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The Role of Urea Types in Minimizing Leaching Loss to Maximizing Its Use Efficiency

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

The research aimed to investigate the behavior of nitrogen (N) when different types of urea fertilizers are used in *Alfisol*. Traditional chemical fertilizers have a low N use efficiency, around 30 to 35 percent, posing a significant challenge for improvement. This study sought to assess the effectiveness of urea coated with various materials compared to regular urea and prilled urea, focusing on how they affect N release dynamics and leaching losses. Results showed that urea coated with certain materials, such as CSPC @3% and neem-coated urea, resulted in lower levels

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of NH⁴ + -N in the leachate compared to conventional and prilled urea. Specifically, CSPC @3% exhibited a gradual release pattern, with NH₄+-N levels decreasing from 55.00 to 54.00 µg between the 0th and 50th day of leachate collection (DLC). Moreover, $NO₃$ -N levels were lowest in CSPC @3%, ranging from 17.71 to 31.00 µg during the same DLC period. These findings suggest that uncoated urea undergoes hydrolysis upon application, leading to conversion into various forms of nitrogen, including available, ammonical and nitrate. However, nitrate despite being present in smaller quantities is particularly susceptible to leaching losses. Therefore, the use of coated urea formulations like CSPC @3% and neem-coated urea can help minimize such losses, thus enhancing nitrogen use efficiency.

Keywords: Corn starch based superabsorbent coated @3% prilled urea (CSPC @3%); neem coated urea; leaching loss; NUE (Nitrogen Use efficiency).

1. INTRODUCTION

Nitrogen holds a paramount position among essential plant nutrients, recognized for its indispensable role in numerous biological functions. It serves as a foundational element in key plant compounds such as chlorophyll, amino acids, proteins and enzymes, which are vital for facilitating plant growth and fostering overall development. Despite being abundant in the atmosphere, plants cannot directly utilize atmospheric nitrogen (N_2) due to its triple bond nature. Instead, they rely on nitrogen in the form of nitrate $(NO₃)$ or ammonium $(NH₄⁺)$ for nourishment, with most plants absorbing nitrogen in the $NO₃$ form, except for rice, which prefers NH₄+[1].

In agricultural soils, nitrogen availability varies but generally falls within the range of 0.02% to 0.4% on a weight basis. Indian soils, in particular, tend to be low in available nitrogen due to factors such as poor organic matter content and high temperature [2]. To compensate for this deficiency and prevent nitrogen loss from soils, external nitrogen sources, such as fertilizers, are crucial for crop production.

Urea fertilizer holds a prominent position in the global nitrogen fertilizer market due to its costeffectiveness, high nitrogen content (46%) and ease of production. In India, urea accounts for a significant portion of nitrogen fertilizer consumption. However, the efficiency of conventional urea fertilizers is often compromised by factors such as ammonia volatilization, denitrification, leaching and immobilization, leading to low nitrogen use efficiency (NUE), typically ranging from 30 to 35 per cent [3,4].

To address these challenges and improve NUE, various technologies have been developed, including controlled-release urea (CRU) fertilizers [5]. CRU fertilizers release nitrogen gradually over time, mimicking organic nitrogen sources and reducing the risk of nitrogen loss [6]. Coating urea with materials like neem oil or biodegradable polymers has shown promise in enhancing NUE by regulating nitrogen release and minimizing losses [7,8,9].

Among biodegradable polymers, starch-based superabsorbents have gained attention for their environmentally friendly properties [10]. Starch, derived from sources such as cereal grains and tubers can effectively reduce leaching loss of nitrogen when used as a coating material for urea fertilizers [11]. This study explores the effectiveness of corn starch-based superabsorbent in mitigating nitrogen (N) leaching losses. With this aim, the research evaluates the performance of urea coated with various materials, comparing it to prilled urea and ordinary urea. The focus is on understanding how these different urea formulations impact the leaching losses.

