Mitigating Rapid Release of Nitrate from Rejected Sago Starch-coated Urea and Uncoated Urea

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ABSTRACT

Urea is the most widely used nitrogen (N) fertilizer as it has a high N content (46%), is inexpensive, easily available, and can be conveniently stored. However, the high water-solubility and rapid hydrolysis of urea in the soil leads to much N loss. Rejected sago starch (RSS) was used to coat urea to prevent rapid release of N. A soil leaching experiment was conducted over 30 days to determine the effectiveness of RSS-coated urea in retaining soil N availability in the form of exchangeable NH_4^+ and available NO_3^- compared with uncoated urea. The soil used in the leaching experiment was Bekenu Series (Sandy loam, Typic Paleudults). This study compared seven different treatments: soil alone (S), 5 g of uncoated urea (U), 5 g of 2% RSS-coated urea (CU1), 5 g of 3% RSS-coated urea (CU2), 5 g of 4% RSS-coated urea (CU3), 5 g of 5% RSS-coated urea (CU4), and 5 g of 6% RSS-coated urea (CU5). The RSS-coated urea (CU1, CU2, CU3, and CU4) significantly reduced N leaching due to the coating on the urea that serves as a barrier which slows down the conversion of N into NH_4^+ and NO_3^- . Gradual released of N helps in retaining more soil exchangeable NH_4^+ in all RSS-coated urea than uncoated urea. Optimize use of RSS-coated urea in CU1 (2% of RSS) did not only mitigates NO_3^- leaching, but it is also increasing soil TOM, TOC, total N, soil exchangeable NH_4^+ , and available NO_3^- although all the RSS-coated urea has minimal effects on soil pH.

Key words: coated urea, urea hydrolysis, natural polymer, nitrogen loss

INTRODUCTION

Urea is one of the major sources of nitrogenous fertilisers that is widely used in agriculture because of the high nitrogen (N) (46%) concentration (Rose *et al.* 2018). However, due to its solubility and mobility in the soil, urea should be applied in a controlled manner to ensure efficient soil N use and uptake by crops. Otherwise, approximately 20 to 70% of the N from urea application is lost through ammonia (NH₃) volatilisation and nitrate (NO₃-) leaching which leads to low soil N availability, low N uptake and use efficiency, and causing adverse environmental impacts. Thus, it is important to retain soil N availability in the form of exchangeable ammonium (NH₄+) and available NO₃- which is readily available for plant uptake (Zhang *et al.* 2019). Some studies on improving soil N availability and N use efficiency were based on agronomic, molecular, and genetic approaches. However, a

sustainable way to improve soil N retention and N uptake and N use efficiency is by coating the urea prills using environmentally friendly materials such as rejected sago starch (RSS). Coating urea is a process of encapsulating urea prills using thin-walled materials or layers embedded in homogeneous or heterogeneous matrices to form capsules that protect urea surface from being rapidly solubilised or hydrolysed when reacting with soil water. As stated by Suzzi *et al.* (2012), the thickness of the film layer for urea coating varies between 5 µm and 100 µm which depends on the granular dimension and coating functionality. The main purpose of urea encapsulation is for gradual release of N from urea and synchronisation of the release of core material rate with a certain N concentration and time to ensure soil N availability. Such mechanisms could be physically imparted to the urea prills by coating to reduce the dissolution rate as summarised in Figure 1.

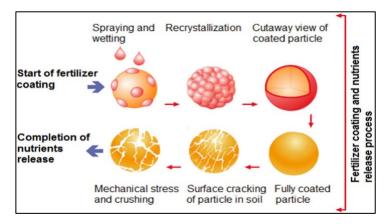


Figure 1. Slow release of nitrogen from coated materials Source: Naz and Sulaiman (2016)

N release from coated urea takes place through partial degradation of the thin layer of coating materials (Figure 1). When coated urea is applied to soil, the coating becomes porous and breaks down causing a burst release of N from urea. For this mechanism, coating materials for urea encapsulation should be hydrophilic. According to Naz and Sulaiman (2016), the coating should be partially hydrophilic to provide the water flow through coating and favour the flow of N. In addition, the coating materials should be partially hydrophobic to avoid the disruption of coated film and fast release of N from urea prills. Most of the coating materials used in previous studies were mainly inorganic and organic compounds that slow down the oxidation of urea by delaying the activities of nitrosomonas and nitrobacter in the nitrification process. However, these inorganic compounds are expensive, non-biodegradable, and have adverse effects on beneficial soil microorganisms (Dong *et al.* 2013).

