ACS Publications
Most Trusted. Most Cited. Most Read.

Search text, DOI, authors, etc.

Advanced Search

Read   Publish   Subscribe   Help

ACS AGRICULTURAL SCIENCE & TECHNOLOGY

October 20, 2025
Volume 5, Issue 10
Pages 1947-2089

ACS AGRICULTURAL SCIENCE & TECHNOLOGY

About the Cover:

The cover art illustrates the development of a nanocomposite coating system for urea granules, combining castor-oil-derived polyurethane and montmorillonite clay. The process produces coated fertilizers capable of synchronizing nitrogen release with plant demand, improving nutrient uptake, and reducing environmental losses. Greenhouse experiments with *Brachiaria brizantha* demonstrate enhanced biomass production and nitrogen use efficiency, highlighting the potential of bio-based nanocomposite coatings as sustainable alternatives for advanced controlled-release fertilizers. Some illustrative elements were created with the assistance of ChatGPT (OpenAI). **View the article.**

Download Cover

In this issue:

» Reviews
» Viewpoints
» Articles
» Mastheads

‹ PREVIOUS ISSUE
VIEW ALL ISSUES
ASAPs

Get e-Alerts

Submit Manuscript

Article

Role of Nanocomposite Structure in Polyurethane Coatings for Slow-Release Fertilizers: A Case Study with *Brachiaria brizantha*

Vinícius Ferraz Majaron, Cassio Luiz Vellani, Alexandre Antonio Fidelis Martins Junior, Sendy Marques Soares, Fernando Ferrari Putti, Murilo Daniel de Mello Innocentini, Alberto Carlos Campos Bernardi, Wagner Luiz Polito, Caue Ribeiro, and Ricardo Bortoletto-Santos*

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: We developed a nanocomposite coating system based on castor oil-derived polyurethane (PU) and montmorillonite for the controlled release of urea. The incorporation of low amounts of nanoclay effectively slowed nitrogen diffusion through an ion exchange mechanism, resulting in a reduction from 70 to 20% in 215 h (treatment with less than 5%). Greenhouse experiments using *Brachiaria brizantha* demonstrated that the coated fertilizers promoted improved nitrogen uptake and biomass production compared to uncoated urea. Sequential harvests showed that the benefits were consistent across growth stages, with a more evident cumulative effect over 135 days. The results highlight the critical role of nanocomposite structure in enhancing nutrient use efficiency and reducing environmental losses. This approach enables the use of thinner coatings without compromising performance, providing a sustainable alternative for the development of advanced controlled-release fertilizers.

KEYWORDS: urea, clay, castor oil, controlled release, fertilizer

■ INTRODUCTION

The world population has increased by 1.2 billion since 2010 and reached 8 billion individuals in 2023, making the development of technologies for better agronomic efficiency evident.[1] Fertilizers have played a fundamental role in increasing production per hectare, meeting global food demand, and enhancing the quality of human life.[2] Although urea is worldwide the most used nitrogen-based fertilizer due to its physical characteristics and high nitrogen content, ∼45% by mass,[3,4] its high solubility can lead to transformations in the soil and different processes of gas emissions, such as ammonia (NH_3) volatilization and nitrous oxide (N_2O) emission.[5−8] In this context, technologies to synchronize the release of fertilizers with the plant's demand emerge as an alternative to minimize environmental impacts and increase fertilizer use efficiency.

Coatings with biomaterials have attracted attention over synthetic polymers due to their biodegradability and ability to be incorporated into the soil.[9−11] Recently, we have demonstrated that nanocomposite coatings can adjust the release rate based on the electrostatic interactions between the active sites of the load (e.g., clay minerals as montmorillonite or bentonite) and nutrients (e.g., ammonium, phosphate, and potassium, among others).[12−14] It opens the possibility of versatile coating systems, where the chemical interaction plays a more significant role than the physical barrier, as typically seen in many products.

Clay minerals, such as montmorillonite and bentonite, are typically organized in lamellar structures, in which micrometer-sized platelets are stacked at nanometric distances (∼1 nm).[5,12] When dispersed within a polymeric matrix, these lamellae can be exfoliated or intercalated, leading to a nanoscale distribution that significantly alters the transport properties of the coating. This structural arrangement justifies classifying these systems as nanocomposites. In parallel, polyurethane (PU) has been widely studied as a coating material for fertilizers due to its excellent adhesion to urea surfaces, mechanical resistance, and controlled degradation profile.[10,11,15] The use of castor oil-based PU further adds the advantage of employing a renewable and biodegradable polyol source, which aligns with the current demand for more sustainable agricultural inputs.

Despite advances in polymeric coatings, most studies emphasize the physical barrier effect provided by the polymer layer, while the potential chemical interactions between nanostructured fillers (e.g., clays) and nutrient ions remain less explored. Thus, the knowledge gap addressed in this work lies in investigating how nanoclay dispersion within a biodegradable PU matrix not only modifies the water permeation pathway but also promotes ionic interactions that can modulate the kinetics of nutrient release.

Therefore, here we propose a nanocomposite-based coating system over urea granules, testing it in a soil-plant system (greenhouse). The coating system was based on nanocomposites produced from castor oil polyurethane with montmorillonite finely dispersed in the polymer matrix, evaluating its effectiveness in terms of dry mass and efficiency.
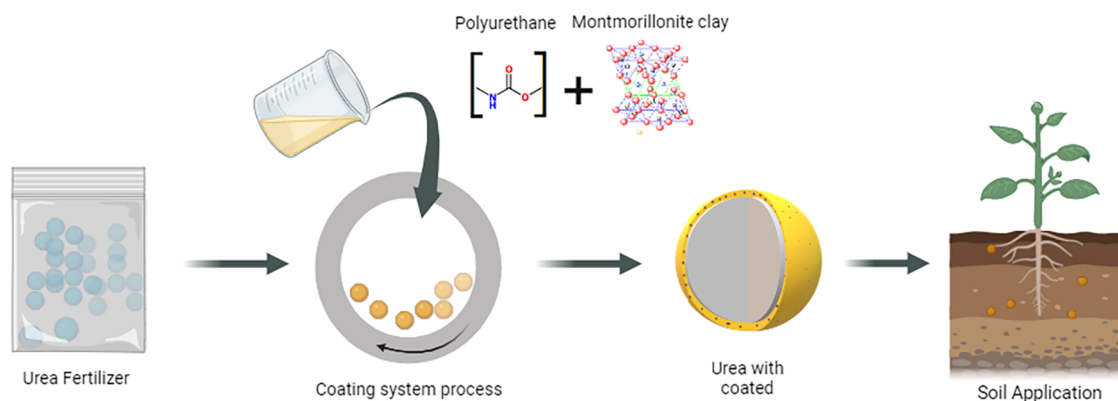
Figure 1. Schematic of the coating process for urea granules.

