits practical applications. Instead of these problems, many studies in this area of research are under consideration to overcome these challenges.

3. Coating methods

Different coating methods are commercially applied to produce slow-release fertilizers for nitrogen delivery. Some examples of these methods are fluidized bed coating, pan coating, and rotary drum coating technologies [35].despite of certain limitations associated with rotary drum and pan coating technologies, they are commonly used for synthesis of slow-release urea. Achieving uniform coating on urea granules using the rotary drum method often resulted in significant material loss. In this process, the fertilizer particles are agitated by the pan’s rotation while being sprayed with the coating solution through nozzles. Generally, throughout the showering operation, high temperature air was applied over the wet coatings for drying purposes. The production of controlled release fertilizer using the rotary pan method was used for many years, but the quality of the product had many drawbacks. The primary limitation of this method was uneven and inadequate thickness of coating layer [36].

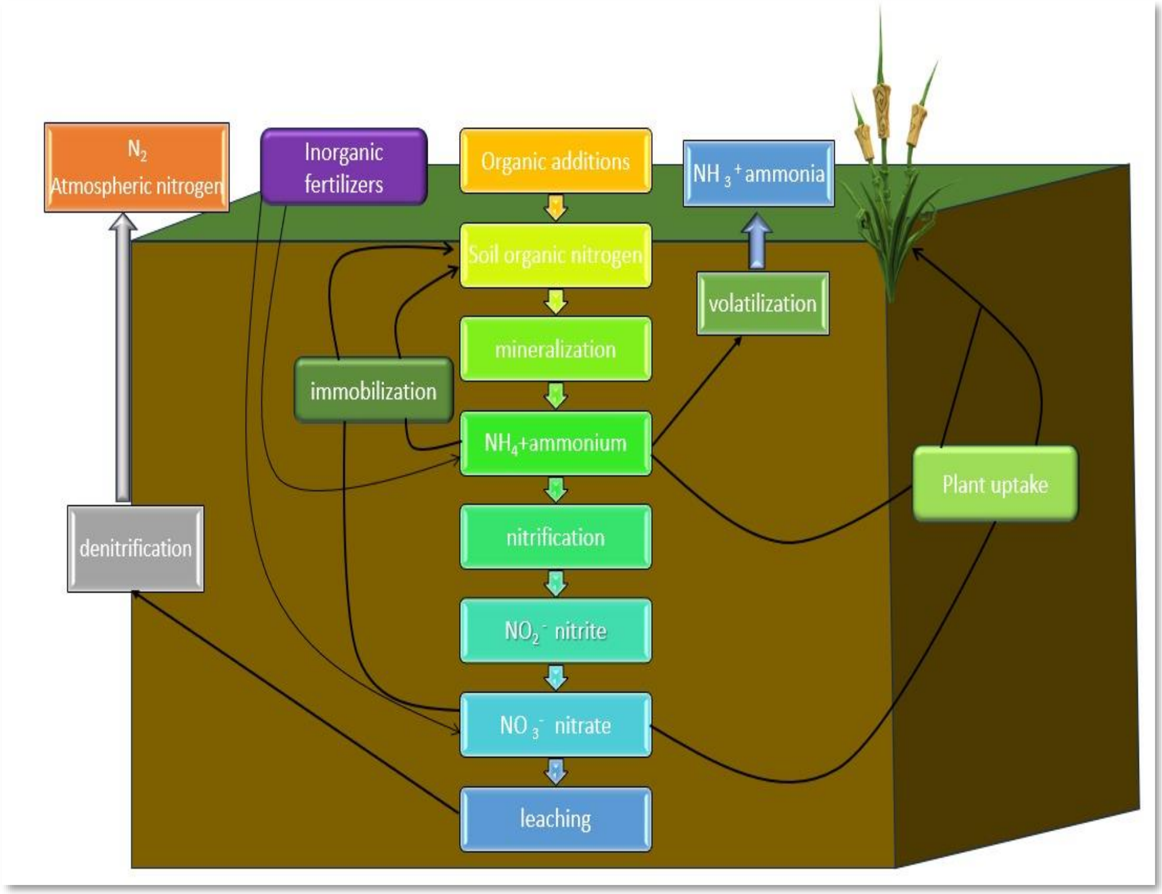

Figure 1. Simple nitrogen cycle for non-coated urea

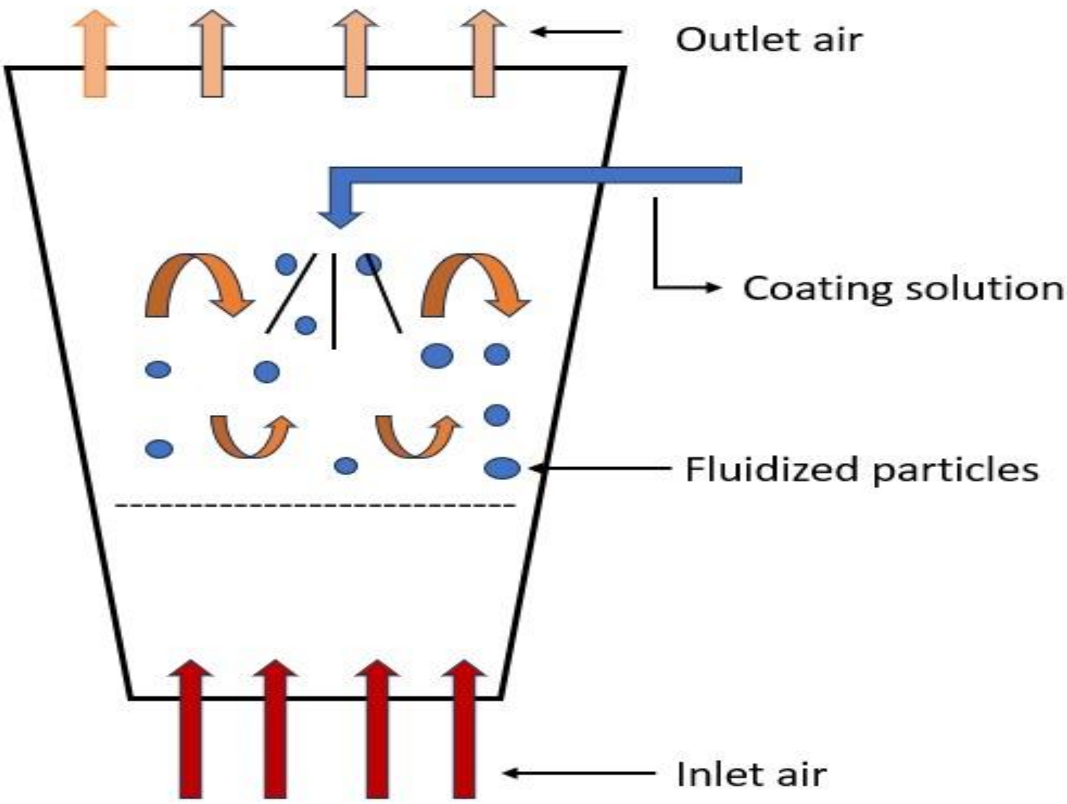

Figure 2. Top-Spray fluidized bed coating

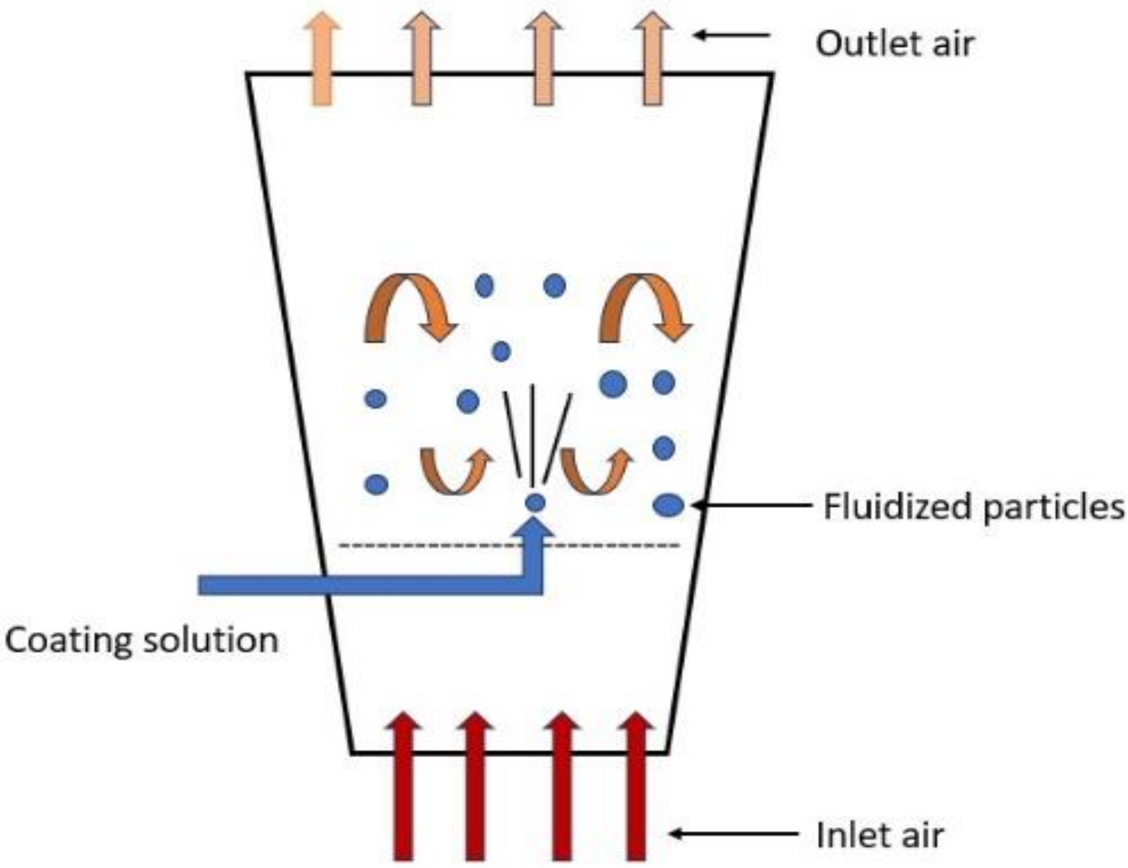

Figure 3. Base-spray fluidized bed coating

Table 1. Advantages and Limitations of Commonly Used Fertilizer Coating Materials

Materials	Advantages	Limitations