The focus of this study was using a low cost and environmentally friendly material for urea coating, hence the choice of RSS. Low quality sago starch is considered as rejected starch as it is expelled from the rotary sieves, extractors, and sieve bend machines during the processing of the refined sago starch flour. RSS is almost similar to high-quality starch flour except for its texture which is slightly coarse (does not meet the standards of premium quality sago starch). We considered using the RSS as coating material to encapsulate urea prills because it contains polymer chains of glucose units with a high degree of regularity with crystalline clusters of double helices which consist of the two glucans of amylopectin

and amylose. Amylopectin is a major component in most starches. It is characterised by an extensively branched structure and is composed of short chains α -(1,4)-linked D-glucosyl units that are interconnected through α -(1,6)-linkages (Miao and BeMiller 2023; Vamadevan and Bertoft 2014). Amylose is a minor component and has essentially longer linear chains than amylopectin (Miao and BeMiller 2023).

There is limited information on using natural biopolymers from waste materials such as RSS for urea coating. In our previous study, RSS-coated urea has potential as coating material for urea because the starch degrades in a slow manner and gradually released N in the form of NH₄⁺ and NO₃⁻. Urea hydrolysis causes a higher concentration of NH₃ in the soil solution, especially when the soil microsite is high in pH. When urea coated with RSS, the acidic nature of RSS used for urea coating temporarily decreased the pH of soil microsite which led to the low concentration of NH₃ and the amount of N loss *via* NH₃ were reduced compared with uncoated urea (Kavitha *et al.*, 2022). In this study, we expected that RSS-coated urea could mitigate N loss *via* minimizing NO₃⁻ leaching from soil. Thus, the soil leaching study was carried out to determine the optimum amount of RSS-coated urea that could mitigate N leaching from the soil compared with uncoated urea. This study provides information on the mechanism of N release from different formulations of RSS-coated urea compared with uncoated urea. This study partly shows that use of appropriate coating material for urea prills does retain N and benefits planters, economy, society, and the environment.

MATERIALS AND METHODS

Selected Properties of Rejected Sago Starch-Coated Urea

The uncoated urea prills used in this study are produced by ASEAN Bintulu Fertilizer Sdn. Bhd., Bintulu, Sarawak, Malaysia, and was purchased from Poson Perniagaan, Bintulu, Sarawak, Malaysia. The RSS used for urea coating was collected from Sago Link Sdn. Bhd. at Mukah, Sarawak, Malaysia. The procedures of coating urea with RSS and their characterizations have been reported in our previous study (Kavitha *et al.*, 2022). The coating materials of RSS were prepared by diluting different amounts of RSS (0.4 g, 0.6 g, 0.8 g, 1 g, and 1.2 g) with 5 mL of the distilled water in 50 mL beakers to obtain different concentrations (2%, 3%, 4%, 5%, and 6%) of the RSS coating materials. All of those RSS formulations used for urea coating were indicated as CU1 (2% RSS), CU2 (3% RSS), CU3 (4% RSS), CU4 (5% RSS), and CU5 (6% RSS) representing coated urea. Uncoated urea was indicated as U. The preliminary characterisations of selected properties of uncoated urea and RSS-coated urea are given in Table 1.

Table 1. Selected characterization of uncoated urea and RSS-coated urea

Parameter	U	CU1	CU2	CU3	CU4	CU5
N content (%)	46 ± 0.12	45 ± 0.99	44 ± 0.40	44 ± 0.57	43 ± 1.46	42 ± 0.53
Dissolution rate (second)	84.67 ± 1.76	1088.33 ± 0.88	971.67 ± 1.20	818 ± 3.06	767 ± 2.08	729 ± 0.58
Thickness of coating (mm)	None	0.39 ± 0.04	0.41 ± 0.04	0.43 ± 0.03	0.44 ± 0.04	$\begin{array}{c} 0.45 \pm \\ 0.05 \end{array}$

Note: The values given are means followed by \pm standard error; U is urea only; CU1-CU5 is coated urea.

