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ORIGINAL PAPER

Effect of Coated Urease/Nitrification Inhibitor Synergistic Urea on Maize Growth and Nitrogen Use Efficiency

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Abstract
Controlling the dissolution of urea and inhibitors, improving the regulation ability of inhibitors to soil nitrogen transformation, and reducing the negative impact of nitrogen fertilization on the environment are the research hotspots in the field of slow/controlled-release fertilizer around the world. This study used natural rubber (NR)-modified epoxy resin (ER) as coating materials to prepare coated controlled-release urea (CU) and coated inhibitor synergist particles. Six treatments comprising different nitrogen (N) fertilizations were set up: CK (no nitrogen fertilizer), U (urea), CU and coated urease/nitrification inhibitor synergistic urea (CISU) of NCU (coated N-(n-butyl) thio-phosphoric triamide (NBPT) particles + CU), DCU (coated 3,4-dimethylpyrazole phosphate (DMPP) particles + CU), and NDCU (coated (NBPT + DMPP) particles + CU). The results of ammonia (NH_3) volatilization and soil column leaching experiments showed that cumulative NH_3 volatilization losses were reduced by 33, 22, and 27% and inorganic nitrogen leaching losses were reduced by 33, 31, and 43% from NCU, DCU, and NDCU treatments, respectively, in comparison with the U treatment. Moreover, results of the pot experiment revealed that CISU treatment could enhance soil N supply continuously and improve maize yield and its N use efficiency (NUE). In comparison with CU, NCU, and DCU, the NDCU treatment significantly increased the maize yield by 5, 15, and 31%, and the NUE by 8, 15, and 27%, respectively. The NDCU exhibited better agronomic effectiveness with a higher NUE than NCU and DCU. It is recommended that coated urease + nitrification inhibitor particles and coated urea could be combined for preparing a novel, environment friendly coated urease/nitrification inhibitor synergistic urea having high agronomic efficacy, NUE, and low N loss.

Keywords Ammonia volatilization · NBPT · DMPP · Maize yield · Nitrogen leaching

1 Introduction

Currently, urea (46% N) is the main synthetic nitrogenous fertilizer in China and accounts for more than 50% of the total N fertilizers produced (Sanz-Cobena et al. 2011; Li et al. 2015). Soil broadcasting is the most common way of applying urea prior to irrigation or precipitation, which results in its rapid hydrolysis. Various researchers have reported that more than 50% of the soil applied N is lost via surface runoff, leaching, and volatilization, resulting in a low N use efficiency (NUE; Azeem et al. 2014; Huang et al. 2017; Pereira et al. 2017). Excessive and non-judicious fertilization decreases the crop yield and leads to several environmental concerns such as air and water pollution as well as soil quality degradation (Geng et al. 2016; Xiao et al. 2019; Chojnacka et al. 2020).

In agricultural production, controlled-release urea and inhibitors have been developed and applied to fill the gap between soil nutrient supply and crop nutrient requirements, which can reduce N losses and improve N utilization efficiency. However, the previous studies mainly dealt with using the organic/inorganic materials to control the slow dissolution of urea or directly adding conventional urease/nitrification inhibitors to slow down its hydrolysis (Li et al. 2020a). The controlled-release urea coated with organic polymer materials overcomes the rapid dissolution of urea in soil (Tian et al. 2019). However, it is impossible to manage

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the hydrolysis and conversion of urea after dissolution. At the same time, the concerns regarding the non-renewability and non-biodegradability of the coating materials along with the related environmental risks have confined the large-scale and long-term implications of commercialized slow-release fertilizers (Xie et al. 2019). Inhibitors upon their direct application to the soil are exposed to series of problems including adsorption, fixation, and degradation, which affect their efficiency (Abalos et al. 2014). Furthermore, there are different opinions on whether the inhibitor can increase crop yield. Abalos et al. (2014) recommended that nitrification inhibitors (NIs) and urease inhibitors (UIs) can increase crop productivity as well as NUE (average increase of 7.5% and 12.9%, respectively). Yang et al. (2016) performed a meta-analysis and concluded that DCD significantly increases crop yield by 6.5%, while DMPP does not.

The development of synergistic urea provides an effective opportunity to control the simultaneous dissolution of urea and inhibitors and, at the same time, alleviate their detrimental impacts on environment. The synergistic urea is prepared by coating the inhibitor particles with coated urea. It can efficiently prevent the direct contact between the inhibitor and soil due to the existence of a protective film on its surface, which reduces the degradation and fixation losses of the inhibitor in the soil environment and prolongs its effectiveness period.

Santos et al. (2020) reported that a new type of controlled-release urea prepared by coating an organic polymer on the urease inhibitor could regulate the slow release of urea and inhibitor efficiently. Similarly, Li et al. (2020b) prepared controlled-release urea by combining the organic polymers (epoxy resin) or inorganic materials (ground phosphate rock) with urease/nitrification inhibitors. However, the slow degradation rate of the resin film shell after the completion of N release adversely affected the soil. In addition, the controlled-release urea coated with inorganic materials could not meet the one-time fertilization requirements of maize and other major crops owing to its relatively poor and uncontrolled N release abilities. At present, the direct application of urease/nitrification inhibitor and urea has been widely reported.

In this study, coated controlled-release urea (CU) and coated NBPT, DMPP, and NBPT + DMPP particles were prepared using the optimal combination of natural rubber (NR)-modified epoxy resin (ER) as membrane material. The coated urease/nitrification inhibitor synergistic urea (CISU) were prepared by mixing CU and coated inhibitor particles, respectively. The CISU achieved the dual regulation of the dissolution of urea, and the transformation process of N and inhibitors. Moreover, ammonia volatilization and soil leaching tests were performed to study the effects of CISU on soil NH_3 volatilization and soil N leaching loss. For this purpose, a pot experiment was conducted to study the effects of CISU on soil urease activity, soil N supplying capacity, maize yield, and NUE. By studying the effect and mechanism of CISU on reducing the N loss and improving the NUE, it can provide theoretical basis and technical means for the development of a novel high efficiency urea.

