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# Effect of γ-PGA Coated Urea on N-Release Rate and Tomato Growth

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**Abstract:** The anionic polymer γ-polyglutamic acid (γ-PGA) was used to coat urea and slow its dissolution. Three types of slow release urea (SRU) fertilizers (polymer coated urea with pore constriction, polymer coated urea with enzyme inhibitor and polymer coated urea with pore constriction and enzyme inhibitor) were prepared and tested for the N-release rate. After using SRU, the effect on the tomato growth was analyzed. The extracts of SRU were analyzed for $NH_3/NH_4^+$-N and $NO_3^-$-N. The N-release rate was used to determine the optimum ratio of ingredients. The results show that the three types of SRU met the dissolution rate standards recommended by the Committee of European Normalization. γ-PGA SRU increased the chlorophyll content of tomato (flowering stage) by an average of 100% compared with that grew in untreated urea. The results from soil analysis (0-60 cm in tomato pots) indicate that the content of $NH_3/NH_4^+$-N in SRU-treated pots was 25%-61% higher than that in soil from urea-treated pots during the growing period，while the content of $NO_3^-$-N was nearly 50% lower after the tomato had been harvested. Newly formulated SRU fertilizer increases nitrogen uptake and reduces loss of applied nitrogen. Plant growth is enhanced, a valuable resource is conserved, and the aquatic environment benefits from decreased level of nitrate in agricultural run-off.

**Key words:** γ-PGA; slow release urea (SRU) fertilizer; nitrogen release rate; tomato growth

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## 0 Introduction

Urea is an excellent source of nitrogen and used in most nitrogenous fertilizers. Urea is catalytically converted to $NH_3$ and $CO_2$ by urease within 4-5 days after application[1]. A fraction of the nitrogen is absorbed by plants as $NH_3/NH_4^+$ and the remainder is converted by soil microbial action to nitrite, nitrate, nitrous oxide and nitrogen. Leaching of excess nitrogen as $NO_3^-$-N leads to loss of a valuable resource and contributes to serious environmental problems[2]. The nitrogen content of conventional fertilizers is in the range of 30%-40%[3-5]. Application of slow release urea(SRU) technology increases ammonia uptake by plants and reduces nitrate in the runoff water from agricultural lands. Therefore, it is one of the most effective ways to improve fertilizers.

The physical integration method was used to make the slow release urea fertilizers (SRUs)[6], in this process, molten urea was mixed with liquid polymer, which formed particles of solid urea coated with a porous polymer film. The dissolution rate and porosity of the polymer film control the release rate of urea and the conversion rate of urea to $CO_2$ and $NH_3$ depends upon the activity of urease in the soil. Finally, the rate of nitrification is controlled by microbial action in the soil. Conceptually, the rate of urea dissolution, the conversion rate of urea to $NH_3/NH_4^+$ and its rate of conversion to $NO_3^-$ can be controlled by using a porous polymer coating to decrease urea dissolution rate (the pore size of the polymer coating can be decreased using $ZnSO_4$/$CuSO_4$ as a pore constriction agent), and by inhibiting urease and nitrification[7].

*γ*-polyglutamic acid (*γ*-PGA) is an anionic polymer produced by polymerizing glutamic acid in which peptide bonds form between the α-$NH_2$ and *γ*-COOH groups of glutamic acid [8]. Glutamic acid affects the biological activity of various cell and increases the efficiency of the fertilizer. As a biodegradable polymer material, the release of the glutamic acid would promote water uptake and nutrient absorption [9].

To date, the use of *γ*-PGA coat urea with pore constriction and/or enzyme inhibitor and analysis of the N-release of these SRUs and the effect on the tomato growth have not yet been reported [10]. In this paper, three types of SRU fertilizers were prepared by using urea as nitrogen source, different sustained-release material, different combinations of control components and sustained-release material of different ratios, then the optimal formulation was tested. The efficacy of each SRU fertilizer was characterized by measuring the effect of N-release on tomato growth. Results confirm that *γ*-PGA coated urea increases nitrogen uptake from fertilizer and increases plant growth while reducing loss of applied nitrogen.

## 1 Materials and Methods

### 1.1 Samples, Reagents and Equipments

1) Samples: Soil both for the leaching and tomato growth studies was obtained from the China Three Gorges University research botanical garden. The soil was compact, slightly alkaline and yellow-brown in color. The physical and chemical properties of the soil are displayed in Table 1. Tomato seeds (miscellaneous 9) were from Institute of Vegetables and Flowers, Chinese Academy of Agricultural Sciences.

