J. Appl. Res Plant Sci. Vol. 6(1), 01-07, **2025**, https://doi.org/10.38211/joarps.2025.06.288

Research Article

OPEN ACCESS

Available on https://www.joarps.org
Journal of Applied Research in Plant Sciences
(JOARPS)
ISSN: 2708-3004 (Online), 2708-2997 (Print)

Efficiency of Nano-silicon Coated Urea with Various Fertilizing Techniques on Maize (*Zea mays* L.) Performance and Nitrogen Content

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Article Received 12-08-2024, Article Revised 03-12-2024, Article Accepted 14-02-2025

ABSTRACT

Environmental deterioration and nitrogen (N) losses are closely interrelated. In the realm of nitrogenous fertilizers, urea holds a prominent position due to its unique characteristics and high N content. While urea is valued for its ease of application, excessive use often leads to significant losses through leaching and volatilization. Coating urea with biodegradable materials offers a potential solution by enabling the steady release of N. In recent years, nanotechnology has been employed in various ways to coat urea, improving its efficiency. With the dimensions of nano-fertilizers and N losses in mind, a field experiment was conducted at the Soil Fertility Research Institute (SFRI) in Tandojam, Pakistan. The study investigated the effects of nano-silicon (nSi)-coated urea on the growth, N uptake, and nitrogen use efficiency (NUE) of maize plants. Nano-Si was used as a urease inhibitor with urea (160 kg N ha^{-1}) and combined with different coating materials, namely vegetable oil and palm stearin, to assess binding reliability. Two fertilization application techniques broadcasting and placement were also evaluated. The highest agronomic performance was observed when nSi-coated urea with palm stearin was applied, while coating with vegetable oil was less effective but still outperformed broadcast urea. NUE and N uptake were significantly improved when nSi and urea were combined, compared to other treatments. Additionally, plants demonstrated the ability to utilize nano-Si, a sustainable byproduct derived from rice husks. The overall findings of this study are promising and provide valuable insights for future strategies to enhance nitrogen use efficiency while mitigating environmental degradation.

KEYWORDS: Nano-technology, Synchronized nitrogen release, Staple crops, Eco-friendly adhesives, Nitrogen utilization

INTRODUCTION

Nitrogen is an essential nutrient that influences metabolic, physiological, and biochemical processes in plants. Available amounts of N are required for crops to produce amino acids, nucleic acids, nucleotides, enzymes, and hormones (Lawlor et al., 2001). A common nitrogen-based fertilizer is urea with a high (46%) nitrogen concentration and is widely recognized as the major and most affordable source of N in the farmer's community (Kira et al., 2019). Global urea production capacity has increased by 17 Mt (+8%) and is expected to reach 230 Mt in 2024, up from 225 Mt in 2021 (Skorupka & Nosalewicz, 2021). There are several factors that influence the ammonia soil emission potential, including fertilizer application methods, cultivation systems, soil type and pH (Babar et al., 2022). Due to the urease enzyme, conventional urea accelerates the hydrolysis rate of urea in soil (Davies et al., 2022). Pollutants such as ammonia (NH_3) contribute significantly to secondary inorganic aerosol formation, which degrades air quality and negatively affects human health (Nair & Yu, 2020). Emitted NH_3 can also increase soil acidification and eutrophication, and decrease biodiversity through nitrogen (N) deposition (Jiang et al., 2017). Fertilizers play an integral role in promoting agricultural productivity and sustainability. A number of alternative approaches are being used worldwide to enhance the nitrogen use efficiency of urea fertilizers and increase its uptake by crops (Arif et al., 2019). Effectively managing nitrogen is a challenge for reducing losses, enhancing crop yield, and improving use efficiency (Gil-Ortiz et al., 2021). Efficiencies in nutrient use and crop productivity can be improved through the adoption of innovative strategies (Salim et al., 2020). The use of controlled release urea (CRU) allows nutrients to be applied to crops over a long period of time. The plants will be able to absorb urea more effectively if nutrients are gradually supplied. According to studies (Naz and Sulaiman, 2016), semi-permeable coating materials can delay initial absorption and prolong nutrient supply. Although material selection for coating is a crucial stage as they are directly related to urease activity, a restraint hydrolysis rate is indispensable (Babar et al., 2019). In addition to being eco-friendly to the soil, urease

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inhibitors and binders should also be friendly towards the environment.