2 Materials and Methods

2.1 Preparation of Coated Urea with the Synergistic Effect of Coated Urease/Nitrification Inhibitor

In this study, three different types of inhibitor particles (NBPT particles, DMPP particles, and NBPT + DMPP particles) were prepared, based on the different inhibitors. Briefly, NBPT (DMPP, NBPT + DMPP) powder, phosphate rock powder, and starch were mixed thoroughly in specific proportions and were loaded into a disc pelletizer for pelletizing. The coated urea (CU) and inhibitor were prepared by following the method of Qi et al. (2021). The CISU was prepared by mixing CU and coated inhibitor particles, respectively. Depending on the type of inhibitors, they were named NCU, DCU, and NDCU.

2.2 Characterization of N Release from the CU

A nitrogen release experiment was conducted to learn the best mass proportion of NR for ER modification. The N release characteristics of the CU were evaluated using the national standard method GB/T 23348–2009 (GAQS, IQPRC, SA 2009). Briefly, 10.0 g CU was placed into a 250-mL glass bottle containing 200 mL distilled water at 25 °C. Total N concentration in the solution was determined using the Kjeldahl method (Kjeldahl 1883) after 1, 3, 5, 7, 10, 14, 28, 42, 56, and 84 days until cumulative N release rate was ≥ 80%, which is a common benchmark for complete release (Yang et al. 2013). Three replicates were set up for CU.

2.3 Nitrogen Loss Potential of the Coated Urease/Nitrification Inhibitor Synergistic Coated Urea

Two experiments were conducted to evaluate the N loss potential (volatilization and leaching losses) in the U, CU, NCU, DCU, and NDCU treatments.

The soil used in this study, including these two experiments and the pot experiment described later, was collected from the experimental station of the College of Resources and Environment, Shandong Agricultural University, China (36.16° N, 117.15° E). The basic physical and chemical properties of the top soil (0–20 cm) were characterized, which indicated a soil type of brown earth, and soil texture of clay loam, soil organic carbon of 10.10 g kg^{-1}, total N of 0.86 g kg^{-1}, available N of 38.50 mg kg^{-1}, available P of 22.75 mg kg^{-1}, available K of 107.11 mg kg^{-1}, EC of 145.04 μS cm^{-1}, and pH of 6.5.

For the evaluation of NH_3 volatilization loss, the U, CU, NCU, DCU, and the NDCU were mixed thoroughly with 250 g soil at 0.6 g N kg^{-1} dry soil in plastic boxes. In addition, boxes containing only 250 g soil without fertilizer (CK) were also prepared. After the soil moisture was adjusted to 60% of field water holding capacity (WHC) with distilled water, a Petri dish containing 10 mL boric acid (3%) indicator solution was placed on the soil as a trap for capturing the volatilized NH_3. The boxes were sealed and incubated at 25 °C in the dark. The boric acid traps were replaced with new ones at regular intervals during the 40 days of incubation and titrated with sulfuric acid standard solution (0.005 mol L^{-1}) for NH_3 quantification.

Similarly, a column leaching experiment was conducted for the evaluation of N leaching loss potential of the fertilizers. The PVC columns (6.0 cm in diameter and 15.0 cm in height) were first packed with a thin layer of quartz sand, then 2000 g soil, and finally a thin layer of quartz sand again. The fertilizers at 0.6 g N kg^{-1} of dry soil were applied to the top 5 cm of soils. Distilled water was added to saturate the soil for 24 h. Then, 100 mL distilled water was added to the column every 4 days for a total of 1000 mL water in 40 days. The leachate was collected for NH_4^+-N and NO_3^--N determination using an AA3 continuous flow analyzer (BL-TECH, Germany). Soil inorganic N contents were calculated as the sum of NH_4^+-N and NO_3^--N.

2.4 Pot Experiment

The pot experiment was conducted at Shandong Agricultural University Resources and Environment Experimental Station from June 2020 to September 2020. The pots were arranged by following a completely randomized design (CRD). Six treatments of different N fertilizations were set up: CK (no N fertilizer), U (conventional urea, base fertilizer stage: jointing stage = 1:1), CU (30% NR-modified ER-coated controlled-release urea), NCU (coated NBPT particles + CU), DCU (coated DMPP particles + CU), and NDCU (coated NBPT + DMPP particles + CU). During the experiment, plastic pots (lower diameter 23.0 cm, upper diameter 35.0, height 43.5 cm) were used, and 15 kg of soil were put in each pot. The N fertilizers were applied at 0.15 g N kg^{-1} soil. Calcium superphosphate was used as phosphorus fertilizer at 0.1 g P_2O_5 kg^{-1} dry soil and potassium chloride as potassium fertilizer at 0.1 g K_2O kg^{-1} dry soil. Prior to the pot filling, 15 kg of topsoil (0–20 cm) was mixed with the phosphorus fertilizers, potassium fertilizers, CU, NCU, DCU, and NDCU, while urea was applied in splits as basal fertilizer (50%) and topdressed (50%, at the jointing stage). Five seeds of maize (*Zea mays* Ziyu 2) were sown in each pot on 10th June 2020, and thinned to one seedling at the 5-leaf stage.