**Table 1 Physical and chemical properties of the test soil**

| pH | Content/ mg•$kg^{-1}$ | | | | | | Moisture /% |
|---|---|---|---|---|---|---|---|
| | Organic matter | Total-N | $NH_4^+$-N | $NO_3^-$-N | Organic phosphorus | Available potassium | |
| 7.28 | 15 750.00 | 910.00 | 37.00 | 82.00 | 128.13 | 266.53 | 25.4-38.8 |

2) Reagents: Pure urea was obtained from Hubei Yihua Chemical Industry Co. Ltd. Hubei, China; *γ*-PGA (MW100 000-1 000 000 and degree of polymerization, 1 000-15 000) was obtained from Hubei Zhengyuan Chemical Industry Co. Ltd. Hubei, China; $ZnSO_4$, $FeSO_4$, and thiourea were reagent grade.

3) Equipments: K9840 Kjeldahl apparatus (Hanon Instruments China); UV-3010 UV-Vis spectrophotometer ( Hitachi, Japan).

### 1.2 Methods

1.2.1 Preparation of SRU

The SRU fertilizers were prepared by first mixing molten urea in *γ*-PGA and then adding the pore constrictors and inhibitors as appropriate. In the first step, *γ*-PGA was dissolved in deionized water, mixed for 1.0-1.5 h at 80 ℃ on a hot plate with a magnetic stirrer, and then cooled to room temperature. In the second step, $ZnSO_4$(pore constrictor), $FeSO_4$ (urease inhibitor), thiourea (nitrification inhibitor) at a mass ratio of 1.0∶1.5 were ground and mixed with ethanol, respectively, as appropriate for formulating a given fertilizer to obtain a homogeneous suspension. The suspension was stirred with the *γ*-PGA/molten urea until well blended and then heated at 130-140 ℃ and stirred for 30-45 min. The mixture was cooled at room temperature, the particles of ~3 mm in the fertilizer were tested.

The following convention was used to designate the three types of SRU: polymer coated urea with pore constrictor (PCU/PC); polymer coated urea with enzyme inhibitor (PCU/EI); polymer coated urea with pore constrictor and enzyme inhibitor (PCU/PC/EI). Preparation of the mixtures for each type of SRU fertilizer is shown in Table 2 (PCU/PC), Table 3 (PCU/EI) and Table 4 (PCU/PC/EI).

**Table 2 Preparation of fertilizers with γ-PGA coated urea and pore constrictor (PCU/PC)**

g

| Formula of PCU/PC | Urea | *γ*-PGA | $ZnSO_4$ (PC) |
|---|---|---|---|
| PCU/PC-1 | 450 | 0.45 | 1.00 |
| PCU/PC-2 | 450 | 2.5 | 1.00 |
| PCU/PC-3 | 450 | 4.5 | 1.00 |
| PCU/PC-4 | 450 | 2.5 | 4.50 |
| PCU/PC-5 | 450 | 2.5 | 0.45 |

1.2.2 Water extraction of nitrogen from untreated urea and SRU fertilized soil

10.00 g of urea and PCU/PC, PCU/EI or PCU/PC/EI were placed into a 100 mesh nylon bag which was closed and immersed into a 250 mL beaker filled with distilled water [11]. The beakers were placed

**Table 3 Preparation of fertilizers with γ-PGA coated urea and enzyme inhibitor (PCU/EI)**

g

| Formula of PCU/EI | Urea | $\gamma$-PGA | EI | |
|---|---|---|---|---|
| | | | $FeSO_4$ | Thiourea |
| PCU/EI-1 | 450 | 2.5 | 0.90 | 0 |
| PCU/EI-2 | 450 | 2.5 | 1.50 | 0 |
| PCU/EI-3 | 450 | 2.5 | 2.70 | 0 |
| PCU/EI-4 | 450 | 2.5 | 0 | 0.90 |
| PCU/EI-5 | 450 | 2.5 | 0 | 1.50 |
| PCU/EI-6 | 450 | 2.5 | 0 | 2.70 |
| PCU/EI-7 | 450 | 2.5 | 0.50 | 1.00 |
| PCU/EI-8 | 450 | 2.5 | 0.75 | 0.75 |
| PCU/EI-9 | 450 | 2.5 | 1.00 | 0.50 |