The permeability to water vapor was proposed to infer the diffusion of water into the granule, and the subsequent dissolution of micronutrients is critical. A greenhouse experiment was conducted using Palisade grass (*Brachiaria brizantha*), demonstrating that the total nutrient uptake is enhanced by the longer N release, which is also beneficial for reducing N-compound emissions to the atmosphere.

MATERIALS AND METHODS

Materials. Castor oil was generously provided by A. Azevedo Oils (Brazil). 4,4′-diphenylmethane diisocyanate and montmorillonite were purchased from Univar (Brazil) and Sigma-Aldrich. Urea was purchased by Yara Brazil S.A. 4-(dimethylamino)benzaldehyde, hydrochloric acid, and trichloroacetic acid were purchased from Sigma-Aldrich for urea quantification. Decarbonated deionized water (with a resistivity of 18.2 MΩ cm) was used from a Milli-Q system (Barnstead Nanopure Diamond, Thermo Fisher Scientific Inc.) for all quantification analyses.

Preparation of Coated Fertilizer Granules. Commercial urea granules were coated with a castor oil-based polyurethane (PU) prepared from 4,4′-diphenylmethane diisocyanate and castor oil at a 60:40 weight ratio, respectively. This composition was selected due to the high reactivity of 4,4′-diphenylmethane diisocyanate with hydroxyl groups from castor oil, ensuring the formation of a cross-linked polymeric network with adequate mechanical resistance and adhesion to the fertilizer surface. The coating process was carried out using a metallic turntable coater that rotated at 30 rpm, with airflow heating at 50 ± 2 °C, and equipped with 25 cm side shields to minimize material loss during application and promote homogeneous distribution of the polymer over the granules.

The polymer coating layer was standardized at 4% by weight (wt %), corresponding to the application of 40 g of polymer per kilogram of fertilizer. This percentage was previously established as an optimal balance between coating efficiency and process cost, ensuring adequate coverage of the granules without excessive polymer consumption. In addition to the neat polyurethane coating, montmorillonite (Mt) nanoclay was incorporated into the polymer matrix in amounts ranging from 2 to 10 wt % (based on urea weight). The presence of nanoclay in the coating was expected to modify the barrier properties of the film, enhancing resistance to water permeation through a tortuosity effect and potential ionic interactions between the clay layers and urea molecules. The dispersion of montmorillonite into the castor oil phase was performed under mechanical agitation, allowing the clay layers to be exfoliated or partially intercalated before the reaction with 4,4′-diphenylmethane diisocyanate. This step is crucial for achieving a uniform distribution of the nanoclay within the polymer matrix and preventing agglomerates that could act as defects in the coating layer. The castor oil-based polyurethane coating was sprayed using an airbrush-type disperser, as shown in the Supporting Information (Video S1), which allowed for fine control of droplet size and deposition rate,

resulting in more uniform films compared to manual or bulk coating techniques.

Figure 1 schematically illustrates the preparation of coated urea granules, including the dispersion of nanoclay in castor oil, the synthesis of polyurethane, and the subsequent application of the coating. After the coating process was completed, the prepared fertilizers were stored in sealed plastic bags under controlled laboratory conditions, avoiding contact with air and air moisture before the experiment began.

Characterization. The total nitrogen content in the samples and treatments was determined through elemental analysis using a CHNS/O 2400 Series II Elemental Analyzer (PerkinElmer). Values were measured using quadruplicates and masses up to 10 mg to perform the analysis. The residual charge for montmorillonite was determined at different pH levels using the Zetasizer Advance equipment (Malvern Panalytical, United Kingdom).

The interface between the urea and the coating was examined using scanning electron microscopy (SEM) analysis. SEM analyses were performed using a JEOL JSM 6510 instrument equipped with an energy-dispersive X-ray analysis system. The beads were placed on a carbon tape fixed to a metal support (stub) surface and coated with gold in an ionization chamber (Baltec Med. 020). The SEM images obtained from the analysis were taken at an accelerating voltage of 10 kV using a secondary electron detector on the JSM 6510 instrument (JEOL).

The permeation of water vapor was tested in a lab-built device. Polyurethane membranes (flat membranes) with a thickness of 0.30−0.50 mm and a useful diameter of 2.5 cm were placed between two chambers with identical temperature (25 ± 1 °C) and relative humidity (RH). The wet chamber received a pulse of distilled water, rapidly increasing the RH to ∼90−95%, while the dry chamber initially had a RH of ∼30−35%. The temporal variation of RH in both chambers was recorded by calibrated capacitive-hygrometric sensors (1s sampling interval), indicating that water vapor permeates through the membrane. The time-lag and slope of the RH trace in the dry chamber were used qualitatively to compare the relative transmission between formulations. For surface inspection, distilled water was applied to the membranes, and the droplet behavior was recorded by optical microscopy.

Water-Release Assay in Water. The immersion release assay was performed using water as the medium, and allowed us to evaluate the urea release rate over time and the performance of the coating system. The water release experiment was conducted at a controlled temperature (25 °C). The methodology involved immersing 0.5 g of the fertilizer (coated or uncoated) in a beaker containing 250 mL of distilled water, with gentle agitation to ensure homogenization and uniformity of the urea released into the medium. Uncoated urea served as a control.

Aliquots of 0.5 mL were collected periodically every 24 h for 14 days. These samples were analyzed to determine the concentration of urea released. Urea quantification was performed using a Shimadzu UV-1601 PC spectrophotometer, following an adaptation of the