2.5 Collection and Determination of Potted Test Samples

At the (June 20th), jointing (July 10th), tasseling (August 10th), flowering (August 17th), and maturation (September 22nd), three pots were randomly taken from each treatment. The plant height was measured during the growth period of maize. After maize roots were removed, the fresh soil from each pot was thoroughly mixed and extracted with 1 mol L^{-1} KCL for NH_4^+-N and NO_3^--N determination with an AA3 continuous flow analyzer. Urease activity was measured by the sodium phenate-sodium hypochlorite colorimetric method (Santos et al. 2020) using air-dried soil (< 1 mm). Maize was harvested on September 22 and different yield attributes, i.e., ears per plant, grains per ear, and 100-grain weight, were recorded. Plant and grain samples were first oven-dried at 105 °C for 30 min and then at 75 °C to constant weight for calculating the amount of dry matter accumulation (DMA). The dry samples of plant and grain were digested with H_2SO_4/H_2O_2 and N contents were determined by the Kjeldahl method (Kjeldahl 1883). Moreover, grain yield, N utilization efficiency (NUTE), N fertilizer apparent utilization efficiency (NFUE), partial factor productivity of applied N (NPFP), and NUE were calculated by the following formulas:

$$\text{Grain yield} = \text{plants per pot} \times \text{ears per plant} \times \text{grains per ear} \times 100 - \text{grain weight}/100$$

$$\text{NUTE}\left(gg^{-1}\right) = \text{grain yield}/\text{N accumulation in aboveground parts}$$

$$\text{NFUE}(\%) = (\text{N accumulation in aboveground parts of fertilization treatment} - \text{Naccumulation in aboveground parts of CK}/\text{total } N \text{ supplied by fertilizer} \times 100)$$

$$\text{NPFP}(gg^{-1}) = \text{grain yield}/\text{total N supplied by fertilizer}$$

$$\text{NUE}(gg^{-1}) = \text{grain yield}/\text{total N supplied by soil and fertilizer}$$

Soil apparent nitrification rate was calculated as (Li et al. 2020a, b):

$$\text{Soil apparent nitrification rate }(\%) = NO_3^- - N / \left(NH_4^+ - N + NO_3^- - N\right) \times 100$$

3 Results

3.1 Nitrogen Release Characteristics of CU

The cumulative N release curve of CU had a short stagnation period within 1 to 3 days, and the cumulative N release was 8% (Fig. 1). However, a slight change in the cumulative release curve of N was observed from 3 to 7 days, with the cumulative release of N was observed to be 20%. An acceleration in the cumulative N release curve was observed from 7 to 56 days and during this period, the cumulative N release was 71%. When the cumulative N release reached 80%, the controlled-release period of CU was 67 days. The cumulative release of N during the cultivation period was 89%. These results depicted that the CU could be effectively used to achieve the controlled dissolution of conventional urea and can prevent its dissolution.

3.2 NH_3 Volatilization

The NH_3 volatilization rate of the CK was proved to be relatively stable (Fig. 2). A large amount of NH_3 from the treatment comprising the U application was measured in the first week of incubation, whereas the peak NH_3 volatilization (1.13 mg N-NH_3) was observed at day 3 (Fig. 2a). Compared with U, the NH_3 volatilization decreased in the early stage of cultivation in CISU treatment and became stable during the cultivation period. On the 35th day of culture, the volatilization rate of CU, DCU, and NDCU was significantly higher than that of U, which indicated that CISU still released N during the later period of culture. Compared with U, the NH_3 volatilization rate was significantly reduced by 22–27% in CISU (Fig. 2b). In addition, NH_3 volatilization from the NDCU treatment was significantly lower than that from the U and DCU treatments, whereas there were no significant differences between CU, NCU, and NDCU.

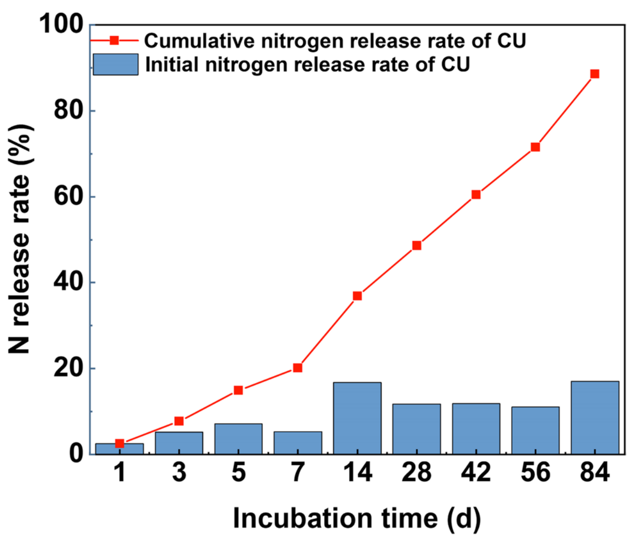

Fig. 1 Nitrogen release curves of the CU. CU, 30% natural rubber-modified resin-coated controlled-release urea

3.3 Nitrogen Leaching Loss

The leaching rate of NH_4^+-N in U treatment increased first and then decreased (Fig. 3) reaching a maximum (5.51 mg day^{-1}) on the 8th day (Fig. 3a). After leaching, the cumulative leaching rate of NH_4^+-N was 61% under U application (Fig. 3b), whereas the leaching rate of NH_4^+-N in NCU and NDCU treatments peaked on the 24th and 36th days, respectively. Compared with U, the peak value of NH_4^+-N leaching rate in NCU and NDCU decreased by 53 and 66%, and the peak value was delayed by 16 and 28 days, respectively. On the 40th day, the cumulative leaching amount of NH_4^+-N changed significantly among the various N fertilizer treatments. The leaching amount of NH_4^+-N from U was the highest, and the order was DCU > CU, NCU > NDCU. Due to the protective effect of the coating layer and inhibitors, CISU significantly reduced the N leaching losses, where DCU and NDCU treatments performed relatively better.

