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ROLE OF NANOCOMPOSITE STRUCTURE IN POLYURETHANE COATINGS FOR SLOW-RELEASE FERTILIZERS: A CASE STUDY WITH *BRACHIARIA BRIZANTHA*

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Abstract: Despite the indispensable use of agricultural fertilizers to achieve current levels of productivity, chemical nutrients have their effectiveness limited by problems, such as NH_3 volatilization and soil immobilization. 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 hours for treatments PUrMt3.5 and PUrMt5, compared to PUrMt0. Greenhouse experiments using *Brachiaria brizantha* demonstrated that the coated fertilizers promoted improved nitrogen uptake and biomass production compared to uncoated urea. Moreover, 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.

FUNÇÃO DA ESTRUTURA NANOCOMPÓSITA EM REVESTIMENTOS DE POLIURETANA PARA FERTILIZANTES DE LIBERAÇÃO LENTA: UM ESTUDO DE CASO COM BRACHIARIA BRIZANTHA

Resumo: Apesar do uso indispensável de fertilizantes agrícolas para atingir os níveis atuais de produtividade, os nutrientes químicos têm sua eficácia limitada por problemas como a volatilização de NH_3 e a imobilização do solo. Dessa forma, foi desenvolvido um sistema de revestimento nanocompósito à base de poliuretana (PU) derivada de óleo de mamona e montmorilonita para liberação controlada de ureia. A incorporação de pequenas quantidades de nanoargila retardou efetivamente a difusão de nitrogênio por meio de um mecanismo de troca iônica, resultando em uma redução de 70% para 20% em 215 horas para os tratamentos PUrMt3.5 e PUrMt5, em comparação com PUrMt0. Experimentos em casa de vegetação utilizando *Brachiaria brizantha* demonstraram que os fertilizantes revestidos promoveram melhor absorção de nitrogênio e produção de biomassa em comparação com a ureia sem revestimento. Também, cortes sequenciais mostraram que os benefícios foram consistentes em todos os estágios de crescimento, com um efeito cumulativo mais evidente ao longo de 135 dias. Os resultados destacam o papel crítico da estrutura nanocompósita no aumento da eficiência do uso de nutrientes e na redução de perdas ambientais. Essa abordagem permite o uso de revestimentos mais finos sem comprometer o desempenho, fornecendo uma alternativa sustentável para o desenvolvimento de fertilizantes avançados de liberação controlada.

Palavras-chave: ureia, argila, óleo de mamona, liberação controlada, fertilizante.

1. Introduction

The global population has grown by 1.2 billion since 2010, reaching 8 billion people in 2023, which highlights the urgent need for technologies that improve agronomic efficiency (Guiné, 2024). Fertilizers have been essential for boosting crop yields, meeting global food demands, and enhancing quality of life. Among them, urea remains the most widely used nitrogen fertilizer due to its favorable handling properties and high nitrogen content (~45% by weight) (Majaron et al., 2020). However, its high solubility leads to nitrogen losses through soil transformations and gaseous emissions, notably ammonia (NH_3) volatilization and nitrous oxide (N_2O) release (Bortoletto-Santos et al., 2020). To address these inefficiencies, strategies that align nutrient release with plant uptake have gained attention for improving fertilizer use efficiency and reducing environmental impact.

Biobased coatings have emerged as promising alternatives to synthetic polymers due to their biodegradability and compatibility with soil ecosystems. Recent findings demonstrate that nanocomposite coatings can fine-tune nutrient release by exploiting electrostatic interactions between nutrients (such as ammonium, phosphate, and potassium) and active sites on dispersed fillers like montmorillonite or bentonite. This mechanism introduces a paradigm shift: chemical affinity becomes more relevant than the physical diffusion barrier commonly seen in conventional coatings.

In this study, we propose a nanocomposite coating system applied to urea granules and tested under greenhouse conditions. The coatings were formulated from castor oil-based polyurethane with uniformly dispersed montmorillonite, aiming to regulate nutrient release. The system's performance was evaluated using Palisade grass (*Brachiaria brizantha*), with a focus on dry biomass production and nutrient use efficiency. The results indicated improved nitrogen uptake due to the prolonged release dynamics.