Table 1. Code, Material, and Total N Contents of the Different Treatments

code	material	total N (%)
SC	soil control	
Ur	urea (uncoated)	45.3 ± 0.2
PUrMt0	urea + castor oil-based polyurethane (4 wt %)	44.5 ± 0.2
PUrMt2	urea + castor oil-based polyurethane (4 wt %) + montmorillonite (2 wt %)	44.7 ± 0.3
PUrMt3.5	urea + castor oil-based polyurethane (4 wt %) + montmorillonite (3.5 wt %)	44.3 ± 0.2
PUrMt5	urea + castor oil-based polyurethane (4 wt %) + montmorillonite (5 wt %)	44.4 ± 0.3
PUrMt10	urea + castor oil-based polyurethane (4 wt %) + montmorillonite (10 wt %)	44.4 ± 0.2
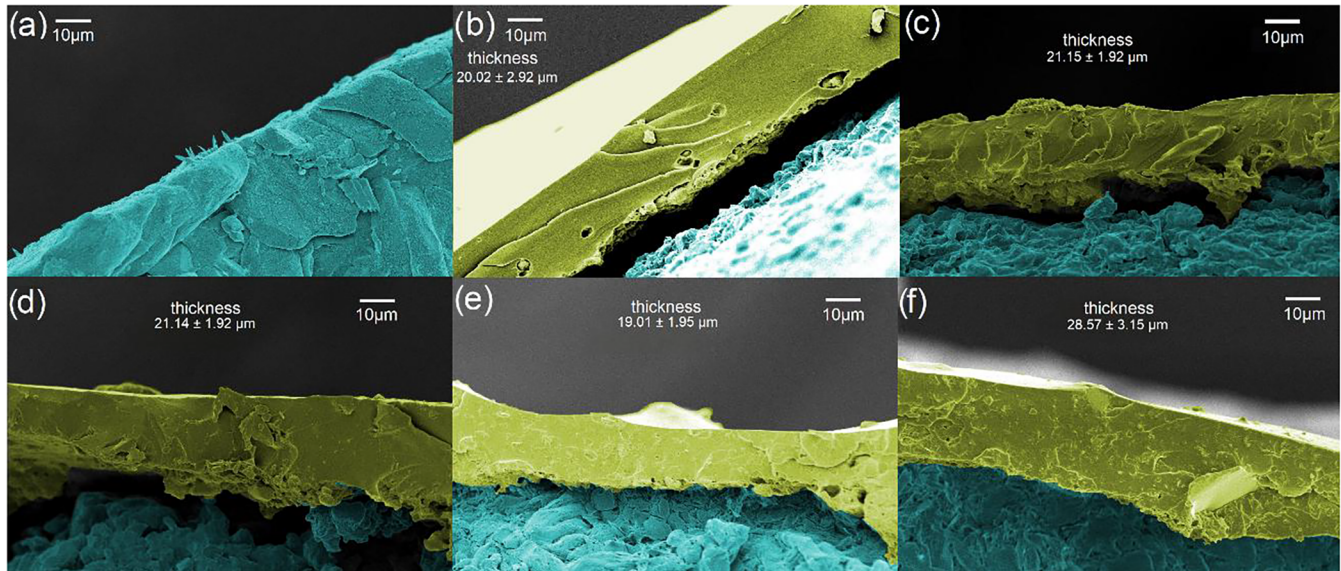
Figure 2. Scanning electron microscopy (SEM) images of (a) uncoated urea and the interface between urea and a castor oil-based polyurethane containing montmorillonite at (b) 0%, (c) 2%, (d) 3.5%, (e) 5%, and (f) 10 wt %, respectively. The urea fertilizer and coating layer are highlighted in green and yellow, respectively. The images were colored using Adobe Photoshop CS5 software.

methods proposed by With et al. and Bortoletto-Santos et al.[15,16] Each aliquot (0.5 mL) was mixed with 2.5 mL of a 10% trichloroacetic acid solution (Sigma-Aldrich) and 0.5 mL of Ehrlich's reagent (0.34 mol L^{-1} 4-(dimethylamino)benzaldehyde in 2.4 mol L^{-1} hydrochloric acid), and absorbance was recorded in the range of 400−500 nm. All experiments were conducted simultaneously to ensure identical laboratory conditions.

Greenhouse Experiment. The greenhouse experiment was conducted with Piatã palisadegrass (Urochloa (syn. Brachiaria) brizantha (Hochst ex A. Rich.) Stapf cv. BRS Piatã), measuring nitrogen (N) uptake and dry mass production, at Embrapa Instrumentation in São Carlos, São Paulo State, Brazil. The soil used was a Haplorthox from an agricultural area in São Carlos, São Paulo State, Brazil (21° 95 12″ S, 47° 85 15″ W; 873 m above sea level), collected from the surface layer (0.30−0.40 m). The soil was sieved (particle size <2 mm), and it presented the following characteristics: 654 g kg^{-1} sand, 53 g kg^{-1} silt, and 293 g kg^{-1} clay; pH (H$_2$O) 5.0; organic matter and total C content of 14 and 8 g kg^{-1}, respectively; cation exchange capacity (CEC) of 44 mmolc kg^{-1}; potassium available of 0.5 mmolc kg^{-1}, and phosphorus content of 1.0 mg kg^{-1}.

The pots were arranged in a randomized block design with five replicates for each treatment, totaling 35 pots filled with 1 kg of soil. The soil was limed with 1.31 g kg^{-1} of limestone and then moistened to the water-holding capacity (WHC) for 30 days. After 30 days, palisade grass (B. brizantha) was sown, and soil moisture was maintained up to the water-holding capacity. Moreover, both potassium (K) and phosphorus (P) were supplied at the time of sowing at 0.035 g-K per kg^{-1} and 0.49 g-P per kg^{-1} of commercial KCl (60% K$_2$O) and triple superphosphate (45% P$_2$O$_5$).

The N-fertilization was made 15 days after seed germination, with two plants grown in each pot. Moreover, 0.05 g-N per kg^{-1} of soil was placed centrally and superficially in each pot. The code, treatments, and total nitrogen for each treatment are shown in Table 1. The first aboveground biomass cut was taken 45 days after fertilization, and the other three cuts were made at 30-day intervals. All the Palisade grass biomass was removed at the fourth cut, which was the last cut. The plant material collected in each section was dried in a stove with forced air circulation at 65 °C for 72 h, then weighed and ground using a benchtop stainless steel knife mill (Wiley mill type) to achieve a particle size of less than 1 mm.

The plants' production was determined by N uptake, dry mass, and applied fertilizer, with comparisons made between treatments regarding the N released. The mean nitrogen concentration (C, mg g^{-1}) of the aerial part of plants was calculated from the nitrogenous uptake (N_{uptake}, mg) and the dry mass production (DM, g), as shown in eq 1. Similarly, the nitrogen use efficiency (NUE, $g_{drymass}$ per $g_{N_{applied}}$) was obtained from eq 2, in which DM is the dry mass production and N applied is the applied nitrogenous amount.[17]

$$C = \Sigma N_{uptake} \times (\Sigma DM)^{-1} \tag{1}$$

$$EU = DM \times N_{applied}^{-1} \tag{2}$$

The plant recovery efficiency (RE, mg$_{increaseN-uptake}$ per mg$_{N-applied}$) was calculated using eq 3. Moreover, the physiological efficiency (PE, $g_{increaseindrymass}$ per $g_{increaseN-absorption}$) was obtained from eq 4.[18,19] U_N and U_0 are the total nitrogenous uptakes by the plants' biomass that received and did not receive fertilizer, respectively.