The leaching rate of NO_3^--N was different from NH_4^+-N. The leaching rate of NO_3^--N under U treatment reached a maximum (1.70 mg day^{-1}) on the 8th day. There were two optimum peaks of NO_3^--N leaching rate in CU during the culture period, which were on the 24th and 36th days, with NO_3^--N leaching rates 2.90 mg day^{-1} and 2.09 mg day^{-1}, respectively. After 4–8 days, the NO_3^--N in DCU and

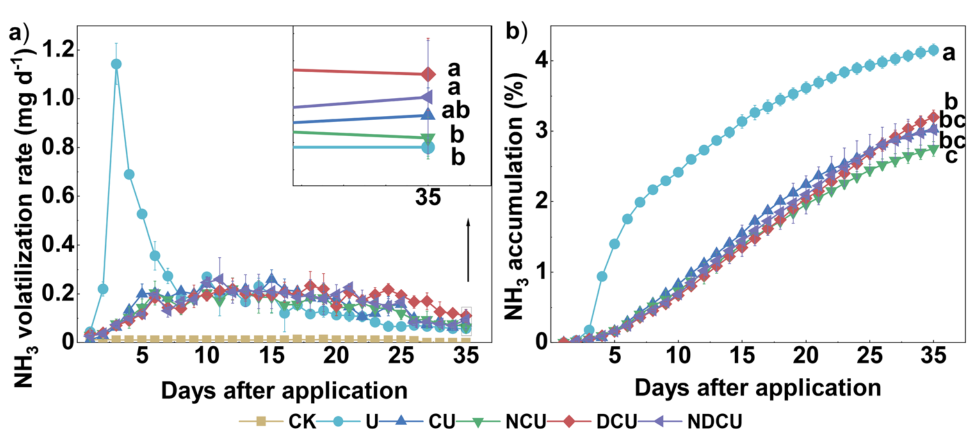

Fig. 2 Effect of CISU on soil NH_3 volatilization. **a** NH_3 volatilization rate; **b** NH_3 accumulation. CK, no N fertilizer; U, conventional urea; CU, 30% natural rubber-modified resin-coated controlled-release urea; NCU/DCU, synergistic urea mixed with coated NBPT/DMPP particles and CU; NDCU, synergistic urea mixed with coated NBPT + DMPP particles and CU