Soil Sampling, Preparation, and Initial Characterization

The soil used for the leaching experiment was sampled at depth of 0-20 cm from an uncultivated area in Universiti Putra Malaysia Bintulu Sarawak Campus (UPMKB), Sarawak, Malaysia. The soil was air-dried for seven days, crushed using a soil mortar and a pestle, after which sieved to pass a 2 mm sieve for a laboratory analysis and the leaching study. Soil pH in water and 1 M KCl were determined at a ratio of 1:2.5 (soil: distilled water/KCl) using a digital pH meter (Seven Easy Mettler Toledo) whereas electrical conductivity (EC) of the soil was analyzed using an EC meter Mettler Toledo (SevenEasyTM Conductivity Meter S30, New Zealand) (Tan, 2005). Soil texture was determined using the hydrometer method whereas bulk density of the soil was determined using the core ring method (Tan, 2005). The total organic matter (TOM) and total organic carbon (TOC) of soil were determined using a loss-on-ignition method (Tan, 2005). Total N was determined using Kjeldahl method (Tan, 2005) and exchangeable NH₄⁺ and available NO₃ were determined using the method described by Keeney and Nelson (1982). Available phosphorus (P) and exchangeable cations of the soil were extracted using the double acid method (Tan, 2005). The available P was determined using the molybdenum blue method (Murphy and Riley, 1962), whereas the exchangeable cations were determined using Atomic Absorption Spectrophotometry (AAnalyst 800, PerkinElmer, Norwalk, CT, USA). The soil cation exchange capacity (CEC) was determined with a leaching method (Cottenie, 1980) followed by steam distillation (Bremner, 1965). The initial characterisations of Bekenu series soil are shown in Table 2.

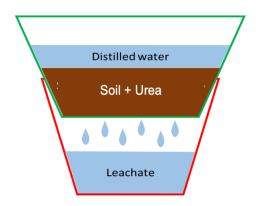
Table 2. Selected physical and chemical properties of Bekenu Series

Property	Current study	Range* (0-36 cm)	
Colour	Dark yellowish brown	Yellowish brown	
pH in water	4.67 ± 0.012	4.6-4.9	
pH in 1M KCl	3.83 ± 0.010	3.8-4.0	
EC (μS cm ⁻¹)	52.00 ± 1.155	NA	
Total organic carbon (%)	1.44 ± 0.330	0.57-2.51	
Organic matter (%)	2.48 ± 0.563	NA	
Total N (%)	0.09 ± 0.009	0.04-0.17	
Exchangeable NH ₄ ⁺ (mg kg ⁻¹)	6.30 ± 0.701	NA	
Available NO ₃ (mg kg ⁻¹)	4.67 ± 0.234	NA	
Available P (mg kg ⁻¹)	1.51 ± 0.180	NA	
	(cmol (+) kg ⁻¹)		
Cation exchange capacity	11.67 ± 0.21	3.86-8.46	
Exchangeable K ⁺	0.16 ± 0.007	0.05-0.19	
Exchangeable Ca ²⁺	0.03 ± 0.004	NA	
Exchangeable Mg ²⁺	0.03 ± 0.005	NA	
Exchangeable Na ⁺	0.22 ± 0.013	NA	
Exchangeable Fe ²⁺	0.19 ± 0.001	NA	
Exchangeable Cu ²⁺	0.02 ± 0.016	NA	
Exchangeable Zn ²⁺	0.17 ± 0.011	NA	
Exchangeable Mn ²⁺	0.02 ± 0.001	NA	
Sand (%)	66	72-76	
Silt (%)	22	8-9	
Clay (%)	16	16-19	
Texture (USDA)	Sandy loam	Sandy clay loam	

Note: The values given are on dry-weight basis; NA: not available; *subjected to the soil development range as stated in Paramananthan (2000).

Soil Leaching Study

A leaching study was conducted for 30 days in the Soil Science Laboratory at University Putra Malaysia Bintulu Sarawak Campus. Soils of 250 g were weighed using a digital balance and filled in polypropylene containers. The soil samples were moistened at 60% of water holding capacity and left overnight to equilibrate. Thereafter, uncoated urea and RSS-coated urea were surface applied throughout the leaching study. It is worth to noted that only uncoated urea and RSS-coated urea were used in this leaching study without applying source of P and K fertilizers because the focus was to determine the beneficial effects of the RSS-coated urea on N availability and retention in the soil compared against uncoated urea. The recommended rate of urea used was 151 kg ha⁻¹ N and the amounts were scaled down from the standard fertilizer recommendation for rice (test crop) cultivation per plant basis. Thereafter, 309 mL of distilled water was added to each container with soil over 30 days (Figure 2). The volume of water applied was based on rainy days over 30 days based on 10 years rainfall data (2009–2019) obtained from the Department of Drainage and Irrigation, Bintulu, Sarawak, Malaysia.