$$RE = (U_N - U_0) \times N_{applied}^{-1} \tag{3}$$
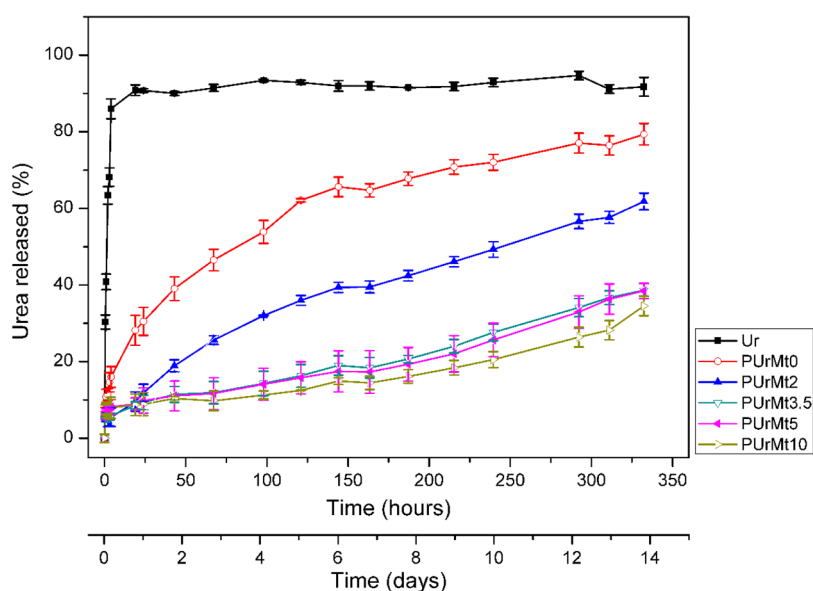
Figure 3. Treatment's release curves in the water immersion assay. The vertical bars correspond to the standard deviation.

$$PE = (DM - DM_0) \times (U_N - U_0)^{-1} \tag{4}$$

Dry mass production and nitrogen absorption rates were calculated from linear regression. The obtained adjustments presented R^2 values above 88 and 95%, respectively. The comparison of treatments in relation to rates, efficiencies, and dry mass in each cut was evaluated by analysis of variance and Duncan's multiple comparisons test, since the data presented variance homogeneity, verified by Bartlett's test. The significance level for the tests was set at 0.05, and the software used for the analysis was R.[20]

■ RESULTS AND DISCUSSION

Figure 2 shows cross-sectional SEM images of urea granules coated with castor oil-based polyurethane containing different proportions of montmorillonite. Figure 2a shows the uncoated urea granule surface, which is rough and irregular. Figure 2b−f present SEM images of the coated urea granules, showing the formation of a homogeneous and evenly distributed layer on the granule surface. The coating layers had similar thicknesses, with values ranging from 19.0 to 24.6 μm. The similar thicknesses are mainly due to the polymer amount being fixed in all treatments (4 wt %), with only the proportion of nano clay dispersed in the polymer matrix varying.

Figure 3 shows the release curves of each treatment in the water immersion assay. The release curve showed that uncoated urea achieved release above 85% in 4 h, and this behavior for urea reflects its high solubility. On the other hand, the granules coated only with polyurethane (PUrMt0) exhibited a slow-release profile, resulting from urea diffusion through the physical barrier formed by the polymer. Montmorillonite (Mt) in the applied coating delayed the release even more effectively. This reduction in the release rate was directly proportional to the increase in the Mt content dispersed in the polymeric matrix.

These results suggest two functions for nano clay in the polymeric matrix: (i) Mt acts as a physical barrier, which prevents direct exposure of the fertilizer to water, as well as reducing the solubilization rate, and (ii) it also interacts with the fertilizer, allowing the urea to remain in the coating for more extended periods. This effect on urea release occurs when using relatively low amounts of nano clay, allowing a

reduction in urea release from 70 to 22% in 215 h for PUrMt0 and PUrMt5, respectively. Moreover, this phenomenon highlights the interaction between the fertilizer and the nano clay, since montmorillonite is a lamellar material with a cationic character (negative residual charge), as shown in Supporting Figure S1 from the ζ-potential measurements. The ζ-potential data indicated that montmorillonite presents a residual negative charge in its structure within the pH range of 1 to 7. This behavior suggests a strong correlation between the interaction potential of the clay interstices and the ammonium ion (NH_4^+) released during the hydrolysis of urea. This interaction can significantly influence the adsorption and mobility of ammonium in the soil, resulting in the retention of the nutrient.

Figure 4 shows the performance of coatings shaped as flat membranes with a thickness of 0.3−0.5 mm in terms of water vapor permeation. The steep increase in relative humidity in the moist chamber in time ∼3500 s did not affect the humidity in the dry chamber even after 12000 s (3.33 h). All samples presented similar behavior, indicating that the treatment of the coatings with montmorillonite did not improve their ability to transmit water vapor. When compared with urea release in water (Figure 3), this result suggests that the higher retention in Mmt-loaded coatings is attributed to the chemical barrier effect (e.g., surface interaction with charged layers) rather than an increase in physical barrier. This result supports the visual observations of each membrane when exposed to water droplets, as shown in Figure 5. The hydrophobic nature is confirmed for all formulations, with no spread or absorption of the droplet. It is worth noting, however, the presence of enclosed air bubbles in some membranes.