**Table 4 Preparation of fertilizers with γ-PGA coated urea and enzyme inhibitor and pore constrictor (PCU/PC/EI)**

g

| Formula of PCU/PC/EI | Urea | $\gamma$-PGA | $ZnSO_4$ PC | EI | |
|---|---|---|---|---|---|
| | | | | $FeSO_4$ | Thiourea |
| PCU/PC/EI-1 | 450 | 2.5 | 1.0 | 0.75 | 0.75 |
| PCU/PC/EI-2 | 450 | 2.5 | 0.5 | 0.75 | 0.75 |
| PCU/PC/EI-3 | 450 | 2.5 | 0.5 | 0 | 0.75 |
| PCU/PC/EI-4 | 450 | 2.5 | 0.5 | 0.75 | 0 |

into an incubator at 25 ℃ and N-release was monitored over a four week period. The extracted samples (250 mL) were collected daily for the first week and then weekly for the remaining three weeks. Samples were stored in polycarbonate bottles for Kjeldahl-N determination. After sampling, 250 mL distilled water was added to maintain the extraction volume. Each SRU mixture was tested in triplicate.

1.2.3 Column leaching experiment

Leaching rates for urea and each SRU treatment were measured by monitoring Kjeldahl-N from a soil leaching column. The leaching column was constructed in the lab and a schematic of the column is displayed in Fig.1. The column contents were held in place with 100 mesh nylon secured at the bottom, from bottom to top there were placed: ① 25 g sand; ② 200 g test soil; ③ 10 g SRU mixed with 25 g sand; ④ 200 g test soil; ⑤ 25 g sand. To simulate rainfall, deionized water was added to the column until the soil was nearly saturate and the column was allowed to stand. After 24 h , 100 mL water was added to the column, leachate was collected, the volume recorded and the leachate analyzed for Kjeldahl-N. Leachate was collected over a period of 120 days; biweekly for 2 weeks, weekly for the next 6 weeks and then each 10 days for the remainder of the study period. The leaching experiments were run in triplicate [12].

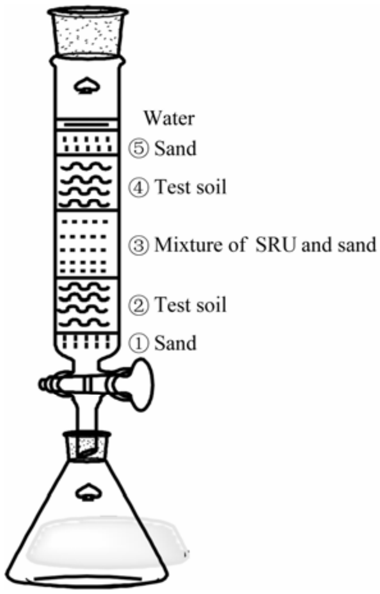


**Fig.1 Schematic of the column used for soil leaching experiments**

1.2.4 Effect of SRU on tomato growth

Tomato seedings were planted in plastic pots (high, 13 cm; top diameter, 8 cm; bottom diameter, 5 cm). The plants were grown in a greenhouse within a temperature range of 18 - 22 ℃. The pots were prepared by placing 1.5 kg of dry soil at the bottom, followed by a mixture of 3.0 kg dry soil and 25.0 g of fertilizer [13]. Each pot contained 3 tomato seedlings and they were watered every 3 days. The pots were weighed before watering and water was added to maintain soil moisture at 50% saturation value. The chlorophyll content of tomato was measured at the seedling, flowering, and mature stages and at harvest. A portion leaf samples (removed costa) extracted with 80% alcohol, which was determined with the spectrophotometric method. Tomato plants used in this investigation were fertilized with different kinds of manure and the approximate duration of each stage is displayed in Table 6. At the same time leaves were collected, soil for the tomato growth studies was obtained by systematic sampling method from tomato pots and core samples (0-60 cm) were collected from each pot for $NO_3^-$-N analysis. The tomato growth experiment was also run in triplicate.

1.2.5 Analytic methods

National standard methods for analysis of slow-release fertilizer (GB/T 23348-2009) were used in this investigation. Total nitrogen (Total-N) content was determined using the Kjeldahl method (Hanon K9840 Kjeldahl apparatus), $NO_3^-$-N and $NH_3/NH_4^+$-N were determined colorimetrically using sulfonic acid, alkaline phenol, and a Hitachi 3010 UV-Vis spectrophotometer [14].