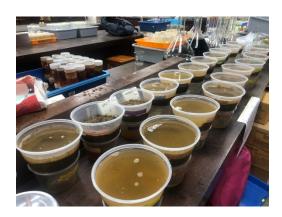


Figure 2. Illustration of leaching study set up (left) and layout of soil leaching study (right)

The treatments evaluated in the leaching study are summarized as below:

S : soil alone

U : soil + 5 g of uncoated urea

CU1 : soil + 5 g of urea coated with RSS (2%) CU2 : soil + 5 g of urea coated with RSS (3%)

CU3: soil + 5 g of urea coated with RSS (4%) CU4: soil + 5 g of urea coated with RSS (5%)

CU5 : soil + 5 g of urea coated with RSS (6%

Leachates and soil chemical analysis

Leachates were collected at three days interval over 30 days of leaching study for determination of pH, exchangeable NH_4^+ and available NO_3^- in the leachate. At 30 days of leaching, the soil samples were air-dried, and analyzed for pH, total N, exchangeable NH_4^+ , available NO_3^- , TOM and TOC using the standard procedures.

Experimental design and statistical analysis

The leaching study was arranged in a completely randomized design (CRD) with three replications of each treatment. Analysis of variance (ANOVA) was used to test treatment

effects whereas means of treatments were compared using Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$. The Statistical Analysis System (SAS) version 9.4 was used for the statistical test.

RESULTS AND DISCUSSION

Soil acidity, exchangeable ammonium, and available nitrate of leachate over 30 days of leaching

Soil alone (S) had the lowest pH throughout the leaching study because of the inherent acidic nature of soil (Bekenu series) used in this study and no urea added in the soil to temporarily increased soil pH (Figure 3). Treatment with uncoated urea (U) had highest pH due to the absence of coating material and rapid hydrolysis of urea that released OH- and neutralized H⁺ (Hamidi et al., 2021). After 18 days of leaching, pH of the leachate in uncoated urea (U) decreased from alkaline (7.7) to slightly acidic (5.9) could be partly due to the conversion of NH₄⁺ to NO₃⁻ through nitrification process. This is possible as nitrification of NH₄⁺ to NO₃⁻ lead to soil acidification (Cai et al., 2023; Walworth, 2013). Whereas the treatments with RSS-coated urea had lower pH than treatment with uncoated urea (U) at 3rd day until 15th day because the presence of coating layer associated with acidulating property temporarily acidified the soil surrounding and prevent the urea from being rapidly hydrolyzed. After 15th day, the pH of the leachate increased to alkaline as the coating dissolved and urea begin to hydrolyze regardless of RSS formulation used to coat urea. In addition, the treatments with RSS-coated urea increased the pH of the leachates because of the inherent content of cations of RSS which contributed to the increased in pH (Kavitha et al., 2022).

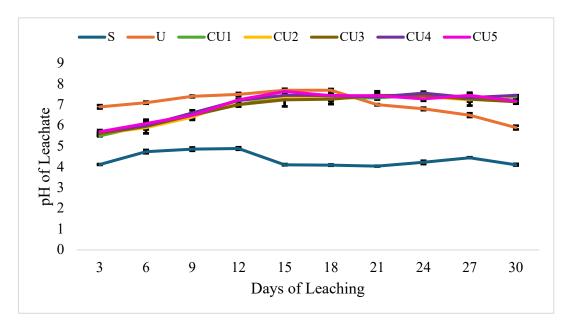


Figure 3. Treatments effects on pH of leachate over thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean.

As shown in Figures 4 and 5, all the treatments with RSS-coated urea (CU1, CU2, CU3, CU4 and CU5) significantly reduced NH₄⁺ leaching from soil compared with soil alone (S)

and uncoated urea (U) because of the RSS used as coating material provided a thin film layer that serves as barrier to retain NH₄⁺ ions in soil. Rejected sago starch is a natural polysaccharide known as one of the materials that has a high affinity for cations, and it is applicable for holding NH₄⁺ ions. The layer of RSS covered on urea prills held NH₄⁺ ions, thus preventing them from being leached. In the related study, using potato starch as urea coating, the starch forms a complex with NH₄⁺ ions, providing a stable bond that reduces N mobility and availability for leaching (Naz and Sulaiman, 2016). In addition, the ability of RSS to retain NH₄⁺ ions are attributed to the high CEC of the starch, known as the capacity, to retain and exchange cations. In our previous findings, the high CEC of RSS enables the starch to attract and bind NH₄⁺ ions, thus preventing the NH₄⁺ movement in the soil profile (Figure 4) (Kavitha *et al.*, 2022).