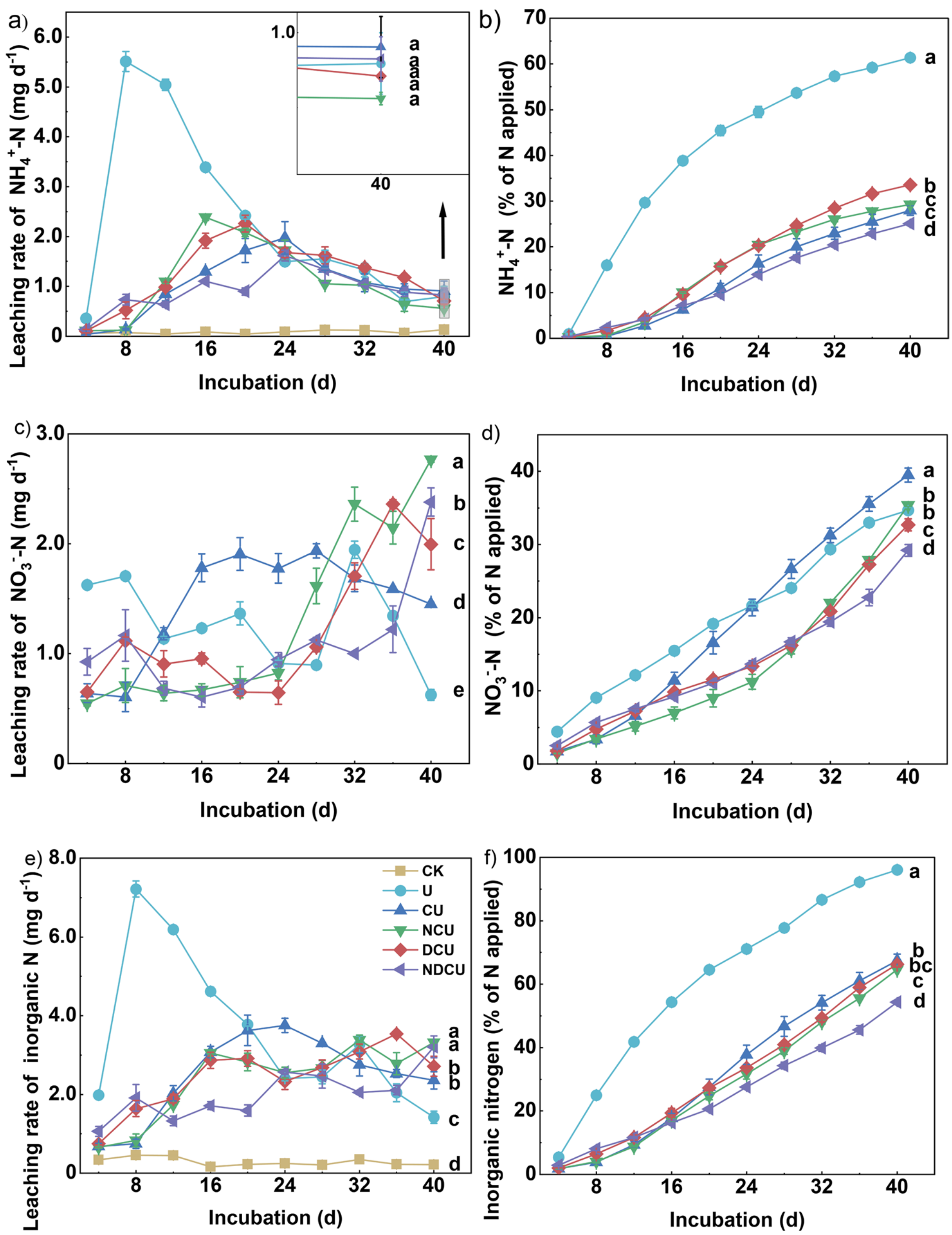

Fig. 3 Effect of CISU on soil N leaching. **a** Leaching rate of NH_4^+-N; **b** cumulative leaching rate of NH_4^+-N; **c** leaching rate of NO_3^--N; **d** cumulative leaching rate of NO_3^--N; **e** leaching rate of inorganic N; **f** cumulative leaching rate of inorganic N. CK, no N fertilizer; U, conventional urea; CU, 30% natural rubber-modified resin-coated controlled-release urea; NCU/DCU, synergistic urea mixed with coated NBPT/DMPP particles and CU; NDCU, synergistic urea mixed with coated NBPT + DMPP particles and CU

NDCU were lower than U, whereas the leaching rates were higher than U treatment during the 12–40 days. On the 40th day, the cumulative leaching amount of NO_3^--N treated with U was 35%. In addition, compared with U, DCU and NDCU significantly reduced NO_3^--N by 6 and 16%, respectively.

The leaching and cumulative leaching rates of inorganic N (Fig. 3e and f) showed that the CISU could reduce N leaching loss and maintain high soil nutrient contents later. A reduction in the soil inorganic N leaching loss was observed by the CU (17%), NCU (28%), DCU (26%), and NDCU (38%), in comparison with the U treatment where NDCU exhibited the most significant effect in reducing the soil N leaching losses, followed by NCU and DCU, and finally the CU treatment. This indicated that the nutrient release of the coated urea was reasonable and could reduce the leaching loss of N. After being combined with the coated inhibitor, the effect of the inhibitor was strengthened, the conversion of dissolved N was delayed, and the leaching losses were reduced.

3.4 Maize Yield, Dry Matter Accumulation, and NUE

In the fertilization treatment, during the maturation stage, an increased maize yield (28–83%) and DMA (9–73%) was observed in comparison with the CK (Table 1). The DMA was significantly higher in CU (4%), NCU (12%), DCU (32%), and NDCU (43%), than the U treatment, whereas the DMA was significantly higher in the DCU

Table 1 Maize grain yield and dry matter accumulation (DMA)

Treatment	Total N uptake (g pot^{-1})	Grain number (pot)	100-grain weight (g)	Yield (g pot^{-1})	DMA (g pot^{-1})
CK	1.32 ± 0.03c	345 ± 13c	30.84 ± 0.76b	106.40 ± 6.78e	207.70 ± 8.75e
U	1.87 ± 0.11b	373 ± 16c	31.03 ± 0.59b	115.74 ± 4.42d	264.81 ± 1.80d
CU	2.02 ± 0.28b	425 ± 9c	32.94 ± 0.72b	140.00 ± 6.15c	301.06 ± 3.57c
NCU	1.99 ± 0.07b	449 ± 16b	32.63 ± 2.16b	146.51 ± 9.89bc	296.55 ± 8.91c
DCU	2.43 ± 0.04a	507 ± 24a	31.67 ± 1.46b	160.57 ± 14.94b	350.72 ± 23.72b
NDCU	2.62 ± 0.05a	506 ± 33a	36.33 ± 0.70a	183.83 ± 10.56a	379.97 ± 25.07a

Different letters indicate significant differences between treatments for a same column ($P < 0.05$). *CK*, no N fertilizer; *U*, conventional urea; *CU*, 30% natural rubber-modified resin-coated controlled-release urea; *NCU/DCU*, synergistic urea mixed with coated NBPT/DMPP particles and CU; *NDCU*, synergistic urea mixed with coated NBPT + DMPP particles and CU

Table 2 Nitrogen utilization efficiency (NUTE), N fertilizer apparent utilization efficiency (NFUE), partial factor productivity of applied N (NPFP), and N use efficiency (NUE) of the different treatments

Treatment	NUTE (g g^{-1})	NFUE (%)	NPFP (g g^{-1})	NUE (g g^{-1})
CK	-	-	-	-
U	65.4 ± 3.6b	24.7 ± 4.9b	54.4 ± 0.7e	41.1 ± 0.5e
CU	70.2 ± 9.1ab	31.1 ± 12.3b	62.2 ± 0.4d	47.0 ± 0.3d
NCU	76.0 ± 1.2a	29.8 ± 2.9b	67.2 ± 1.3c	50.7 ± 1.0c
DCU	66.2 ± 2.0b	49.5 ± 1.6a	71.5 ± 1.9b	54.0 ± 1.5b
NDCU	67.9 ± 0.1ab	57.6 ± 0.2a	79.0 ± 0.2a	59.6 ± 0.2a

Different letters indicate significant differences between treatments for a same column ($P < 0.05$). *CK*, no N fertilizer; *U*, conventional urea; *CU*, 30% natural rubber-modified resin-coated controlled-release urea; *NCU/DCU*, synergistic urea mixed with coated NBPT/DMPP particles and CU; *NDCU*, synergistic urea mixed with coated NBPT + DMPP particles and CU

(16%) and NDCU (26%) treatments in comparison with CU. Moreover, there was a slight difference between the changing trend of maize yield and DMA. Compared with CU, the maize yield was significantly higher in the DCU (15%) and NDCU (31%) treatments. Furthermore, the NDCU treatment performed significantly well in increasing the 100-grain weight, maize yield, and DMA.

The NUTE, NFUE, N-partial factor productivity (NPFP), and NUE reflect the degree of N absorption and utilization of crops from different angles. The CISU increased NPFP (14–45%) and NUE (8–40%) in comparison with the U treatment (Table 2). Similarly, the NDCU treatment significantly improved the NPFP (27%) and NUE (30%) as compared to CU treatment. Alterations in the NUE depicted that stabilization of urea with urease and nitrification inhibitors was very effective in improving the NUE and that coating could further improve NUE, implying less N loss to the environment.