Silicon (Si), constituting about 28% of the Earth's crust, is primarily available through minerals and biogenic silica. Soluble silicon forms, including monosilicic acid (H_4SiO_4), are absorbed by plants at soil concentrations of 0.1–0.6 mM, either passively or via active transport systems in the roots. Once taken up, Si is deposited as amorphous silica in plant tissues, enhancing their structural integrity and stress resistance (Ma & Yamaji, 2006). The recommended dose of silicon (Si) fertilizer for wheat crops depends on factors like soil type, existing soil Si levels, and environmental conditions. However, typical rates range from 100 to 200 kg of Si per hectare, often applied in the form of silicon-rich fertilizers such as calcium silicate, potassium silicate, or diatomaceous earth (Kovács *et al.,* 2022).

Since scientists generally work with nanoparticles these days, Nano-Silicon (nanoparticles) reduces urease activity and is therefore considered an effective urease inhibitor (Sarkar et al., 2022). To develop an eco-friendly nitrogen fertilizer, a variety of natural binders have been tested with different inhibitors, including phenolic aldehyde (Horta et al., 2016). In this way, N-losses and environmental pollution can minimally be achieved through biodegradable adhesive coating materials. Thus, the urea microsites in our current research have been coated with synthetic vegetable oil and Palm Stearin (PS). Palm Stearin actually is a by-product of oil palm and is less valuable in the industry. Both binders can be used without any risk concern. Considering N losses with conventional urea, this study proposes to evaluate N efficiency by using various fertilizing techniques; comparing broadcasting versus placement and coated urea, we assessed the grain yield and nitrogen content of maize in response to Nano-Silicon (used as urease inhibitor) coated urea applications.

MATERIAL & METHOD

Experimental minutiae: A field experiment was led in the fields of the Soil Fertility Research Institute, ARI, Tandojam, Sindh Pakistan. The studied site was located at latitude 25°25'27.2"N and longitude of 68°32'45.9"E. A study evaluated the N efficiency and behavior of maize towards Nano-Silicon coated urea with various fertilizing techniques during the summer of 2023. There were six treatments with single fertilizer urea (160 kg N ha^{-1}) along with the recommended phosphorous (80 kg P_2O_5 ha^{-1}) and potassium (50 kg K_2O ha^{-1}) in the form of triple superphosphate ($Ca(H_2PO_4)$. H2O) and sulfate of potash (K_2SO_4) respectively (Table 1). Broadcasting and placement were compared as coated and commercial urea on the maize crop variety *'Akbar'*. Biodegradable binders as PS and vegetable oil were used to coat urea with urease inhibitor Nano-Si to synchronize N availability for maize plants. Coated urea was prepared manually in the laboratory of the department of Soil Science, Sindh Agriculture University, Tandojam. Palm stearin is a byproduct of oil palm and exported from Malaysia, whereas synthetic vegetable oil (available in the market) was used to compare their binding effects. However, Nano-Silicon (Nano-Si) which is also a natural waste product is exported from Türkiye and is used as a urease inhibitor in current research. The ratio and methodology for coating is followed by Babar *et al.*, 2016. The experiment layout was a Randomized Complete Block Design (RCBD) with four replications. The canal water was used for irrigation. The first irrigation was applied after 20 days of cultivation and a total of six irrigations were applied, each at 15-18 days interval depending on the conditions of the soil. Straight fertilizer (commercial urea) was applied in three splits at the different growth stages of crops, but coated urea was applied once.

Land preparation: The land was prepared according to recommended practices before planting the maize crop. The soil was properly tilled, and seeds were sown using the drilling method at the recommended seed rate of 12-15 kg/ha. The experimental field was divided into four blocks (replications), comprising a total of 24 plots, each measuring 4m x 4m ($16m^2$). Each replication included six treatment plots of $16m^2$, with one meter spacing between replications and treatments. Row spacing was maintained at 75 cm, with 25 cm spacing between plants. Regular weeding was carried out throughout the planting period.