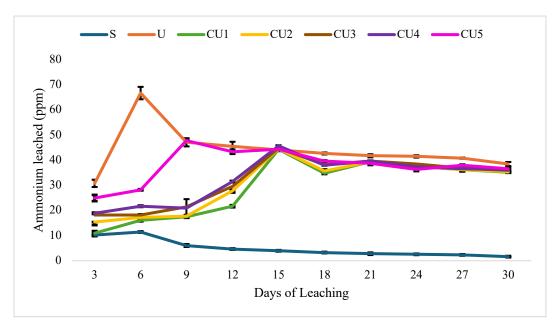


Figure 4. Ammonium leached at three-day interval over 30 days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-5%), and CU5 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean.

The three-day interval losses of NO₃⁻ from soil in the leaching experiment for 30 days is presented in Figure 6 whereas the accumulation leached of NO₃⁻ is showed in Figure 7. Consistent with the amount of NH₄⁺leached, uncoated urea (U) had higher amount of NO₃⁻ leached from soil compared with all RSS-coated urea. The higher NO₃⁻ leached in uncoated urea was due to the rapid hydrolysis of urea and immediate availability of NH₄⁺ (Benlamlih *et al.*, 2021). Without proper retention, the NH₄⁺ ions then further transformed into NO₃⁻ through nitrification. In addition, NO₃⁻ is negatively charged, thus the anion is not retained in soil and repelled by the negatively charged soil surfaces (Hamidi *et al.*, 2021; Wyatt *et al.*, 2019). In other study, it was also reported that NO₃⁻ easily move with soil water particularly in waterlogged soil, resulting high NO₃⁻ leached (Latifah *et al.*, 2021). Regardless of the concentration, all the RSS-coated urea (CU1, CU2, CU3, CU4 and CU5) significantly reduced NO₃⁻ leaching compared with uncoated urea. This could be partly related by the slow-release characteristic of RSS-coated urea that help to minimize the conversion of NH₄⁺ to NO₃⁻ and subsequent leaching. When the N released slowly from RSS-coated urea, less

NH₄⁺ available in the soil and nitrification process delayed, thus reduced NO₃⁻ leaching (Ransom *et al.*, 2020; Singh *et al.*, 2012).

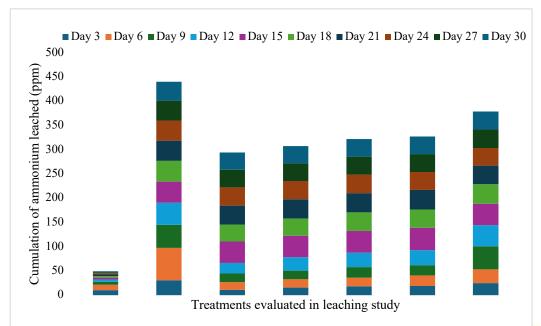


Figure 5. Cumulation amount of ammonium leached at three-day interval over 30 days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-5%), and CU5 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean.

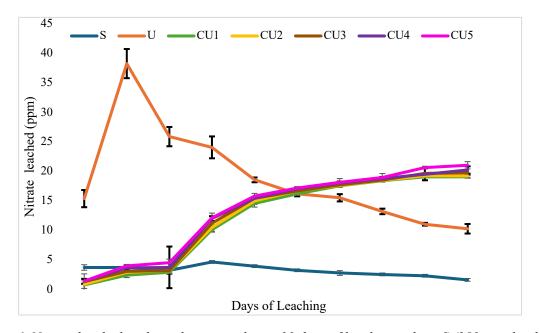


Figure 6. Nitrate leached at three-day interval over 30 days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-5%), and CU5 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean.

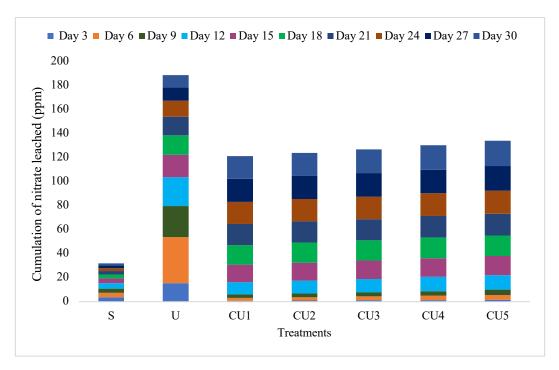


Figure 7. Cumulation amount of nitrate leached at three-day interval over 30 days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-5%), and CU5 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean.