It is worth noting that despite the occasional presence of encapsulated bubbles in some flat membranes (Figure 5), the RH traces indicated no detectable increase in vapor transmission for all compositions, including montmorillonite, up to 12,000 s after the RH step (≈3.33 h). In contrast, urea release during immersion was strongly reduced with increasing montmorillonite content. These results indicate that montmorillonite acts primarily as a chemical barrier through ionic/adsorptive interactions with NH_4^+, rather than by increasing
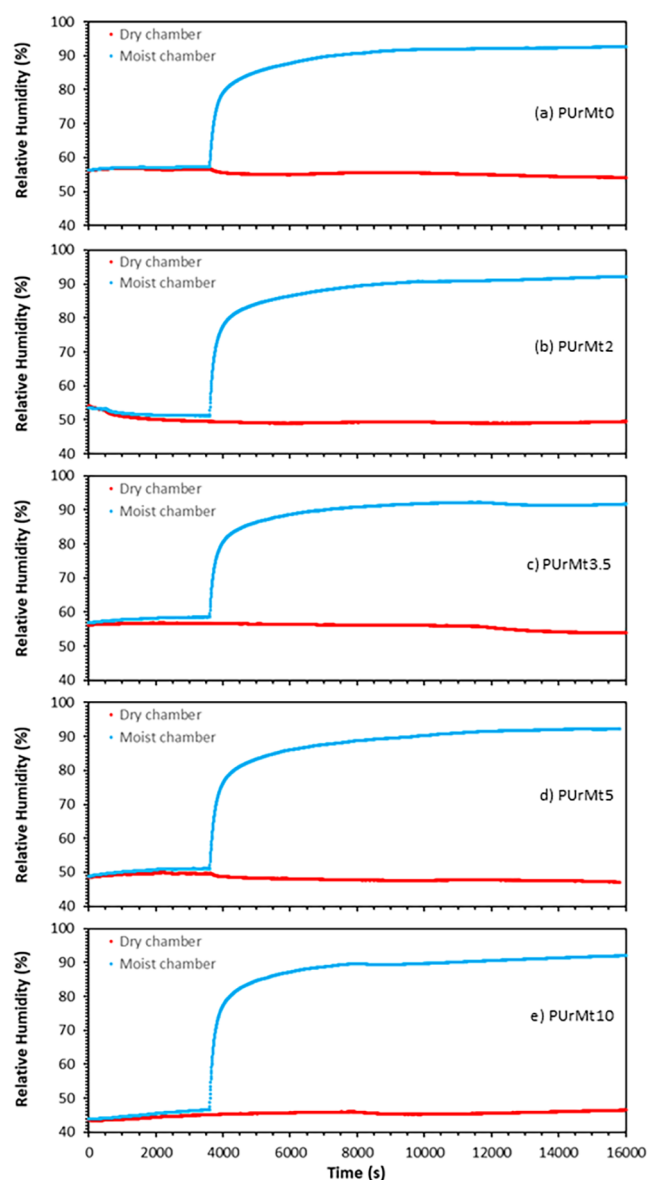
**Figure 4.** Time-dependent profiles of membranes exposed to relative humidity gradients.

the physical barrier (tortuosity). It is also worth noting that montmorillonite presents a residual negative charge in the pH range of 1−7 (Figure S1), which favors the retention of cationic species (e.g., NH_4^+) released during urea hydrolysis,

thereby slowing down the effective diffusion of the nutrient, as well as the coatings on granules present continuous and homogeneous layers (without pores) of 19.0−24.6 μm, as shown in Figure 2.

Figure 6a,b show the dry mass production for each cut and the dry mass production rate, respectively. The results showed that the Soil control (SC) treatment presented the lowest dry mass values in all cuts (Figure 6a), showing the lowest dry mass production rate for the greenhouse experiment (Figure 6b). On the other hand, the dry mass values for the PUrMt5 and PUrMt10 treatments indicated higher dry mass production rates throughout the experiment, which were statistically different from those of the other treatments. The PUrMt2 and PUrMt3.5 treatments exhibited intermediate dry mass production. The dry mass production rates of the montmorillonite treatments presented higher values than those of granules coated only with castor oil-polyurethane (PUrMt0). This result indicates that the presence of nano clay dispersed in the polymeric matrix alters the fertilizer availability, contributing to a better synergy between nutrient release and plant absorption needs. Moreover, the higher dry mass contents in each cut (Figure 6a) and the production rate (Figure 6b), as well as the better use of urea release, suggest that the combination of a physical barrier and Mt interaction in the coating minimizes losses associated with urea, such as ammonia volatilization and nitrous oxide emission, as reported by Bortoletto-Santos et al.[5]

Figure 7a,b show the N uptake for each cut and the N uptake rate, respectively. As observed for dry mass production, the SC treatment showed lower levels of N uptake in all four cuts, revealing a lower uptake rate. Moreover, it is notable that all fertilizers coated with the nanocomposite (PUrMt2, PUrMt3.5, PUrMt5, and PUrMt10) exhibited statistically significant N uptake compared to urea without nano clay (PUrMt0) and the uncoated control (Ur).

This behavior is seen in the N uptake rate throughout the experiment (Figure 7b). It is worth mentioning that PUrMt5 and PUrMt10 presented the highest rate of N uptake among the nanocomposites, e.g., twice the N uptake compared to Ur, suggesting that the better fertilizer availability was more effectively utilized by the plant and resulted in a consequent reduction in losses, as reported by Bortoletto-Santos et al.[5] The low accumulation of dry matter in the first cut is associated with the lack of nitrogen (N) availability, as N is essential for plant development and growth.[21] Moreover, there was an increase in the performance of the treatment with the highest nanoclay content when analyzing the second, third, and fourth
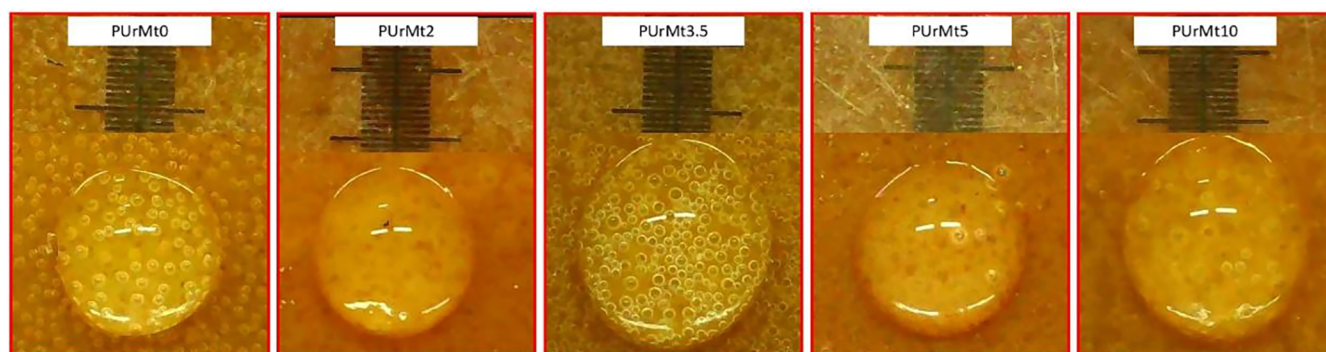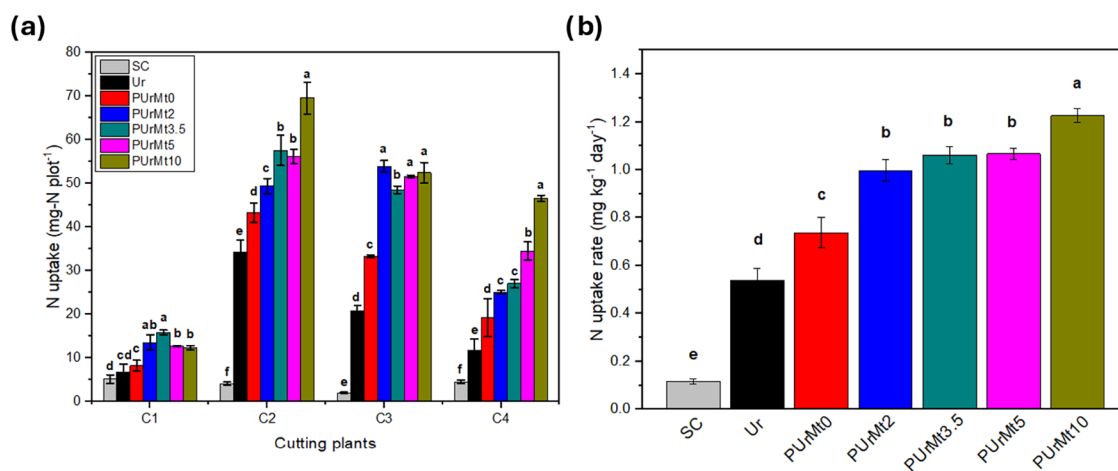