Chlorophyll from tomato leaves was extracted with 80% alcohol and determined with the spectrophotometric method [15].

Data analysis was carried out with Excel (2003) and SPSS software using the *t*-test with $0.05 \geqslant p \geqslant 0.001$ as the criterion for significance.

# 2 Results and Discussion

## 2.1 N-Release Rate for Urea and SRU Treated Urea in Water Extraction

PCU/PC, CPU/EI and PCU/PC/EI were prepared according to the experiment of Section 1.2.3 and conducted water extraction experiments, added mass ratio is shown in Tables 2-4. To develop an empirical model for N-release, 3rd order curve-fitting was carried out upon the results from each water extraction and the leaching curves are displayed in Fig. 2.

Statistical analysis indicates a significant difference between untreated urea and all three types of SRU. The best fit for the N-release data was found out to be a cubic equation which gave a satisfactory fit with the curve-fitting of N-release for optimal formulations of urea and SRUs ( $R^2 > 0.80$). The PCU/PC formulations were significantly different, particularly PCU/PC-2 ($R^2 = 0.858$, $0.001 < p < 0.01$). The other PCU/PC with lower slow release performance maybe as $\gamma$-PGA which has strong water inhibition and ion adsorption; the absorption of water soluble pore constriction would lead to fertilizer loss but it is yet superior to urea. Taking material savings into account, PCU/PC-2 was the best SRU. Among the PCU/EI formulations, PCU/EI-8 had a superior release effect and a higher degree of cubic equation mode corresponding with $R^2 = 0.80$ and $p$ were all of composite standards. But the PCU/EI-4, 5, 6 got a lower release effect according to the $R^2$, $p$ value, so $FeSO_4$ as urease inhibitor may delay the hydrolysis of urea, and reduce loss of volatile $NH_3$. Thiourea, as a nitrification inhibitor was the direct inhibitor $HN_4^+$-N which oxidizes as $NO_3^-$-N and at the same time reduces $NO_3^-$-N leaching and $N_2$ or $N_2O$ and gaseous loss. As for PCU/PC/EI, according to water extraction data of PCU/PC/EI-2, there is a slower release curve than other fertilizer from Fig. 2(c). The amount of resistance solvents, which was 0.5 g, and inhibitors, which was 0.75 g relative to the urea, with $R^2 = 0.92$, and the $p$ values were all composite standards ($0.001 < p < 0.01$). Moreover, PCU/PC/EI-2 not only had high slow-release efficiency, but saved 10% of the material effectively. It was an effective control of SRUs nitrogen release, as shown by the increase in resource utilization rate.

Based on results from the water extraction study, PCU/PC-2, CPU/EI-8, and PCU/PC/EI-2 were found out to be the optimal formulations for the three types of SRU-treated urea and were used for the nutrient release and tomato growth studies described in the following sections.