Soil pH after thirty days of leaching

Figures 8 and 9 demonstrated the higher soil pH at 30 days of leaching in soils with RSS-coated urea (CU1, CU2, CU3, CU4, CU5) than soil alone (S) and soil with uncoated urea (U). Slightly increased in soil pH for treatment with RSS-coated urea particularly in CU1 was because of the delay of urea hydrolysis, that prolonged until 30th day. During urea hydrolysis, the reaction converts urea into NH₄⁺ ions and bicarbonate (HCO₃⁻) ions. The occurrence of NH₄⁺ ions in soil increased soil pH because NH₄⁺ is a cation that displaced H⁺ in the soil, after which raises the soil pH and decreases soil H⁺. As reported by Panja and Adams (2021) and Rana *et al.* (2021), the hydrolysis of urea causes an alkalizing effect on the soil and increased soil pH. The lower of soil pH in uncoated urea was due to the rapid urea hydrolysis that occurred at the earlier stage of leaching study which was corroborated by the higher leached of NH₄⁺ and NO₃⁻ from day 6 to day 18 (Figures 4 and 6). Despite of high N concentration in U among all treatments, the rapid release of N from uncoated urea was corroborated by the higher dissolution rate as indicated in Table 1 (Page 4).

The higher soil pH due to RSS-coated urea showed that the RSS has no glaring effects on acidifying soil although RSS has low pH. This finding suggested that RSS as coating materials for urea encapsulation is environmentally friendly.

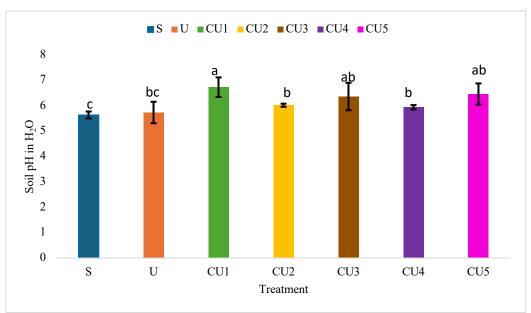


Figure 8. Treatments effects on soil pH in water after thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean. Means with different letter(s) indicate significant differences between treatments according to Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$, that is, a > b > c. Bars represent the mean values \pm SE

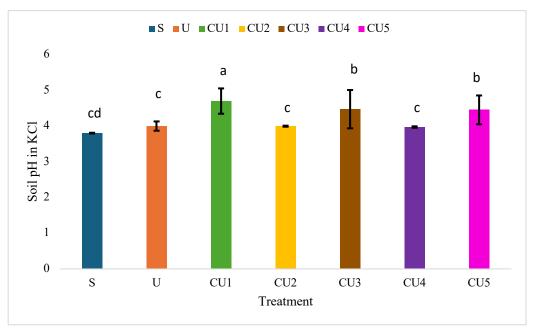


Figure 9. Treatments effects on soil pH in potassium chloride after thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean. Means with different letter(s) indicate significant differences between treatments according to Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$, that is, a > b > c. Bars represent the mean values $\pm SE$

Soil total organic matter and total organic carbon after thirty days of leaching

Soil alone (S) has lower TOM and TOC (Figures 10 and 11) because Bekenu series soil is characterized by low TOM content due to various factors, such as weathering and degradation. Soil with RSS-coated urea (CU1, CU2, CU3, CU4 and CU5) significantly improved soil TOM and TOC compared with soil alone (S) and uncoated urea (U) because of inherent content of RSS which is high in organic matter (Kavitha *et al.*, 2023). Rejected sago starch is a plant-based material that contain C compounds (Rasyid *et al.*, 2020). The C present in these organic compounds contributes to the higher TOM and TOC content in the soil treated with RSS-coated urea than uncoated urea. The higher TOM and TOC in soils with RSS-coated urea also related to the decomposition of organic matter in the RSS. When applied to the soil, RSS coating react with soil water and facilitate the microorganisms in the soil and to further break down the organic compounds in the RSS, which results in the released of C and the incorporation of TOM and TOC into the soil. In a related study using starch as urea coating stated that when starch-coated urea is applied to the soil, the degradation begins with the presence of bacteria, fungi, and algae enzymes which catalyse the process of chemical hydrolysis (Puoci *et al.*, 2008).