Soil and Plant analysis: Before sowing, composite soil samples were collected randomly from each block at a depth of 0-30 cm. Soil samples were air dried, and passed through a 2mm sieve, then stored for further soil analysis of recommended soil tests such as soil texture, electrical conductivity (dSm^{-1}) and pH through 1:2.5 soil water (w/v), organic matter (%), and total nitrogen (%) in soil (Ryan et al., 2001). A soil sample was collected from each repeat after crop harvesting and air dried before being sieved and stored for subsequent soil analysis of total nitrogen (%). In order to analyze the N content in plant tissues, five randomly selected plant samples were collected from each repeat after harvest. Plant samples were collected and transferred to the Laboratory. Before using distilled water, plant samples were washed with tape water, dried in a hot air oven at 65^0C for 48 hours in order to remove all moisture, then ground and made ready for nitrogen extraction.

Agronomic observation: Agronomic observations were recorded at the time of harvesting. Based on five selected plants, data was collected regarding plant height (cm), cob length (cm), stem girth (mm), number of cobs $plant^{-1}$, number of grains cob^{-1}, number of grain rows cob^{-1}, and number of grains row^{-1}. The weight of cobs (g) with husk and without husk, 1000 grain weight (g), and biological yield (kg ha^{-1}) was observed by the following formula.

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Biological yield = total dry plant weight x number of plants per unit area: Grain yield (kg ha^{-1}) was calculated at crop maturity in kilograms per hectare by following the formula (Sapkota *et al*., 2016).

$$\left(\frac{No.of\,rows}{cobs}\right) x \; \frac{\frac{No.of\,cobs}{m2}}{100} \; x \; \frac{weight\ of\ thousand\ grains(g)}{1000} \; x\ 10000$$

Basic chemical and physical properties of experimental soil: According to the chemical and physical properties of the soil at the experimental site before planting, the soil was silty clay loam with a slightly alkaline reaction (7.82), non-saline (0.58 dS m^{-1}), low organic matter (0.067%) and low nitrogen content (0.04%).

Statistical analysis: The collected data was subjected to statistical analysis using Statistix 8.1 version (Statistics, 2006). Four replications with a randomized complete block design (RCBD) were used to determine significant differences among the means were resolved by Analysis of variance (ANOVA) followed by Tukey's HSD (Honest Significant Difference) was applied to compare the treatment effect at alpha 5% (*$p \leq 0.05$).*

RESULTS AND DISCUSSION

The Effect of Nano-Silicon Coated Urea on Nitrogen Content in Soil and Plant: Soil and plant analyses were conducted to assess the effect of Nano-Silicon coated urea (NSCU) on nitrogen content in both soil and plants. The results indicated that Nano-Silicon coated urea increased N content and N-use efficiency in soil and plants. Urea, with a standard N dose of 160 kg N ha^{-1} was applied to all treatments along with different coating materials, including palm stearin (PS), and vegetable oil (VO), combined with a urease inhibitor (Nano-Silicon (NSA)). Nano-Si acid was used to prevent the rapid hydrolysis of urea, thus improving fertilizer efficiency. The highest nitrogen content (0.081%) in soil was recorded in the T5, whcih involved urea coated with palm stearin + Nano-Silicon acid (PSNS-CU). In contrast, the lowest N content (0.042%) was observed in the control treatment (T1, uncoated urea, UCU). Significant differences in nitrogen content were observed between treatments ($p \leq 0.05$), with the following ranking: T5 > T6 > T3 > T4 > T2 > T1.

Regarding plant nitrogen content, the highest was recorded in T5 (2.67%), while the lowest was in T1 (1.51%). A significant difference ($p \leq 0.05$) was noted between treatments. The ranking of treatments in terms of effectiveness was as follows: T5, T6, T3, T4, T2, and T1. The nitrogen content analysis in both soil and plants is summarized in Table 1.