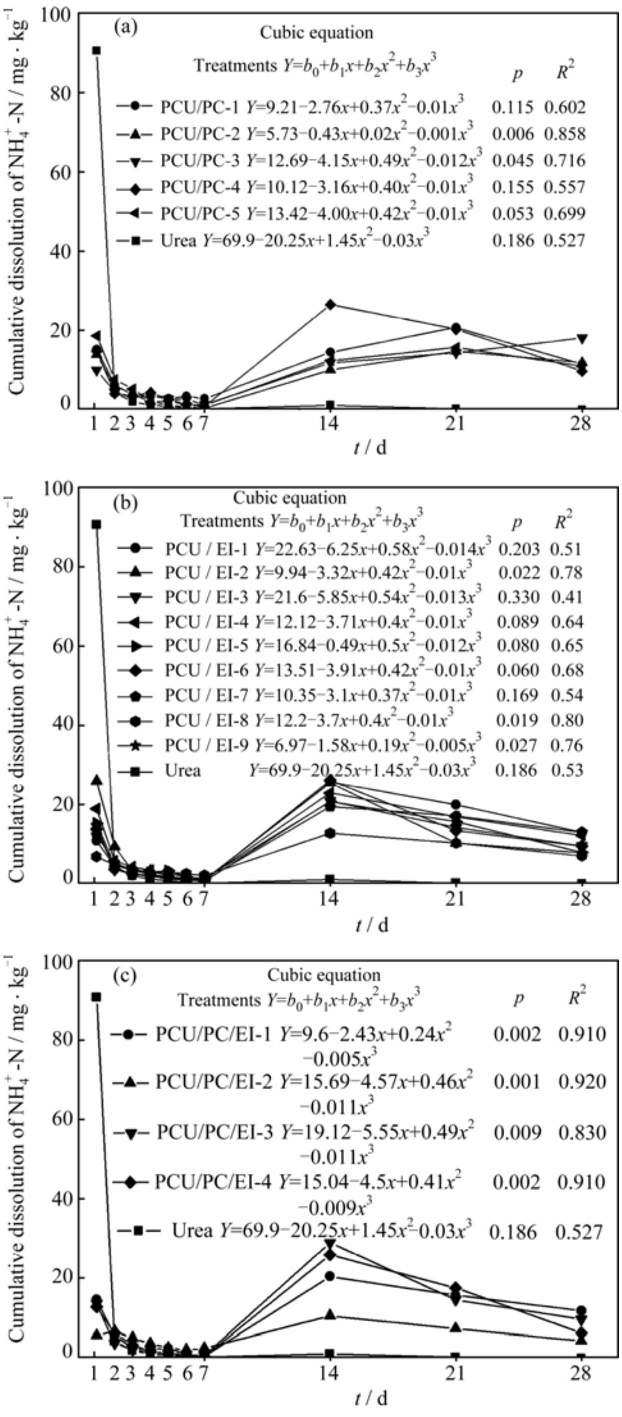


**Fig. 2 Nitrogen release fitted equation and parameter** values of SRU (a)PCU/PC; (b)CPU/EI; and (c)PCU/PC/EI

### 2.2 N-Release Rate for Urea and SRU Treated Urea from Leaching Columns

In order to further evaluate the release effects of SRU treatment, untreated urea and formulations PCU/PC-2, CPU/EI-8, and PCU/PC/EI-2 were tested in a 120 day column leaching study. The procedure is described in Column Leaching Experiment and the results are shown in Fig. 3，which indicates an obvious delay in N-release for the SRUs. After 28 days, the fraction of urea in the accumulated leachate was of 86.5% for urea, 60.86% for PCU/PC-2, 44.36% for CPU/EI-8, and 14.85% for PCU/PC/EI-2, respectively.

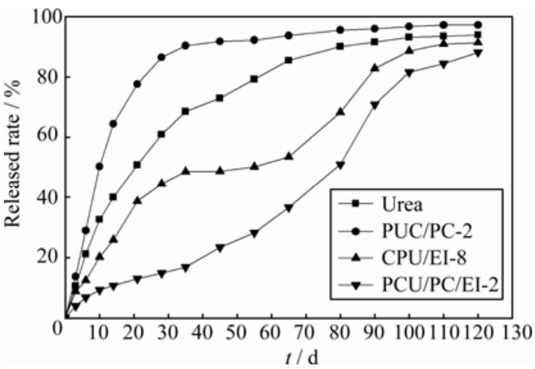


**Fig. 3 Release of nitrogen by SRU fertilizers from the leaching column**

The leaching curves for PCU/PC-2 and urea have similar shapes, indicating a high initial release rate and rapid depletion of nitrogen, roughly a fall “L” shape, leaching consists of 80.08% for 80 days. CPU/EI-8 rapidly released nitrogen for the first 28 days and then the release nearly ceased until day 56. That the curve was roughly the “L” shape could be explained by urease inhibitor lasting from approximately day 28 until day 56. The test results from CPU/EI-8 show that enzyme inhibitor plays an important role for N-release rate; oxidation of $NH_4^+$ was reduced and the urea hydrolysis was delayed, because the experiments were conducted in a sealed vessel. The PCU/PC/EI-2 leaching curve is impressive, roughly in an “M” shape. After a rapid initial N-release, the rate was low but increased gradually. However, PCU/PC/EI-2 led to favorable conditions for growth while reducing the loss of applied nitrogen. More importantly it demonstrates that SRU fertilizers can be controlled to match nutrient requirements and minimize loss of applied nitrogen.