Figure 5. Optical observation of water droplets on the surface of the coating membranes.
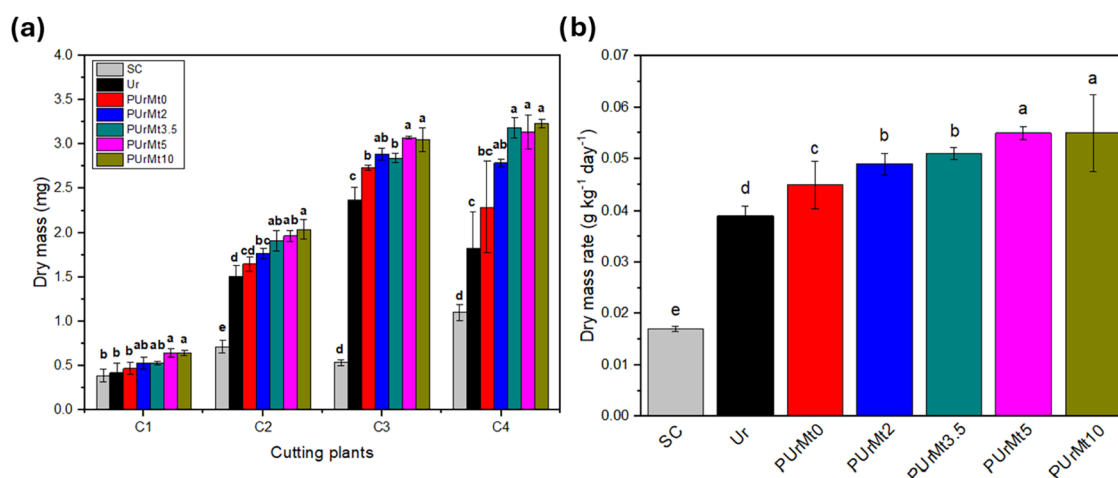
Figure 6. (a) Dry mass production from each cut and (b) dry mass production rate foreach treatment. The values of the bars with the same letter do not differ significantly (Tukey's test; $P < 0.05$).


Figure 7. (a) N uptake from each cut and (b) N uptake rate for each treatment. The values of the bars with the same letter do not differ significantly (Tukey's test; $P < 0.05$).

cuts. This effect suggests that the controlled release of the cationic nutrient, ammonium, interacts with the coating, synchronizing nitrogen availability with the plant's needs and thereby increasing dry matter accumulation.

Concomitant with the dry mass data presented, the variation in N uptake during the experiment showed a significant correlation with the inclusion of montmorillonite in the coating composition. Statistically, higher N values were observed for the PUrMt10, followed by PUrMt5, PUrMt3.5, and PUrMt2, which were statistically equal.

Fertilizing with controlled-release fertilizers had a significant impact on agronomic efficiency (Figure 8) in all four cuts. In the first cut, only the PUrMt5 and PUrMt10 treatments showed greater efficiency ($p < 0.05$). We can see that the montmorillonite coating directly affects the release of N. It is important to note that in the second, third, and fourth cuts, there was an increase in efficiency in the presence of montmorillonite, especially above the percentage of 3.5. Since montmorillonite has the potential to reduce pH, it accelerates the release of nitrogen into the soil.[22] Thus, the results of this article corroborate the work of Liao et al., Yang et al., and Zhao et al.,[23−25] which found that coating with montmorillonite increases the efficiency of nitrogen release. It should be noted that maximum release occurred between the
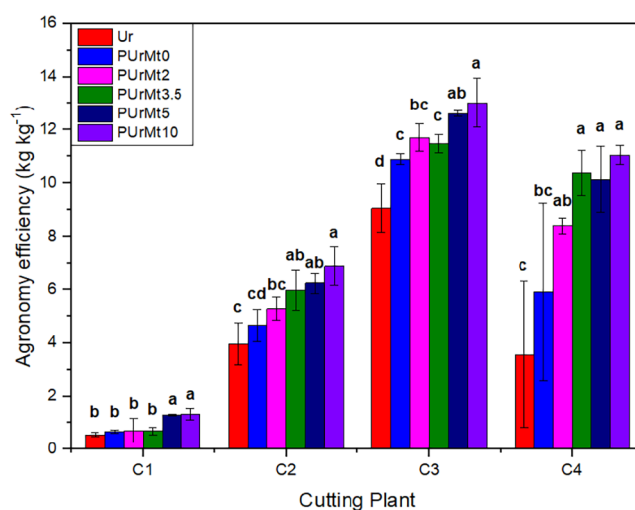
Figure 8. Agronomic N use efficiency from the four aboveground biomass cuts of Palisade planting. Treatments: Ur; PUrMt0; PUrMt2; PUrMt3.5; PUrMt5; PUrMt10.

third and fourth cut, thus leading to greater efficiency in the third cut.