2. MATERIALS AND METHODS

2.1 Soil Collection and Processing

The experimental soil belonging to order *Alfisol* was collected from a field situated at College of Agriculture, V. C. farm, Mandya. (at 12˚34˝ N, 76˚49˝ E, and 713 m above mean sea level) located under the Southern Dry Zone (Zone-6) of Karnataka. The bulk soil samples were collected from the upper 15 cm surface soil. While collection all the stubbles, gravels and stones were removed, shade dried, and passed through a 2 mm size sieve. The important initial soil properties were analyzed following the standard analytical methods and listed in Table 1.

2.2 Experimental Setup

Under greenhouse conditions, an experiment was conducted to study the leaching loss of nitrogen (N) from different N sources applied to soil. Twenty-seven pots of similar size were prepared by cleaning them and making a hole near the bottom surface of each pot. A tube with a diameter of 1.50 cm was securely attached to each hole using an L-bow joint with a rubber case to ensure leak-free leachate collection. To prevent soil particles from entering and ensure clear leachate, a filter paper was placed at the bottom of each pot and secured with gravel. Subsequently, all 27 pots were filled with ten kilograms of air-dried and sieved soil. Gentle tapping was applied to maintain a bulk density of approximately 1.49 Mgm⁻³, simulating $approximately$ 1.49 , simulating conditions similar to those found in cultivable fields.

Table 1. Initial soil physio-chemical parameters

Plate 1. Different types of urea fertilizers

2.3 Imposition of leaching

The pot was filled with 10 kg of *Alfisol* soil and saturated to its maximum water holding capacity (MWHC) by adding the calculated amount of water. The volume of the pot's frustum shape was utilized to determine the precise quantity of irrigation water needed for this purpose.

$$
V = \frac{1}{3} \Pi \ h \ (r2 + R2 + Rr)
$$

Where, V= Volume of frustum (volume of irrigation water), $h=$ height (5 cm), $R=$ upper radius and $r =$ lower radius

1. Make a hole adjacent to bottom

4. Uniformly distributing calculated amount of fertilizer

To reach the MWHC of the potted soil initially, 2625 ml of water was added. Subsequently, leachate was collected at 5-day intervals, starting from day 0 and continuing until day 45. To facilitate leachate collection, an additional 200 mL of water was added each time into a clean plastic jar. During the intervening days, soil moisture was sustained at field capacity by adding water as needed, determined by monitoring weight loss every 24 hours. Leachate was collected at an interval of 5 days and subjected to analysis for its electoral and chemical properties $viz.$, $NH₄$ ⁺, NO₃, cations (Ca⁺ , Mg⁺ , K⁺and Na⁺) and anions (carbonates, bi-carbonates, sulphates and chlorides).

2. Fixing L-bow with rubber 3. Filling of soil

5. Filling a layer of soil

Plate 2. Preparation of pot for leaching study

Plate 3. a) Collection of leachate b) After the collection of leachate

2.4 Determination of Ammonia (NH⁴ +) and Nitrate (NO³ -)

Five milliliters of leachate were distilled with 25 mL of 40 percent NaOH in the Kjeldhal N analyzing instrument. The ammonia released was trapped in 4 percent boric acid containing mixed indicator titrated against 0.05N standard sulphuric acid and expressed as NH_4 +-N [12]. Subsequently, for the same sample contained in a distillation tube 0.50 g of Devarda's alloy was added and repeated the above procedure to get $NO₃$ -N [13].

2.5 Statistical Analysis

The data about leaching losses of N had been instructed to statistical analysis adopting completely randomized block design (CRD) Gomez and Gomez [14]. One-way analysis of variance (ANOVA) was done using statistical package SPSS version 9.1.6.3. Further, the significant difference between treatment means was compared with critical differences at a 5% confidence level.