Sulfur based urea	• Economical and low-cost • Single-layer coating • Slow nutrient release, but with irregular pattern	• **Sensitive to:** • Elevated temperature and light exposure • Mechanical stress • Rough handling during processing • Inadequate sealing • Soil characteristics
Polymer based urea	• Manufactured using synthetic materials • Single-layer coating • Hydrophobic in nature • Simple release mechanism • Release minimally influenced by soil properties • Provides fully controlled nutrient release	• High cost • Predominantly non-biodegradable • Environmentally polluting • Potentially toxic
Starch based urea	• Widely available • Economic • Biodegradable • Environmentally friendly	• Fragile coating layer • Hydrophilic nature • Requires modification for effective use

3.1. Fluidized Bed Spray Coating

Numerous types of fluidized bed coaters are commercially available, all characterized by their ability to keep urea particles suspended during operation by directing air upward from the base of the bed [37]. Coating materials are applied to the suspended granules via nozzles. Among the different fluidized bed techniques, swirling bed coaters have proven most effective for producing controlled-release urea fertilizers. The particle motion during coating and fluidization is the key difference between swirling bed systems and other coatings because particles exhibit random movements in conventional fluidized beds [38]. Urea granules follow a circular trajectory due to circular motion generated by the air flow in swirling beds. The bed is divided into two regions: one region has high velocity particles while the other containing low-velocity particles, according with differences in air flow speed. Gravitational forces in the lower-velocity region balanced the effect of high-velocity air while central region lifted by an air stream. Various spraying methods such as internal bed spray, base spray nozzles and top spray nozzles are used to spray coating solution onto the suspended granules (Figures 2, 3) [39]. Air flow necessary for fluidizing the bed is supplied by an air compressor and a heat source such as an electric heating coil is used to heat the supplied air. The temperature must exceed minimum needed for film formation in order to achieve a uniform and smooth coating on fertilizer particles. Furthermore, sticking of urea granules and its lumps formation can be reduced by elevated air temperature which promotes evaporation of coating solution [40]. The quality of the coated fertilizer can be determined by an air used as fluidizing agent during the coating process. The duration that urea particles spend in the spray region where nozzles are located decides the thickness of the coating layer as they are directly related to each other. Urea granules move more rapidly within the bed as the contact time between the particles and the coating solution decreases when air velocity increases. The effectiveness of coating process and uniformity of the coating layer decreases when contact time becomes shorter. Consequently, the nutrient release behavior of the coated urea is adversely influenced by increasing air velocities. [41].