3.5 Soil NH_4^+-N, NO_3^--N, and Apparent Nitrification Rate of NH_4^+-N

The changing trends of NH_4^+-N and NO_3^--N for U and CISU were slightly different (Fig. 4). The changing curve of NH_4^+-N increased between the seedling and jointing stages followed by rapid decrease under U treatment. The NH_4^+-N decreased by 31% on average as compared to U treatment followed by DCU, CU, NCU, and NDCU treatments, during the seedling stage. However, compared with U, the NH_4^+-N of CISU increased by 48% on average during the flowering stage followed by DCU, NDCU, CU, and NCU treatments. The changing trend of NO_3^--N of CISU was consistent with that of NH_4^+-N. In comparison with the U treatment, the NO_3^--N decreased in the seedling (40%), jointing (11%), and maturation (6%) stages by the NDCU treatment, whereas there were no significant differences between tasseling and flowering stages.

The apparent nitrification rate of NH_4^+-N in U treatment was always high during the growth stage (Table 3). Compared with U, the apparent nitrification rate of NH_4^+-N was decreased at seedling (13%), flowering (16%), and maturation stages (10%) under DCU treatment. The apparent nitrification rate under the U treatment was higher than CU in the maturation stage. The DCU had better inhibitory effects on soil NH_4^+-N nitrification than other fertilization treatments at different growth stages. Compared with the DCU, NDCU did not significantly increase the apparent nitrification rate of NH_4^+-N in the later stages of maize growth.

3.6 Urease Activities

The soil urease activities in the fertilization treatments were significantly higher than that of CK during the growth stage of maize (Fig. 5). Soil urease activities in U treatment increased first and then decreased. Compared with U, soil urease activities of NCU decreased in the seedling (22%), jointing (26%), and tasseling stages (4%). Similarly, the soil urease activities of NDCU were significantly reduced in the

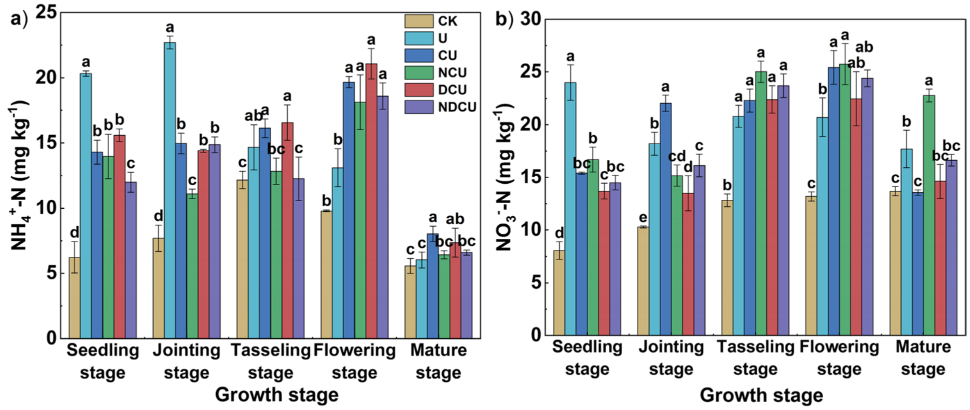

Fig. 4 Soil NH_4^+-N and NO_3^--N contents at different growth stages of maize in the different treatments of the pot experiment. Different letters indicate significant differences between treatments for a same growth stage ($P<0.05$). CK, no N fertilizer; U, conventional urea; CU, 30% natural rubber-modified resin-coated controlled-release urea; NCU/DCU, synergistic urea mixed with coated NBPT/DMPP particles and CU; NDCU, synergistic urea mixed with coated NBPT + DMPP particles and CU

Table 3 Soil apparent nitrification rate (%) at different growth stages of maize in the different treatments

Treatment	Seedling stage	Jointing stage	Tasseling stage	Flowering stage	Mature stage
CK	56.5 ± 5.4a	57.4 ± 2.2a	51.4 ± 4.1c	57.4 ± 3.0ab	71.2 ± 2.3bc
U	54.0 ± 3.0a	44.5 ± 1.6c	58.7 ± 3.3b	61.3 ± 5.6a	74.0 ± 5.8ab
CU	51.9 ± 1.6a	59.6 ± 1.0a	58.0 ± 2.1b	56.5 ± 3.7ab	62.8 ± 2.0d
NCU	54.5 ± 1.3a	57.7 ± 1.4a	65.9 ± 3.8a	58.7 ± 3.2a	78.0 ± 1.1a
DCU	46.8 ± 1.9b	48.4 ± 3.4b	57.3 ± 1.7b	51.6 ± 1.8b	66.4 ± 3.8 cd
NDCU	54.8 ± 0.9a	52.0 ± 1.9b	65.7 ± 3.3a	56.8 ± 1.1bc	71.5 ± 0.4bc

Different letters indicate significant differences between treatments for a same growth stage ($P<0.05$). *CK*, no N fertilizer; *U*, conventional urea; *CU*, 30% natural rubber-modified resin-coated controlled-release urea; *NCU/DCU*, synergistic urea mixed with coated NBPT/DMPP particles and CU; *NDCU*, synergistic urea mixed with coated NBPT + DMPP particles and CU

seedling (21%), jointing (25%), and tasseling stages (9%) in comparison with the U treatment. The results showed that NBPT significantly inhibited soil urease activities during the early stage of maize growth. It provided sufficient N supply for the mid-late stages of maize growth (Fig. 4) and matched soil nutrient supply with maize nutrient demand. Among CISU, NDCU has a better ability to regulate and transform soil N.