3. RESULTS AND DISCUSSION

3.1 Ammonical N content of Leachate Collected after Successive leaching of Soil

Variations in the ammonical N content of leachate during leaching of soil applied with different urea fertilizers are given in Table 3. Changes in ammonical N content on the day of leaching (0th day) among the treatments were non-significant. Initially (5th DLC), NH_4 ⁺ -N content in the leachate was significantly higher in treatment T2 (84.73 µg) that received CU followed by T3 (75.94 µg) received PU and T8 (74.14 µg) that applied with PCSA @3%. Although treatment T8 (PCSA @3%) and T9 (PCSA @6%) were found to be statistically at par with each other (74.14 µg in both treatments). Further, the significantly lowest value of NH_4 + -N was recorded in the control (41.00 µg) followed by T6 received CSPC @3%.

Subsequently, the NH_4 ⁺ -N content of leachate decreased with increasing days in treatments T1, T2, T3, T5, T7, T8 and T9. Whereas, treatments T4 and T6 have shown increasing to till 25th day of leachate collection. Further, irrespective of treatment plummet of NH_4 ⁺ -N content was noticed. However, at the 50th DLC, the maximum

NH⁴ + -N content was recorded in CSPC @3% (59.00 µg) which was statistically at par with NCU (54.00 μ g). Further, the least NH₄+ -N content was noticed in the control (9.00 µg) followed by CU (12.00 μ g).

Under the controlled condition, the highest concentration of NH₄+-N in CU was recorded on day 7, indicating that virtually all the urea was hydrolyzed within ten days [15]. Due to the uncoating CU and PU when came in contact with water and urease Enzyme, it was activated and complete hydrolysis occurred and liberated as free ammonia at a faster rate. Whereas in coated urea (neem coated and corn starch-based superabsorbent) due to the coated layer which acts as a semipermeable membrane. With the influence of soil temperature, moisture penetrates inside through that membrane and dissolves the nutrient core which builds up the osmotic pressure inside the coated granule. They can reduce N losses due to their potential to delay N release patterns [16].

The decrease in leaching of NH_4 ⁺ -N could be due to loss of NH₃ by volatilization or transformation of NH_4 ⁺ -N to NO_3 ⁻ -N by nitrification. Along with this NH_4 ⁺ ions are positively charged they may get absorbed by negatively charged soil particles. These results are in confirmatory with Mohanty et al. [17], Abbasi et al. [18] also reported that application of neem coated urea delayed the NH₄+ reduction.

3.2 Nitrate N Content of Leachate Collected after Successive Leaching of Soil

The leaching of $NO₃$ -N followed a similar trend as that of NH_4 ⁺ (Table 4). There was no significant difference among treatments on the initial day (0th DLC). Application of different urea fertilizers showed a significant loss of $NO₃$ -N content from the 5th day of leaching fractionation.

Sparingly, higher $NO₃$ -N content was observed in CU *i.e*., T2 (33.00 µg) which increased up to the 30th day (77.00 µg) and reduced in successive days and had less concentration at the last leachate (56.00 μ g). The same trend was followed by T3, T9, and T8 where the concentration increased from 30.00 to 74.00, 28.00 to 72.00, and 28.00 to 70.00 µg up to the 30th day of leachate fractionation after that it reduced to 52.00, 51.00 and 49.00µg, respectively. It was interesting to note a lesser

Table 3. Effect of different types of urea fertilizers on NH₄+ -N content of leachate collected from soil after successive leaching

Note: Leachate was collected at 5 days interval

Table 4. Effect of different types of urea fertilizers on NO₃⁻-N content of leachate collected from soil after successive leaching

Note: Leachate was collected at 5 days interval

amount of $NO₃$ -N initially in coated urea fertilizer (neem coated and corn starch based superabsorbent) but the concentration steadily increased up to the collection of 5th leachate (30th DLC) and it showed a decrease in concentration till to the end. However, in NCU $(T4)$ NO₃ -N content increased from 23.00 to 59.00 µg and decreased to 33.00 µg. Whereas, in CSPC $@3\%$ (T6) NO₃ -N content increased from 22.00 to 57.00 µg and was reduced to 31.00 µg in the last leachate collection (50th day).

The higher content of $NO₃$ -N in conventional and prilled urea may be due to the rapid rate of urea hydrolysis and nitrification rate which causes faster conversation of $NH₄$ ⁺ to $NO₃$ ⁻ which resulted in maximum leaching in the form $NO₃$ $(99 %)$ compared with NH₄⁺ [15]. Further, this may be due to repulsion between negatively charged nitrate ions and negatively charged soil particles.