Table 1. The Effect of Nano-Silicon Coated Urea on Nitrogen Content in soil and plant

S.#	Treatments	N (%) in Soil	N (%) in Plants
1	T1 (UCU 160 kg N ha^{-1} broadcasting)	0.042 f	1.51 e
2	T2 (UCU 160 kg N ha^{-1} placement)	0.048 e	1.75 d
3	T3 (PSCU 160 kg N ha^{-1})	0.063 c	2.41 b
4	T4 (VOCU 160 kg N ha^{-1})	0.056 d	2.25 c
5	T5 (PSMS-CU 160 kg N ha^{-1})	0.081 a	2.67 a
6	T6 (VOMS-CU 160 kg N ha^{-1})	0.071 b	2.49 ab

** Means followed by using Tukey's HSD, at $p \leq 0.05$*

*UCU= Uncoated urea
*PSCU=Coated urea with palm stearin
*VOCU= Coated urea with vegetable oil
*PSMS-CU=Coated urea with palm stearin + Nano-Silicon acid
*VOMS-CU= Coated urea with vegetable oil + Nano-Silicon acid
HSD= Honest significant difference

We used Nano-Silicon coated urea to reduce environmental pollution caused by urea volatilization. According to (Chen *et al*., 2017) Volatilization is a common problem in all types of soil, whether it's due to ammonia volatilization, leaching, or denitrification. Controlled release urea can be defined as "A fertilizer containing N in a form that delays its availability for plant uptake and uses after uptake", according to the Association of American Plant Food Control Officials such delays in initial availability or an extended period of continued availability may occur through a variety of mechanisms. The coating used for urea acts as a semi-permeable membrane to slow down the hydrolysis rate. According to Beig *et al.* (2020), coating materials act as a barrier by forming a physical layer on urea microsite that prevents water through penetrating it. This controls the release of N from urea. As a result, this approach enhances NUE and consequently N content in soil and plant. Another study explored the effectiveness of encapsulated urea as controlled-release urea on wheat farming discovered the massive increase in N availability the soil, which resulted in a significant improvement in yield (40.5% (Babar *et al*., 2019)). In our current

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research, we found the same response from maize as recorded a significant increase in N concentration in T5, T6, and T3 treatments respectively. These treatments consisted; palm stearin and vegetable oil as coating materials and Nano-Silicon acid as urease inhibitors.

Agronomic and yield parameters of maize in response to Nano-Silicon coated urea: The details of growth parameters are presented in Table 2. It was observed through one-way ANOVA that various agronomic parameters of maize were significantly affected by the urease inhibitor (Nano-Si). These parameters included; plant height (cm), stem girth (mm), the weight of cob with husk (g), the weight of cob without husk (g), number of grain cob^{-1}, number of grains row^{-1}, number of cobs $plant^{-1}$, cob length (cm) and the number of grain rows cob^{-1}. Yield credentials such as; 1000 grain weight (g), grain yield (kg ha^{-1}), and biological yield (kg ha^{-1}) are available in Table 3. The response of applied treatments as coated urea with Nano-Silicon acid was found significant as compared to commercial urea. The maximum growth constraints in terms of plant height (183 cm), stem girth (16.8 mm), weight of cob with husk (187.9 g), weight of cob without husk (163 g), number of grains per cob (457.6), number of grains per row (35.4), number of cobs per plant (1.6), 1000-grain weight (223.9 g), grain yield (6650 kg ha^{-1}), and biological yield (12308 kg ha^{-1}) were observed in T5. These parameter showed a highly significant difference between all treatments ($p \leq 0.01$), except for cob length (cm) and the number of grain rows per cob, where T3 and T6 showed no significant difference ($p \geq 0.05$) and had the highest recorded cob length of 16.6 cm and 16.5 cm, respectively. However, there was a significant difference between other treatments (T1, T2, T4, and T5) in cob length (cm) and the number of grain rows per cob. Results demonstrated the positive effect of T5 in terms of cob length and number of grains per row, followed by T6, T3, T4, T2, and T1. However, T1 (UCU) had the narrowest cob length (12.6 cm) and the least number of grains per row (12.8). Moreover, coated urea with different coating materials along with addition of urease inhibitors in the soil (PSCU, PSMS-CU, and VOMS-CU) had a positive impression on maize compared to other treatments