4 Discussion

Earlier studies reported that crop N demand is an "s-shaped" curve during the growth stage (Geng et al. 2016; Zheng et al. 2017). The coated controlled-release fertilizer can adjust the nutrient release rate as per their demand during the different growth stages of crops and, thereby, can synchronize the nutrient release curve and the crop's demand for nutrients. Nitrogen (N) release characteristics curve of coated controlled-release urea is a critical factor for evaluating its performance, which is an important indicator for matching the degree of nutrient release and crop requirements. Li et al. (2020a, b) reported that the controlled-release periods of N, hydroquinone (HQ), and dicyandiamide (DCD) for the controlled-release urea prepared by coating the inhibitor-coated urea and epoxy resin were 56, 42, and 14 days, respectively. Yang et al. (2013) suggested that the N release curve of biopolymer coated controlled-release urea can be divided into three stages, viz., stagnation, acceleration, and the lag period, respectively. The study showed that the CU could release N slowly, having a controlled-release period of up to 67 days, which are in line with the findings of the current study. The results of the current study were consistent with the nutrient release stagnation stage of CU during the culture period of this experiment. The coated controlled-release urea nutrients are released slowly and, hence, provide sufficient N supply to the soil leading to an improvement in the N supplying capacity of the soil as per their demand during the fertility period of maize. According to Li et al. (2020a, b), the resin film slowed down the release of N and inhibitors (HQ and DCD). Since the NBPT and DMPP contents in soil need to be determined by the high-performance liquid chromatography (HPLC) (Santos

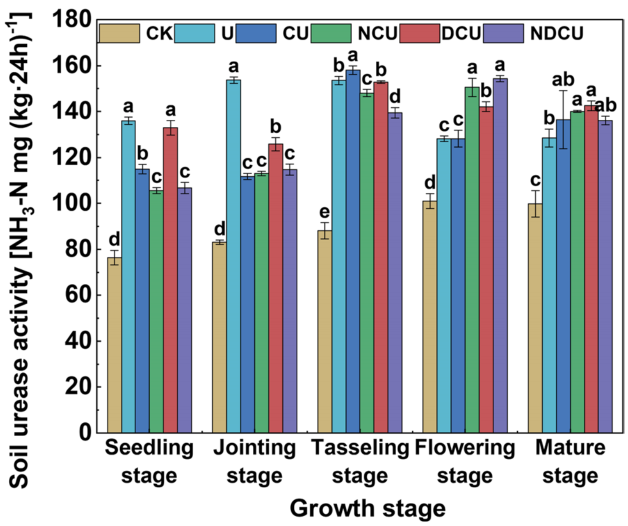

Fig. 5 Soil urease activity at different growth stages of maize in the different treatments of the pot experiment. Different letters indicate significant differences between treatments for a same growth stage ($P < 0.05$). CK, no N fertilizer; U, conventional urea; CU, 30% natural rubber-modified resin-coated controlled-release urea; NCU/DCU, synergistic urea mixed with coated NBPT/DMPP particles and CU; NDCU, synergistic urea mixed with coated NBPT + DMPP particles and CU

et al. 2020) which makes it difficult to determine the activities of NBPT and DMPP in CISU and the controlled-release performance of the organic membrane shell on the inhibitor. Furthermore, there is uncertainty about the true DMPP and NBPT application rates with the coated fertilizers due to eventual loss of inhibitors while coating the fertilizer. For this reason, we used other methods to prove the sustained release effect of the physical film on N, NBPT, and DMPP. Firstly, current experiment discussed and verified the effects of U, CU, NCU, DCU, and NDCU application on NH_3 volatilization and leaching losses. The results of indoor experiments explained that NDCU treatment caused a significant reduction in the NH_3 volatilization and leaching losses as compared to U and CU. Secondly, the fertilization efficiency of CISU was verified by pot trials, where NDCU treatment resulted in a tremendous yield increment in comparison with U and CU treatments. Moreover, the indoor and pot trials verified the hypothesis that CISU can cause slow leaching of the inhibitor and improve the holding period of the inhibitor and its ability to regulate soil N during the maize reproductive period. This may be due to the presence of modified surface resin film shells in CISU, which halted the direct contact between inhibitor, urea, and soil. So, it reduced the degradation and fixation losses of inhibitor, while reducing its leaching and, at the same time, improving the regulation effects of N by the inhibitor.