A lesser $NO₃$ -N concentration in the leachate from the coated urea fertilizer (CSPC @3% and NCU) of the leaching study suggests that a somewhat longer period is needed for the release of urea from the coating. In the case of neem-coated urea, the alkaloid present in the neem oil might have inhibited the ureaseproducing microbial activities [16]. The corn starch-based superabsorbent was coated with a material that has the property of water retaining, they can retain large quantities of water and nutrients. The stored water and nutrients are released slowly. This results in slow release in the amount of $NO₃$ -N was noticed in leachate. These results are corroborated with Islam et al. [19].

3.3 Soluble Cations in Leachate Collected after Successive Leaching

Nitrate leaching can deplete the soil exchangeable cations such as Ca²⁺, Mg²⁺, and K⁺ which might have increased soil acidity. Anyhow among the cations maximum quantity of leaching occurs in Ca^{2+} followed by Mg^{2+} . As soil is light textured (sandy loam) indicating greater loss of Ca^{2+} . Highest Ca^{2+} content was demonstrated in T2 (CU) that decreased from 9.34 to 2.96 meq L^{-1} followed by PU T3 decreased from 9.30 to 3.07 meq L-1 , T9 (PSCA $@6\%$) from 8.47 to 3.13 meq L⁻¹ that was on par with T8 (PSCA @3%) reduced from 8.44 to 3.14 meq L-1 . The least amount of calcium was revealed that decreased in trend from 8.22 to 4.10 meg L^{-1} and 8.26 to 4.01 meg L^{-1} detected

in CSPC @3% and NCU. Upon 1st leaching (0th DLC), the significantly highest magnesium content was recorded in T2 and decreased from 7.01 to 2.58 meq L^{-1} received CU treatment followed by T3 (6.98 to 2.51 meq L^{-1}), followed by T9 (6.35 to 1.94 meq L^{-1}) treatment on par with T8 (6.33 to 1.92 meq L^{-1}). Similarly, T7 and T5 are on par with each other submitting 6.29 to 1.86 and 6.24 to 1.85 meq L^{-1} , respectively. Further, the minimum magnesium content was found in control (6.21 to 1.61 meq L^{-1}) and NCU $(6.20 \text{ to } 1.80 \text{ meq } L^{-1})$ which is on par with CSPC $@3\%$ (6.17 to 1.72 meq L⁻¹). Irrespective of treatments, the difference due to applied urea was found to be non-significant. However, at 50th DLC, the highest leachate quantity of Na⁺ was found in T2 $(2.88 \text{ meq } L^{-1})$ followed by T5 (2.86 meq L-1), T3 (2.81 meq L-1), T9 (2.79 meq L⁻¹), T7 (2.71 meq L⁻¹), T6 (2.69 meq L⁻¹) and lower content Na⁺ was recorded in control (2.33 meq L^{-1}) followed by T8 (2.59 meq L^{-1}). The concentration of potassium leaching was followed in the order of coated urea $(T6 > T4 >$ $T5 > T7$) physical blending $(T8 > T9)$ uncoated urea (T3 > T2 > T1) with 1.91, 1.89, 1.76, 1.79, 1.69, 1.68, 1.60, 1.58 and 1.55 meq L-1 , respectively. Similar trend was attended until the 15 days. Further, exactly opposite trend was noticed i.e., uncoated treatments followed by physical blending and coated urea treatments. From the 20th day concentration of potassium in leachate was followed in the order of T2 > T3 > T9 >T8 > T7 > T5 > T4 > T6 with 1.36, 1.35, 1.30, 1.28, 1.20, 1.22, 1.19 and 1.15 meq L-1 and potassium content decreased to 1.17, 1.16, 1.11, 1.09, 1.01, 0.99, 0.93 and 0.92 meq L-1 when collected at 50th DLC, respectively.