### 2.3 Effect of SRU Treated Urea on Tomato Growth

SRU fertilizer performance, compared with that of untreated urea was also tested by measuring the fraction of nitrogen absorbed by tomato, the effect on tomato growth, and by determining Total-N, $NO_3^-$-N, and $NH_4^+$-N in pot soil at different stages of tomato growth. Untreated urea and SRU fertilizers PCU/PC-2, CPU/EI-8, PCU/PC/EI-2 were tested as described in Effect of SRU on Tomato growth and results are shown in Table 5 (chlorophyll content a and b of leaves) and Table 6 (N-content of pot soil). From the pot experiment, it was found out that the chlorophyll content of plants at maturity and harvest with the fertilizer PCU/PC-2, and CPU/EI-8, PCU-PC/EI-2 SRUs was 13%-55% higher than that with urea[16]. From maturation to harvest, $NH_3/NH_4^+$-N in SRU-treated pots was 25%-61% higher than in soil from urea-treated pots during the growing period while soil $NO_3^-$-N was nearly 50% lower after the tomato had been harvested. The level of $NH_4^+$-N in SRU containing soils initially increased and then decreased, but was higher than in those with urea. This proves that more $NH_4^+$-N was available to the plants and less was converted to $NO_3^-$-N , therefore, the SRU treatments examined improved the utilization of applied nitrogen.

**Table 5 Content of chlorophyll content(a+b) of tomato leaf(FW) in different growth period with SRU formulations and the untreated urea**

mg•g$^{-1}$

| Manure | Seedling | Flowering | Mature | Harvest |
|---|---|---|---|---|
| Contrast | 0.95 | 1 010.00 | 1.17 | 0.88 |
| Urea | 1.15 | 1 820.00 | 1.69 | 1.38 |
| PCU/PC-2 | 1.16 | 1 910.00 | 2.15 | 1.62 |
| CPU/EI-8 | 1.02 | 1 640.00 | 2.62 | 2.13 |
| PCU/PC/EI-2 | 1.10 | 2 570.00 | 3.22 | 2.52 |

**Table 6 Soil nitrogen content during tomato growth with SRU formulations and untreated urea**

mg•kg$^{-1}$

| Manure | C(Total-N) | | | | C($NO_3^-$-N) | | | | C($NH_4^+$-N) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Seedling | Flowering | Mature | Harvest | Seedling | Flowering | Mature | Harvest | Seedling | Flowering | Mature | Harvest |
| Contrast | 730.00 | 680.00 | 620.00 | 530.00 | 82.28 | 89.73 | 90.60 | 77.70 | 30.65 | 38.45 | 49.15 | 32.60 |
| Urea | 1 560.00 | 1 400.00 | 1 420.00 | 1 370.00 | 137.25 | 163.05 | 170.40 | 132.05 | 45.28 | 53.05 | 55.28 | 43.05 |
| PCU/PC-2 | 1 030.00 | 1 140.00 | 1 190.00 | 1 190.00 | 101.44 | 123.20 | 138.40 | 103.60 | 40.48 | 66.29 | 82.48 | 57.29 |
| CPU/EI-8 | 1 000.00 | 1 070.00 | 1 170.00 | 117.00 | 76.62 | 88.43 | 94.62 | 66.43 | 67.62 | 88.43 | 94.62 | 64.43 |
| PCU-PC/EI-2 | 980.00 | 1 040.00 | 1 140.00 | 115.00 | 74.55 | 83.10 | 85.60 | 57.90 | 52.60 | 78.96 | 98.50 | 86.43 |

## 3 Conclusion

In this article, the anionic polymer ($\gamma$-PGA) was used to slow down N-release from urea and other materials were added to enhance the effect by reducing the pore size and inhibiting urease and nitrification. Soil incubation, followed by water extraction, was used to optimize the ingredient ratios for three SRU formulations. Leaching curves for all three SRU formulations had significantly slighter slopes than for untreated urea. The optimal blend of each formulation was tested for N-release in a leaching column and by monitoring chlorophyll and soil nitrogen in potted tomato during their growth cycle. After 28 days, the fraction of urea in the accumulated leachate was of 86.5% for urea, 60.86% for PCU/PC-2, 44.36% for CPU/EI-8, and 14.85% for PCU/PC/EI-2. In the tomato growth study, SRU treatment increased the availability of the chlorophyll content of tomato leaves during the flowering stage. The $NH_4^+$-N in SRU containing pots was more than in pots containing untreated urea during the growing period, but $NO_3^-$-N content was nearly 50% lower in the pot soil (0-60 cm) at harvest. Results confirm that $\gamma$-PGA coating, with pore restrictor and enzyme inhibitor, increases nitrogen uptake from urea, enhancing plant growth and reduces the loss of applied nitrogen. This investigation demonstrates that SRU fertilizers can be controlled to match plant nutrient requirements and minimize the loss of applied nitrogen. This is an important step in the search for the perfect fertilizer, maximizing agricultural production and minimizing environmental impact.

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