Table 2. Agronomic parameters of maize in response to Nano-Silicon coated urea

S#	Treatments	Plant height (cm)	Stem girth (mm)	Wt. of cob with husk (g)	Wt. of cob without husk (g)	Cob length (cm)	No. of grain rows/ cob
1	T1 (UCU 160 kg N ha^{-1} B*)	151.6 e	12.3 f	98 f	75.07 f	12.6 e	12.8 e
2	T2 (UCU 160 kg N ha^{-1} P*)	142.5 f	13.4 e	120.3 e	99.3 e	13.4 d	13.6 d
3	T3 (PSCU 160 kg N ha^{-1})	169 c	15.9 b	139 c	106.5 d	15.2 b	15.2 b
4	T4 (VOCU 160 kg N ha^{-1})	160.5 d	14.27 d	132.6 d	118.2 c	14.45 c	14.46 c
5	T5 (PSMS-CU 160 kg N ha^{-1})	183 a	16.8 a	187.9 a	163 a	16.6 a	16.5 a
6	T6 (VOMS-CU 160 kg N ha^{-1})	173.2 b	14.87 c	151 b	131 b	15.15 b	15.6 b

Means followed by the same letter in the column are not significantly different using Tukey's HSD,test at $p \geq 0.05$
B*: broadcasting; P*: placement (Treatments details are same as in Table 1)

All the required characterization of Nano-Silicon (Nano-particles) involving morphological analysis by Transmission Electron Microscopy (TEM), crystal size and structural analysis by X-ray diffraction (XRD), and the elemental profile by Energy Dispersive X Ray Analysis (EDX) in our previous study at Turkiye (Taskin et al., 2023). Based on nitrogen release analysis, coated urea granules released N more slowly than uncoated urea (Table 1). As compared to the control and Nano-Si coatings, palm stearin and Nano-Si significantly reduced N release from urea granules. The dissolution rate constants of coated urea were lower than those of uncoated urea. As observed by Umar et al., in 2022, urea coated with Nano-Zn released 35% and 28% of N respectively, and it took approximately 15 days for 80% of N release. Despite direct exposure of urea to soil environment and action of urease enzyme, the complete release of N from uncoated urea (control) took the first 5 days of the experiment. Affendi et al. (2020) illustrated a similar trend by reporting complete dissolution of uncoated urea granules within 18 hours of the experiment. It may be that stearic acid and paraffin wax pose a resistance to water penetration because they are hydrophobic (Khalifeh and Burleigh, 2018), and reduce water penetration. Due to reduced water sorption, N releases from coated granules are observed more slowly (Umar et al., 2022). Stearic acid is a non-toxic, biodegradable, and environmentally friendly material (Hornberger et al., 2012), which may delay the exposure of urea to the urease enzyme. In the current study we kept the same goal in mind to incorporate a biodegradable urease inhibitor with a natural coating material. It was also reported that stearic acid reacts with calcium hydroxide and forms calcium stearate which increases the strength of the coating (Affendi et al., 2020). Acids are involved in hydrolysate processes of Nano-Silicon formulations which may react and control the soil pH at a urea microsite.

H~~h~~igher yield of maize is linked with N-supply towards plants. Our study endorses the importance of N in terms of growth and yield constraints. Therefore, coated urea resulted in significant and superior yield parameters along with nitrogen efficiency compared with straight urea. Coated urea with palm stearin and