The higher Ca^{2+} and Mg^{2+} concertation, in the beginning, indicated high exchangeable Ca2+ forms were transformed into soluble. After this stage, the Ca^{2+} and Mg^{2+} concentrations continued to decline slowly until the end of the leaching period. In addition, Ca^{2+} and Mg^{2+} content in the leachate of all the treatments was higher than control, which may imply that urea fertilizer contributed to the release of soluble $Ca²⁺$ and Mg²⁺. However, there was no difference in Ca^{2+} and Mg^{2+} leached between the treatments that received different urea fertilizers. However, after the 35th day, the significance regarding Ca2+ and Mg2+ was noticed because of the decrease in pH which most efficiently affected the replacement of bonded Ca²⁺ and Mg2+ in the soil solution. However, the higher content in coated urea is mainly due to the $NO₃$. N release pattern of coated urea [17].

The hydron ions produced during nitrification can release Ca^{2+} and Mg^{2+} by exchange from soil colloids, resulting in a high amount of $Ca²⁺$ and Mg2+ leaching from coated urea at the end. Initial higher K⁺ concentration in the leachates was due to preliminary treatment of the saturated soils with deionized water which attended there was no significant difference. The release of K⁺ and Na⁺ is a slow process indicating a decrease in the concentration of K⁺ and Na⁺ in leachate [11].

NH₄⁺ and K⁺ compete for the same binding sites on the clay colloids which revealed lower fixation of K⁺ found with an increased in NH₄⁺ content in soil which may get bonded with soil colloids or may converted to the $NO₃$ -N. As in uncoated urea, the NH⁴ ⁺ was leached in a higher amount initially indicating lesser replacement of K⁺ which increases concentration in leachate. But in coated urea due to the behavior of slow releasing initially, the K⁺ was leached with water as potassium held by soil colloids which was easily displaced. Further, lower in $K⁺$ content at the end may be due to the complete leaching of watersoluble and exchangeable K⁺. Similar results are reported by Mohamed et al. [20].

3.4 Soluble Anions in Leachate Collected after Successive Leaching

The chloride ion content in the leachate initially peaked but gradually declined with successive leaching, showing variations among treatments after the 10th day. Initially, higher chloride levels were noted in treatments T6 (CSPC @3%) and T4 (NCU), while uncoated urea treatments (CU and PU) exhibited the lowest chloride content. Chloride in soil primarily exists in soluble form and moves readily into the soil solution, resulting in higher concentrations in leachate, especially in sandy loam soil with high hydraulic conductivity. Total carbonate content initially showed no significant differences among treatments but varied notably after the 10th day of leachate collection. The variation in the chlorine concentration in leachate among the treatments was not significant initially till 10th day of leachate collection. Relatively higher chloride content was recorded in the treatment T6 that received CSPC @3% i.e., 8.56 meq L-1 after 1st leaching which decreased to 4.13 meg L^{-1} after 10th leaching which is on par with NCU that decreases the concentration of chloride from 8.51 to 4.09 meq L-1 followed by NCPU (8.48 to 3.75 meq L-1) which on par with CSPC @6% $(8.43 \text{ to } 3.51 \text{ meq } L^{-1})$. The minimum amount of chloride content was leached in uncoated urea