The coating applied to the fertilizers affected the recovery efficiency of the nitrogen applied to the soil (Figure 9). There
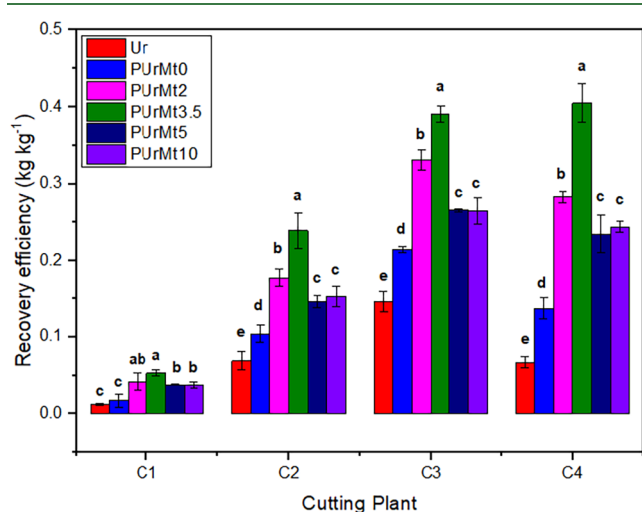
Figure 9. Recovery N use efficiency from the four aboveground biomass cuts of Palisade planting. Treatments: Ur; PUrMt0; PUrMt2; PUrMt3.5; PUrMt5; PUrMt10.

was an increase in the efficiency of nitrogen recovery in the use of fertilizer during the experiment because fertilizers coated with a polyurethane nanocomposite, associated with nanoclay, had controlled availability, reducing losses due to volatilization and thus becoming more efficient. The nanoclay treatments showed higher recovery efficiency values than the granules coated only with castor oil-polyurethane (PUrMt0).

As with the accumulation of dry mass, the efficiency results (RUE) suggest that the nanoclay + polyurethane system allowed better control and availability of the nitrogen fertilizer, contributing to improved synergy between the nitrogen absorbed and its release into the soil. The urea coated with the nanoclay at a percentage of 3.5 showed greater efficiency ($p < 0.05$), which is probably due to the nanoclay having the potential to reduce pH, which accelerates the release of ammonium, and, in this case, at a percentage of 3.5, it reached the threshold of maximum efficiency.

The recovery N use efficiency is associated with the type of coating applied to the fertilizer granule, since urea has a high volatilization and/or leaching rate in the soil, the efficiency is increased with a nanoclay + polyurethane coating. This behavior is observed in studies on the development of controlled-release fertilizers, where similar results are reported, as seen in Zhang et al.,[26] who found that several experiments with coated urea resulted in increased efficiency. Studies show that clay and polyurethane coatings reduce volatilization and leaching losses, thereby increasing N recovery efficiency.[27]

Our results confirm that the structural modification of polymeric coatings plays a crucial role in the slow release of coated fertilizers. The increase in nanoclay (montmorillonite) loading has been observed to be effective in increasing the release period, as well as to confer better agronomic efficiencies. The analysis of sequential cuts in *B. brizantha* indicates that the effect is perceived even in the first stages of production, but the total effect (sum of production after 135 days) is much more evident. It highlights the advantages of the coating strategy and the importance of microstructure design (e.g., nanocomposite structure) in enhancing performance.

■ AUTHOR INFORMATION

Corresponding Author

Ricardo Bortoletto-Santos − *Postgraduate Program in Environmental Technology, University of Ribeirão Preto (UNAERP), Ribeirão Preto, SP 14096-900, Brazil;* ⊙ orcid.org/0000-0002-4447-8239; Phone: +55 16 3603-6774; Email: ricbortolettosantos@hotmail.com, rbortoletto@unaerp.br

Authors

Vinícius Ferraz Majaron − *São Carlos Institute of Chemistry (IQSC), University of São Paulo (USP), São Carlos, SP 13566-590, Brazil; Nanotechnology National Laboratory for Agriculture (LNNA), Embrapa Instrumentation, São Carlos, SP 13561-206, Brazil*

Cassio Luiz Vellani − *Postgraduate Program in Environmental Technology, University of Ribeirão Preto (UNAERP), Ribeirão Preto, SP 14096-900, Brazil*

Alexandre Antonio Fidelis Martins Junior − *Nanotechnology National Laboratory for Agriculture (LNNA), Embrapa Instrumentation, São Carlos, SP 13561-206, Brazil*

Sendy Marques Soares − *Postgraduate Program in Environmental Technology, University of Ribeirão Preto (UNAERP), Ribeirão Preto, SP 14096-900, Brazil*

Fernando Ferrari Putti − *São Paulo State University (UNESP), School of Sciences and Engineering, Tupã, SP 17.602-496, Brazil*

Murilo Daniel de Mello Innocentini − *Postgraduate Program in Environmental Technology, University of Ribeirão Preto (UNAERP), Ribeirão Preto, SP 14096-900, Brazil*

Alberto Carlos Campos Bernardi − *Embrapa Southeast Livestock, Rodovia Washington Luiz, São Carlos, SP 13560-970, Brazil*

Wagner Luiz Polito − *São Carlos Institute of Chemistry (IQSC), University of São Paulo (USP), São Carlos, SP 13566-590, Brazil*

Caue Ribeiro − *Nanotechnology National Laboratory for Agriculture (LNNA), Embrapa Instrumentation, São Carlos, SP 13561-206, Brazil;* ⊙ orcid.org/0000-0002-8908-6343

Complete contact information is available at: https://pubs.acs.org/10.1021/acsagscitech.5c00509

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Guiné, R. P. F. The challenges and strategies of food security under global change. *Foods* **2024**, *13*, No. 2083.

(2) do Valle, S. F.; Giroto, A. S.; Gestal Reis, H. P.; Guimarães, G. G. F.; Ribeiro, C. Synergy of Phosphate-Controlled Release and Sulfur Oxidation in Novel Polysulfide Composites for Sustainable Fertilization. *J. Agric. Food Chem.* **2021**, *69* (8), 2392−2402.

(3) Motasim, A. M.; Samsuri, A. W.; Nabayi, A.; Akter, A.; Haque, M. A.; Abdul Sukor, A. S.; Adibah, A. M. Urea application in soil: Processes, losses, and alternatives—A review. *Discovery Agric.* **2024**, *2*, No. 42.

(4) Majaron, V. F.; da Silva, M. G.; Bortoletto-Santos, R.; Klaic, R.; Giroto, A.; Guimarães, G. G. F.; Polito, W. L.; Farinas, C. S.; Ribeiro, C. Synergy between castor oil polyurethane/starch polymer coating and local acidification by *Aspergillus niger* for increasing the efficiency of nitrogen fertilization using urea granules. *Ind. Crops Prod.* **2020**, *154*, No. 112717.

(5) Bortoletto-Santos, R.; Plotegher, F.; Majaron, V. F.; da Silva, M. G.; Polito, W. L.; Ribeiro, C. Polyurethane nanocomposites can increase the release control in granulated fertilizers by controlling nutrient diffusion. *Appl. Clay Sci.* **2020**, *199*, No. 105874.

(6) Swify, S.; Mažeika, R.; Baltrusaitis, J.; Drapanauskaitė, D.; Barčauskaitė, K. Review: Modified urea fertilizers and their effects on improving nitrogen use efficiency (NUE). *Sustainability* **2024**, *16*, No. 188.