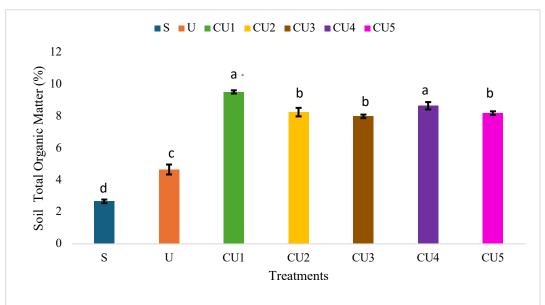


Figure 10. Treatments effects on soil organic matter after thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean. Means with different letter(s) indicate significant differences between treatments according to Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$, that is, a > b > c. Bars represent the mean values $\pm SE$

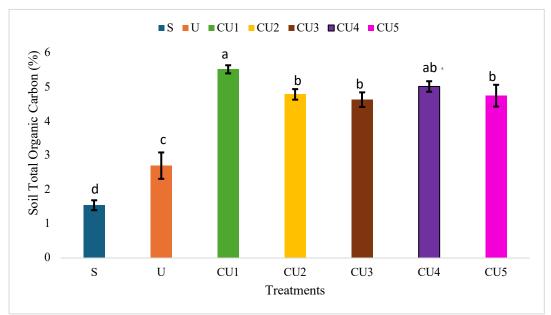


Figure 11. Treatments effects on soil total carbon after thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean. Means with different letter(s) indicate significant differences between treatments according to Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$, that is, a > b > c. Bars represent the mean values \pm SE

Soil total nitrogen, exchangeable ammonium, and available nitrate after thirty days of leaching

Soil total N after thirty days of leaching as shown in Figure 12 showed that soil alone (S) had the lowest soil total N. In soil with uncoated urea (U), the retention of total N was lower than total N in all soils with RSS-coated urea (CU1, CU2, CU3, CU4 and CU5) although with high percentage of N as showed in Table 1, Page 4. Despite with lower N content, all treatments with RSS-coated urea significantly improved soil total N because RSS-coated urea ensured a slow release of N into the soil. The slow release of N into the soil is related to the lower dissolution rate and the thickness of all RSS-coated urea compared with uncoated urea (Table 1, Page 4). The RSS-coated urea mechanism involves a coated film physically creating a barrier during urea dissolution. The retention of soil N is important because N availability able to sustain N supply in soil (Wei *et al.*, 2020). The study of Thind et al. [9] stated that the coated urea lowers the discharge rate of N in the field, which result in lessening the leaching of harmful NO₃- into the groundwater and hindering the volatilization of NH₃ into the atmosphere. The coating on the urea prills surfaces determines the dissolution rate in water when the coated urea is applied to the soil (Guo *et al.*, 2005).

In line with retention in soil total N, the retention of soil exchangeable NH₄⁺ and available NO₃⁻ in soil with RSS-coated urea were higher compared with soil alone (S) and uncoated urea (U) (Figures 13 and 14). Soil alone (S) had the lowest concentration of soil exchangeable NH₄⁺ and available NO₃⁻ because there was no source of N added in the treatment. Uncoated urea (U) had lower soil exchangeable NH₄⁺ and available NO₃⁻ because most of N in the soil were leached and loss from soil as described previously in Figures 4 and 6. Nitrogen formed from urea regardless of NH₄⁺ or NO₃⁻ are easily leached due to several factors such as high solubility and mobility and lack of adsorption to soil particles

(Singh and Craswell, 2021). The retention of NH₄⁺ and NO₃⁻ in the soil after 30 day of leaching with RSS-coated urea is possible because the RSS coating provides a thin layer that serves as a barrier that slows down the release of N (Lakshani *et al.*, 2023), which in turn delays the conversion of urea into NH₄⁺ and NO₃⁻.

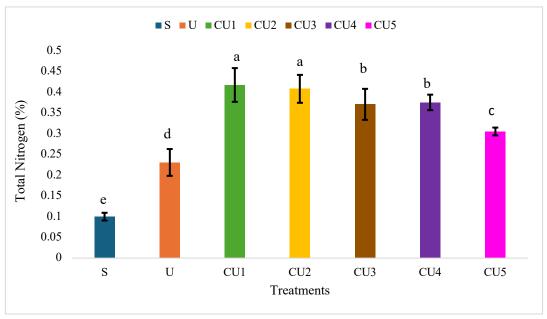


Figure 12. Treatments effects on total nitrogen after thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean. Means with different letter(s) indicate significant differences between treatments according to Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$, that is, a > b > c. Bars represent the mean values \pm SE