fertilizer in CU from 7.67 to 2.45 meq L-1 and PU from 7.93 to 2.85 meq L^{-1} and in was leached. There was no significant difference was recorded due to different treatments till 10th DLC but could find significant difference from $20th$ to $50th$ DLC. Higher concentration of total carbonates of 7.53 and 7.43 meg L^{-1} at 0th DLC was observed in T_2 (CU) and T_3 (PU), respectively. Further, at $50th$ DAL the content was decreased to 1.44 and 1.85 meq L^{-1} in the same treatments (T₂ and T₃, respectively) which were recognized as lesser carbonate content. It was followed by $T₉$ (PSCA $@6%$) and T₈ (PSCA $@3%$) with 7.16 and 6.73 meq L⁻¹ at 0th DLC decreased to 2.05 and 2.31 meq L⁻¹ at 50th DLC. Initially least total carbonates content in the leachate was noticed with 5.66 and 5.70 meq L^{-1} in T₆ (CSPC @3%) and T⁴ (NCU) indicating decremental rate throughout the leaching experiment but contenting higher concentration at the end compared to other treatments with 3.27 and 3.16 meq L-1 . Further, the lesser and decreasing trend was observed in control. The maximum quantity of sulphate was leached in initial leaching (0th DLC) with values of 1.28 and 1.25 meq L^{-1} in treatments T_6 and T_4 , respectively and further successive leaching decreased its quantity recorded 0.39 and 0.36 meq L-1 , respectively at $50th$ DAL. The subsequent values of $SO₄²⁻$ in treatments T_5 and T_7 removing from 1.17 and 1.15 to 0.28 and 0.26 meq L^{-1} , respectively. Application of uncoated urea indicated lesser amount of sulphate leaching. The treatments T₃ and T_2 constitute the sulphate content 1.01 and 0.95 meq L^{-1} in early day leachate collection and decreased 0.12 and 0.08 meg $L¹$ at the end of leachate collection.

Initially higher levels were observed in treatments T2 (CU) and T3 (PU), with decreasing trends over time. Treatments with coated urea formulations showed lower initial total carbonate content but maintained higher levels compared to uncoated urea treatments throughout the leaching experiment. Sulfate content in the leachate was initially higher and decreased steadily over time. Treatments with coated urea formulations exhibited higher initial sulfate levels compared to uncoated urea treatments, with concentrations decreasing over successive leaching events. Sulfate sulfur is prone to rapid leaching losses from the soil, especially in the presence of monovalent cations, leading to higher concentrations in the soil solution and subsequent leachate. Urea application enhances sulfate concentration in the soil solution, contributing to its increased leaching [21,22].

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Fig. 1. Cumulative amount of cations in leachate collected after ten successive leaching from soil

Fig. 2. Cumulative amount of anions in leachate collected after ten successive leaching from soil

4. CONCLUSION

Nitrogen is indispensable for plant growth and development, playing a vital role in various biological processes. Despite its abundance in the atmosphere, plants require nitrogen in forms such as nitrate and ammonium, which are not readily available from the air. Agricultural soils often lack sufficient nitrogen levels, necessitating the use of external nitrogen sources like fertilizers to sustain crop productivity. Urea fertilizer, with its high nitrogen content and costeffectiveness, is extensively used in agriculture globally. However, conventional urea fertilizers suffer from drawbacks such as nitrogen losses through volatilization, leaching, and

denitrification, leading to low nitrogen use efficiency. To address these challenges, controlled-release urea (CRU) fertilizers have been developed, including those with biodegradable coatings like starch-based superabsorbents. In this study, we investigated the leaching losses of nitrogen from various urea fertilizers applied to soil under greenhouse conditions. The experiment revealed significant differences in ammonium and nitrate leaching among different urea formulations. Ordinary urea and uncoated prilled urea fertilizers exhibited higher initial leachate nitrogen content (upto 30th DLC) compared to CSPC @3% and NCU, indicating a faster release of nitrogen from uncoated urea. However, coated urea

formulations demonstrated a delayed release pattern, resulting in lower nitrogen leaching over time. Furthermore, the study assessed the leaching of soluble cations and anions, revealing variations in chloride, total carbonates, and sulphate concentrations in the leachate among different treatments. CSPC @3% and NCU urea formulations exhibited higher initial levels of total carbonates and sulphates compared to other treatments which includes urea, prilled urea neem coated prilled urea and physical blending of prilled urea wuth corn starch based superabsorbent coating urea. Overall, the findings highlight the potential of coated urea fertilizers, particularly those incorporating starchbased superabsorbents, to mitigate nitrogen losses through leaching and improve nitrogen use efficiency in agricultural soils. These innovations in urea fertilizer technology hold promise for enhancing sustainable agricultural practices, reducing environmental impacts. Further research and field trials are warranted to validate these findings and optimize coated urea formulations for widespread adoption in agriculture.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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