(7) Zhang, Y.; Wang, W.; Yao, H. Urea-based nitrogen fertilization in agriculture: A key source of N_2O emissions and potential mitigation strategies. *J. Plant Nutr.* **2022**, *69*, 663−678.

(8) Castejón-del Pino, R.; Sánchez-Monedero, M. A.; Sánchez-García, M.; Cayuela, M. L. Fertilization strategies to reduce yield-scaled N_2O emissions based on the use of biochar and biochar-based fertilizers. *Nutr. Cycl. Agroecosyst.* **2024**, *129*, 491−501.

(9) Majaron, V. F.; da Silva, M. G.; Pfeifer, M.; Bortoletto-Santos, R.; Velloso, C. C. V.; Klaic, R.; Polito, W. L.; Ribeiro, S. J. L.; Bernardi, A. C. C.; Farinas, C. S.; Ribeiro, C. Interaction of *Aspergillus niger* in Double-Coated Urea Granules Reduces Greenhouse Gas Emissions from N Fertilization. *J. Soil Sci. Plant Nutr.* **2023**, *23*, 3751−3760.

(10) da Cruz, D. F.; Bortoletto-Santos, R.; Guimarães, G. G. F.; Polito, W. L.; Ribeiro, C. Role of Polymeric Coating on the Phosphate Availability as a Fertilizer: Insight from Phosphate Release by Castor Polyurethane Coatings. *J. Agric. Food Chem.* **2017**, *65* (29), 5890−5895.

(11) Costa, C. L.; Bortoletto-Santos, R.; Costa, M. I. C.; Silva, G. C.; da Silva, E. A.; Polito, W. L.; Ribeiro, C.; Bernardi, A. C. C.; Farinas, C. S.; Ribeiro, C. Polymeric-Coated Monoammonium Phosphate with Different Release Profiles for Improving Phosphorus-Use Efficiency in Forage Production. *ACS Agric. Sci. Technol.* **2024**, *4* (1), 72−81.

(12) Pereira, E. I.; Minussi, F. B.; Cruz, C. C. T.; Bernardi, A. C. C.; Ribeiro, C. Urea−Montmorillonite-Extruded Nanocomposites: A novel slow-release material. *J. Agric. Food Chem.* **2012**, *60*, 5267−5272.

(13) Sarkar, S.; Datta, S. C.; Biswas, D. R. Effect of fertilizer loaded nanoclay/superabsorbent polymer composites on nitrogen and phosphorus release in soil. *Proc. Natl. Acad. Sci., India, Sect. B* **2015**, *85*, 415−421.

(14) Beig, B.; Niazi, M. B. K.; Jahan, Z.; Hussain, A.; Zia, M. A.; Mehran, M. T. Coating materials for slow release of nitrogen from urea fertilizer: A review. *J. Plant Nutr.* **2020**, *43*, 1510−1529.

(15) Bortoletto-Santos, R.; Ribeiro, C.; Polito, W. L. Controlled release of nitrogen-source fertilizers by natural-oil-based poly-(urethane) coatings: the kinetic aspects of urea release. *J. Appl. Polym. Sci.* **2016**, *133* (33), No. 43790.

(16) With, T. K.; Petersen, B.; Petersen, T. D. A simple spectrophotometric method for the determination of urea in blood and urine. *J. Clin. Pathol.* **1961**, *14*, 202−204.

(17) Siddiqi, M. Y.; Glass, A. D. M. Utilization index: A modified approach to the estimation and comparison of nutrient utilization efficiency in plants. *J. Plant Nutr.* **1981**, *4*, 289−302.

(18) Dobermann, A.Nutrient Use Efficiency: Measurement and Management. In *Fertilizer Best Management Practices: General Principles, Strategy for Their Adoption and Voluntary Initiatives Versus Regulations*; International Fertilizer Industry Association: Paris, France, 2007; pp 1−28.

(19) Sarkar, D.; Baishya, L. K. Nutrient Use Efficiency. In *Essential Plant Nutrients: Uptake, Use Efficiency and Management*; Rakshit, A.; Singh, H. B.; Sen, A., Eds.; Springer: Cham, 2017; pp 119−146 DOI: 10.1007/978-3-319-58841-4_6.

(20) R Core Team. R. *A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2021 https://www.R-project.org/.

(21) Modesto, V. C.; Andreotti, M.; Nakao, A. H.; Soares, D. D. A.; Froio, L. D. L.; Dickmann, L.; Pascoaloto, I. M.; Fernandes, I. M. D. M. Yield and production components of corn under straw of Marandu Palisade grass inoculated with Azospirillum brasilense in the Low-Land Cerrado. *Front. Sustainable Food Syst.* **2021**, *4*, No. 617065.

(22) Xiang, J.; Zhu, R.; Chen, Q.; Lv, G.; Yang, Y. A novel montmorillonite-based soil amendment for Cd/REEs immobilization and nutrients sustained release. *Appl. Clay Sci.* **2022**, *221*, No. 106464.

(23) Liao, Y.; Liu, L.; Wang, M.; Li, L. X.; Cao, B.; Wang, H.; Huang, W. Q. Preparation and properties of starch-based polyurethane/montmorillonite composite coatings for controlled-release fertilizer. *Polym. Compos.* **2021**, *42*, 2293−2304.

(24) Yang, G.; Zhao, H.; Liu, Y.; Li, Z.; Gao, F.; Zhang, Q.; Zhang, M.; et al. Slow release fertilizers based on polyphosphate/montmorillonite nanocomposites for improving crop yield. *Arab. J. Chem.* **2023**, *16*, No. 104871.

(25) Zhao, Q.; Long, C.; Jiang, Z.; Yin, W.; Tang, A.; Yang, H. Highly stable natural zeolite/montmorillonite hybrid microspheres with green preparation process for efficient adsorption of ammonia nitrogen in wastewater. *Appl. Clay Sci.* **2023**, *243*, No. 106787.

(26) Zhang, G.; Zhao, D.; Liu, S.; Liao, Y.; Han, J. Can controlled-release urea replace the split application of normal urea in China? A meta-analysis based on crop grain yield and nitrogen use efficiency. *Field Crops Res.* **2022**, *275*, No. 108343.

(27) Zhong, X.; Zhou, X.; Fei, J.; Huang, Y.; Wang, G.; Kang, X.; Peng, J.; et al. Reducing ammonia volatilization and increasing nitrogen use efficiency in machine-transplanted rice with side-deep fertilization in a double-cropping rice system in Southern China. *Agric. Ecosyst. Environ.* **2021**, *306*, No. 107183.