3.2. Plasticizers

Uniformity and distribution of the coating layer can be enhanced by using additives such as plasticizers incorporated into coating solutions. Polyethylene and polyvinyl acetate are some common examples of plasticizers used in sulfur coated fertilizers to reduce breakage of the coating. Talc and vermiculite are low-cost powders which have also been reported as effective additives [42]. In another approach, a biodegradable natural polymer such as glycerin and wax used as plasticizers alongside chitosan for coating urea granules. In order to prevent surface cracks and increase the plasticity of the coating, these plasticizers facilitated the formation of smooth chitosan film. With this approach, under standard testing conditions nitrogen release ranged from 0.64 to 0.965 over a 5-hour period [43]. Rindt, Blouin, and Getsinger [44] reported in their studies that water permeability can be lowered by incorporating fertilizers into sulfur coatings; however unintended negative effects may resulted as this method reduces surface adhesion.. To mitigate the rapid burst release of nutrients, a range of additives, such as sealing agents and plasticizers has been used which can adversely impact processing efficiency and economic feasibility of coated urea. Sulfur coated urea production for slow-release applications faces discontinuation due to these challenges.

4. Benefits of Coated Urea

Limiting volatilization of ammonia, nitrous oxide and nitrate leaching, the use of slow-release fertilizers can enhance nitrogen use efficiency (NUE) and reduce nutrient loss, thereby controlling environmental pollution. Additionally, SRFs maintain comparable crop yields by reducing fertilizer application rates by 20-30% of the recommended amounts [45]. By following a sigmoidal pattern, it improves agronomic safety when nutrients are released at an optimal rate and also offers economic benefits through savings in energy, time and labor [46]. Plants especially seedlings can be damaged by conventional fertilizer practices as they often create high local concentrations of ions, leading to osmotic stress [47].

5. Conclusions

Improvement of nitrogen use efficiency and enhancing the efficiency of urea uptake is a major focus for future research. Slow- or controlled- releasing coating technologies can be used to address these challenges. However, most of coating materials which are commercially available are environmentally unfriendly, expensive and non-biodegradable. While sulfur-coated fertilizers have been brought to market, significant limitations remain, including difficulty in achieving uniform and compact coating thickness, unpredictable slow-release behavior due to surface cracks, insufficient impact resistance and abrasion, and complex processing requirements. Sulfur's inherent brittleness and crystalline structure often result in thin, uneven, fragile, and discontinuous coatings. Biodegradable polymers obtained from natural sources present a promising alternative to non-biodegradable materials. Among these, starch stands out as environmentally friendly, biodegradable and low-cost option for use as a coating material in slow-release fertilizers. Modified starches differ markedly from other non-Newtonian fluids in their physical properties, which implies that spray behavior of starch-based solutions is expected to differ from previously reported coating materials.

While modified starches offer superior functional performance compared to native starch, they must be produced in cost-effective and an eco-friendly manner to ensure an optimal balance between performance and affordability for end users. While swirling fluidized bed spray systems have been widely studied for bed hydrodynamics and coatings such as enteric or sugar layers, few studies have focused on characterizing the spray parameters of viscous coating materials. Since using starch as a coating material for slow-release fertilizers is a relatively new area of research, it is essential to characterize its spray behavior both in ambient air and within the fluidized air column to develop an effective and efficient coating process. With environmental regulations becoming increasingly stringent, the adoption of slow-release urea is expected to become a critical requirement. This strategy not only enhances crop yields and minimizes fertilizer usage but also mitigates environmental impacts. Yet, to enable farmers to achieve economically efficient, higher quality & environmental-sustainable crop-production further investigation into novel coatings formulation warranted, and considerable opportunities remain for optimization. To examine tailing effect of nutrient release near the end-of-life of slow-release fertilizer (SRFs) and to validate results, field evaluations under diverse environmental conditions are necessary. Furthermore, practical and commercial implementations of SRFs require standardized procedures and upscaling methodologies development.

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