The N loss leads to a considerable decline in its usage efficiencies and its minimization is inevitable for improving the NUE. The N loss is mainly caused by NH_3 volatilization, leaching, nitrification, and denitrification (Li et al. 2015). Different physicochemical attributes of the soil affect the NH_3 volatilization, i.e., pH, cation exchange capacity (CEC), and soil texture, as well as soil urease activity, which determine the potential of NH_3 volatilization from the soil surface. In addition, environmental and weather indicators (soil temperature, soil humidity, wind force) affect the actual amount of NH_3 volatilization (Li et al. 2015). The current study mainly discussed the effect of CISU in regulating the NUE. Santos et al. (2020) reported similar experimental results and explained that the emission of NH_3 in unfertilized soil was not significant. Moreover, Afshar et al. (2018) reported that N losses are more significant in the first 7 days immediately after the application of the fertilizers. In present study, NH_3 was detected on the first day of fertilization treatment, which might be due to the rapid hydrolysis of U into NH_4^+-N by the activity of urease, resulting in a rapid increase in NH_4^+-N concentration in the fertilized area and accelerating NH_3 emission. A modeling study by Watson (1994) indicated that 0.092% of NBPT was predicted to reduce NH_3 formation by 90% in all tested soil. Furthermore, Gioacchini et al. (2002) showed that NBPT in silt loam and clay loam soils reduced NH_3 volatilization by 89% and 47%, respectively. They further stated that the existence of coated NBPT particle film in NDCU made NBPT release slowly, which helped to suppress the urease activity and delayed the hydrolysis and conversion rate of urea. The nitrate (NO_3^--N) and ammonium (NH_4^+-N) are the primary forms of plant N absorption (Geng et al. 2016; Zheng et al. 2017). However, NO_3^--N is easily leached from plant roots towards ground water and is one of the main ways of N loss in crop planting systems (Zheng et al. 2017). Conventional urea is in contact with the soil environment and rapidly hydrolyzes to produce ammonium bicarbonate (NH_4HCO_3), ammonium carbonate ($(NH_3)_2CO_3$), and ammonium hydroxide (NH_4OH). The NH_4^+-N is converted into NO_3^--N or other forms of N in the presence of ammonia-oxidizing bacteria within 7 days under natural soil conditions. Therefore, the current study determined the cumulative leaching amount of NH_4^+-N, NO_3^--N, and inorganic N and its conversion characteristics over time. Conventional urea is rapidly hydrolyzed after being applied to the soil, thereby increasing the N loss (Geng et al. 2016; Xiao et al. 2019), but the presence of a physical film layer of controlled-release urea can delay the dissolution of urea and reduce N loss (Watanabe et al. 2009). This study showed that NDCU could reduce the loss of N leaching in the early stage of culture. However, the leaching loss of NDCU treatment was more significant than U in the later cultivation stages since no plants absorbed soil N. Contrary to the results of this experiment, Kawakami et al. (2012) reported that the addition of DCD and NBPT to urea did not increase N absorption by reducing NO_3^--N leaching and denitrification. The different experimental conclusions proved that the NBPT and DMPP in NDCU had a strong capacity to regulate N owing to the presence of physical film and could always maintain sufficient N supply in the soil.

Coated controlled-release urea released the nutrient on a sustainable and prolonged basis and, thereby, reduced the NH_3 volatilization and NO_3^--N leaching losses during the early stage of culture. However, the NH_4^+-N contents of CU were higher than NCU and DCU, which increased the risk of NH_3 volatilization and NO_3^--N leaching. Urease inhibitor halted the urease activity and delayed the conversion rate of urea to NH_4^+-N to suppress the NH_3 volatilization. Nitrification inhibitor repressed the activity of ammonia-oxidizing bacteria and delayed the transformation of NH_4^+-N to NO_3^--N. Theoretically, DMPP will increase the risk of NH_3 volatilization. However, DCU can effectively delay the dissolution of DMPP, prolong the "timeline," and reduce the impact on NH_3 volatilization in the whole culture. Therefore, it will not significantly promote the NH_3 volatilization rate and accumulation of CU.

Crop yield and NUE are significant indicators for rational fertilization. Many studies have found that applying coated controlled-release urea significantly increased NUE and yield of crops. Yang et al. (2011) reported that the controlled-release urea increased wheat and maize grain yields by ensuring sustainable release of soil N and thus, met the N requirements for these crops over extended stages. Zheng et al. (2016) stated that long-term application of controlled-release urea had great potential to improve maize yield, NUE, and reduce N loss. The results of this study also demonstrated that coated inhibitor synergistic urea could promote maize growth, improve the maize yield, DMA, and NUE.

Due to the limited ability of urease/nitrification inhibitors to regulate urea hydrolysis and conversion processes when applied alone, they cannot effectively regulate the whole process of N conversion. For example, the urease inhibitors can only delay urea hydrolysis and reduce ammonia volatilization losses, but cannot regulate nitrification and denitrification, and cannot reduce the late leaching losses of N. At the same time, the usual application method of the inhibitor is to directly mix the inhibitor with urea mechanically, and the inhibitor can play a good regulatory role during the vegetative growth stage of maize. However, the inhibitor is affected by the soil environment and undergoes losses such as degradation and fixation, and its ability to regulate N is weakened, resulting in faster late conversion as well as soil N losses. In the present study, we prepared CISU by controlling the slow dissolution of urea and inhibitor separately to effectively solve this problem. The urea and inhibitor were wrapped by the modified resin material separately, which was helpful to prevent the slow release of urea and inhibitor, strengthen the regulating effect of inhibitor on soil nitrogen, improve soil nitrogen supply capacity during maize reproductive period, and increase maize yield and NUE. Compared with CU, NCU, and DCU, the NDCU treatment combined with NBPT and DMPP delayed the slow dissolution of urea, stalled two processes of urea conversion, and significantly reduced soil N volatilization and leaching losses. The reduced N losses could provide sufficient N supply to meet the demand of maize throughout the reproductive period and promote maize growth, thus increasing yield and NUE.

5 Conclusion

The best CISU was NDCU prepared by coating N-(n-butyl) thio-phosphoric triamide and 3,4-dimethylpyrazole phosphate (NBPT + DMPP) and the coated controlled-release urea (CU). The NDCU improved the ability of inhibitors by suppressing the activities of urease enzyme and the nitrifying bacteria to regulate the N conversion and synchronized the soil N supply and crop nutrient requirements. The NH_3 volatilization and the loss of inorganic N were observed to be least in the NDCU treatment. In the NDCU treatment of the pot experiment, soil NH_4^+-N contents were low at the seedling and maturation stages of maize but became high at the reproductive growth stage, well matching the N demand of maize growth. Soil apparent nitrification rates and urease activities in the NDCU treatment were lower than other treatments. Compared with CU, the NDCU caused a significant increment in the DMA contents (26%), yield (31%), and N use efficiency (27%) of maize. The results of this study revealed that synergistic urea reduced the loss of inhibitors, prolonged the duration of inhibitors, and was more environmentally friendly in terms of N loss.

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Declarations

Conflict of Interest The authors declare no competing interests.

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