Besides, the RSS has ability to absorb and retain water due to their hydrophilic nature. Retention of soil exchangeable NH₄⁺ is related to the nature of the of RSS-coated urea that absorb moisture which provides favourable environment for microbial activity and N availability. This is possible because the presence of sufficient moisture in the soil enhances microbial processes that involved in the conversion of urea to NH₄⁺. This may indirectly support the retention of NH₄⁺ in the soil by promoting microbial activity, which can temporarily hold onto NH₄⁺. In our previous study, we found that the morphology of uncoated urea and RSS-coated urea which were analysed under scanning electron microscope (SEM), showed that the uncoated urea granule surface was rough, with fine openings and a porous structure through which water can penetrate to rapidly dissolve the urea prill. On the other hand, a decrease in membrane porosity and uniform layer were observed in surface morphology of the RSS-coated urea. The RSS coated urea slowed the penetration time; thus, the RSS-coated urea will take a longer time to dissolve and gradually release N to the outer surface of the urea. This characteristic is important for increasing the encapsulation efficacy of the released N (Kavitha et al., 2023). The concentration of soil exchangeable NH₄⁺ were higher than available NO₃⁻ in all RSS-coated urea because of the delay in nitrification process. By slowing down the conversion of NH₄⁺ to NO₃⁻, RSScoated urea helps in retaining soil exchangeable NH₄⁺ and available NO₃⁻ in the soil and decreases the risk of leaching (Palermo et al., 2023).

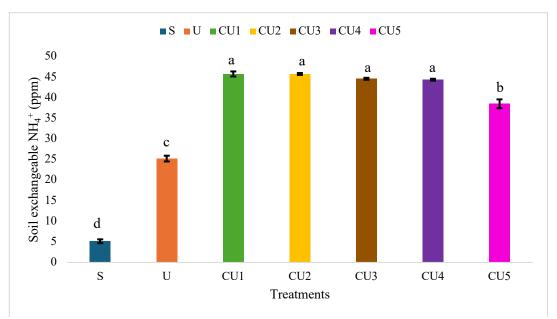


Figure 13. Treatments effects on soil exchangeable ammonium after thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean. Means with different letter(s) indicate significant differences between treatments according to Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$, that is, a > b > c. Bars represent the mean values $\pm SE$

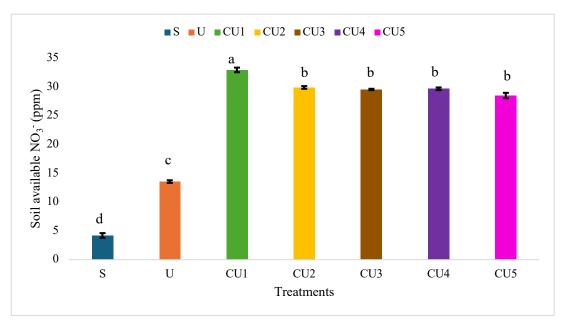


Figure 14. Treatments effects on soil available nitrate after thirty days of leaching, where S (250 g soil only), U (250 g soil + 5.00 g uncoated urea), CU1 (250 g soil + 5.00 g coated urea-2%), CU2 (250 g soil + 5.00 g coated urea-3%), CU3 (250 g soil + 5.00 g coated urea-4%), CU4 (250 g soil + 5.00 g coated urea-6%). Bars represents standard error of the mean. Means with different letter(s) indicate significant differences between treatments according to Duncan's New Multiple Range test (DNMRT) at $p \le 0.05$, that is, a > b > c. Bars represent the mean values \pm SE

CONCLUSIONS

The findings of the leaching study confirmed the ability of RSS-coated urea in mitigating N loss *via* minimizing NO₃⁻ leaching and improving soil N availability and N retention. Soil total N, exchangeable NH₄⁺ and available NO₃⁻ were higher in all soils with RSS-coated urea compared with uncoated urea. Besides that, soil TOM and TOC were also higher compared with uncoated urea (U) particularly in CU1 (2% of RSS coated urea) although it has minimal effects on soil pH. The lower NO₃⁻ leaching in all soils with RSS-coated urea suggest that the coated urea with RSS capable to protect NH₄⁺ from being nitrified to NO₃⁻ compared with uncoated urea. Urea prills could be coated with the RSS to mitigate NO₃⁻ leaching and to improve soil N availability and N retention. The alkalinity of soil after 30 of leaching study confirmed that the RSS has no acidify effects on soil despite of the low pH of the starch used for urea coating.

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