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vegetable oil, along with Nano-Silicon was found effective. In another study conducted by Babar *et al.* in 2022, a positive effect of coated urea enriched with Cu and Zn as urease inhibitors was observed, while using palm stearin as a binder. The results we obtained are consistent with the study conducted by Mathialagan *et al.*, 2020, which investigated the effectiveness of coating materials through a urea characterization study. They prepared coated urea in three models: urea + palm stearin (UPS), urea + allicin (UAL), and urea + allicin + palm stearin (UALPS), while pure urea prills were used as the control sample (U). In a similar manner, nanoparticles also reduce the release of NH_4^+ from nitrogenous fertilizers (Giroto et al., 2017). In accordance with Ditta (2012), nanoencapsulated fertilizers release nutrients slowly to plants. The coating of NPs with bentonite also reduces the dissolution of urea fertilizer. The treatment of Nano-Silicon coated urea significantly improved the growth and yield of maize crops. Three treatments (T5, T6, and T3) showed the highest yield (PSMS-CU, VOMS-CU, and PSCU). Our research indicates the importance of Nano-Silicon coated urea as it reduces nitrogen losses by inhibiting hydrolysis rate of urea and consequently mitigate the ammonia volatilization loss. Coating thickness plays an important role in the release of nutrients (Ahmad et al., 2015). The slowed dissolution of coating reduced the exposure of fertilizer to the soil environment and can also act as urease inhibitor which leads to the slow release of NH_4^+ (Ransom et al., 2020). It was also observed in our study that palm stearin can provide the thicker film on urea granule which consequently reduces the dissolution of PSMS-CU and help to inhibit hydrolysis rate

Table 3. Effect of Nano-Silicon coated urea on maize yield

S#	Treatments	No. of grains/row	No.of grains/cob	No. of cob/plant	1000-grain weight (g)	Grain yield (kg ha^{-1})	Biological yield (kg ha^{-1})
1	T1 (UCU 160 kg N ha^{-1} B*)	25.7 f	293.8 f	1.067 e	105.7 f	2190 f	6857 f
2	T2 (UCU 160 kg N ha^{-1} P*)	28.2 e	327.7 e	1.23 d	114.3 e	3515.7 e	7170 e
3	T3 (PSCU 160 kg N ha^{-1})	33.37 b	384.9 c	1.45 bc	140 d	4800 c	9577 c
4	T4 (VOCU 160 kg N ha^{-1})	29.5 d	357.6 d	1.36 c	161 c	4032.3 d	8897 d
5	T5 (PSMS-CU 160 kg N ha^{-1})	35. 4 a	457.6 a	1.6 a	223.9 a	6650 a	12308 a
6	T6 (VOMS-CU 160 kg N ha^{-1})	31.9 c	425 b	1.48 b	187.4 b	5517.7 b	11647 b

Means followed by the different letter in the column are significantly different using Tukey's HSD,test at $p \leq 0.05$
B*: broadcasting; P*: placement (Treatments details are same as in Table 1)

CONCLUSION

In a summary, urea coating with Nano-Si and palm stearin proved as an effective method. Nano-Silicon coated urea substantially increased the plant growth and yield of maize crop compared to uncoated urea. The higher yield was recorded in three treatments T5, T6, and T3 (PSMS-CU, VOMS-CU, and PSCU). Nano-Silicon coated urea reduced the nitrogen losses such as ammonia volatilization and nitrate leaching, thereby utilization of nitrogen by plants was high. It was proved that nano-Si can act as a cheap, environment-friendly, and efficient source of Si carrier and a urease inhibitor.

RECOMMENDATIONS

Nano-Si coated urea is recommended as an efficient fertilizer. It is suggested to taste the same fertilizer on different crops.

ACKNOWLEDGEMENTS OR NOTES

Authors are highly thankful to Department of Soil Science & Plant Nutrition, Ankara University Turkiye for providing the Nano-Si particles (fertilizer). This research was supported by Sindh Agriculture University Tandojam and Soil Fertility Research Institute, Agriculture Research Centre, Tandojam, Pakistan.

AUTHORS' CONTRIBUTION

Babar, S. K. conceptualized the study and designed the experiments. Abbasi, Z. performed data collection and analysis. Babar, S.K., and Abbasi, Z. wrote the original draft, and Rajpar, I. and Shujrah, H. reviewed and edited the manuscript. Babar, H., supervised the project and secured funding. All authors read and approved the final manuscript**.**

CONFLICT OF INTEREST

All authors have no conflict **of interest**

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