2. Materials and Methods

Commercial urea granules were coated with a castor oil-based polyurethane prepared from 4,4'-diphenylmethane diisocyanate and castor oil in a 60:40 weight ratio, respectively. The coating process consisted of the castor oil-based polyurethane dispersion over urea granules using a metal turntable coater that rotated at 30 rpm, with 25 cm side shields and airflow heating at 50 ºC. The polymer coating layer was kept at 4% by weight (wt%) since 40 g of polymer was applied in 1 kg of fertilizer. Moreover, the montmorillonite percentage dispersed in the polymer matrix varied between 2 and 10 wt% on a urea weight basis.

The total nitrogen content in the samples and treatments was determined through elemental analysis using a CHNS/O 2400 Series II Elemental Analyzer (PerkinElmer). 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 greenhouse experiment was conducted using Palisade grass (*Brachiaria brizantha*) to measure nitrogen (N) uptake and dry mass production. 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_2O) 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.

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 hours, then weighed and ground using a benchtop stainless steel knife mill (Wiley mill type) to achieve a particle size of less than 1 mm.

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

3. Results and Discussion

Figure 1 shows cross-sectional SEM images of urea granules coated with castor oil-based polyurethane containing different proportions of montmorillonite. Figure 1a shows the uncoated urea granule surface, which is rough and irregular. Figures 1b-1f present SEM images of the coated urea granules, revealing the formation of a homogeneous and evenly distributed layer on the granules' 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.

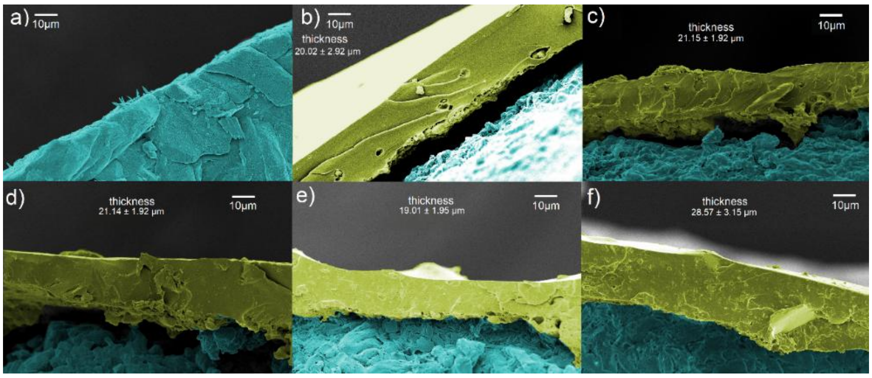

Figure 1. Scanning Electron Microscopy (SEM) images of (a) uncoated urea and the interface between urea and a castor oil-based polyurethane containing montmorillonite at (b) 0%, (c) 2%, (d) 3.5%, (e) 5%, and (f) 10% wt%, respectively. The urea fertilizer and coating layer are highlighted in green and yellow, respectively.

Figure 2 shows the dry mass production rate, respectively. The results showed that the Soil control (SC) treatment presented the lowest dry mass production rate. On the other hand, PUrMt5 and PUrMt10 treatments indicated higher dry mass production rates, 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.

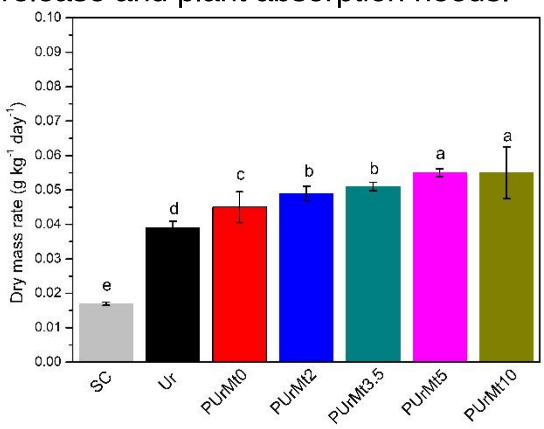

Figure 2. Dry mass production rate for each treatment. The values of the bars with the same letter do not differ significantly (Tukey's test; $P < 0.05$).

Figure 3 shows the N uptake rate. As observed for dry mass production, the SC treatment showed 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). It is worth mentioning that PUrMt10 presented the highest rate of N uptake among the nanocomposites, suggesting that the better fertilizer availability was more effectively utilized by the plant and resulted in a consequent reduction in losses.

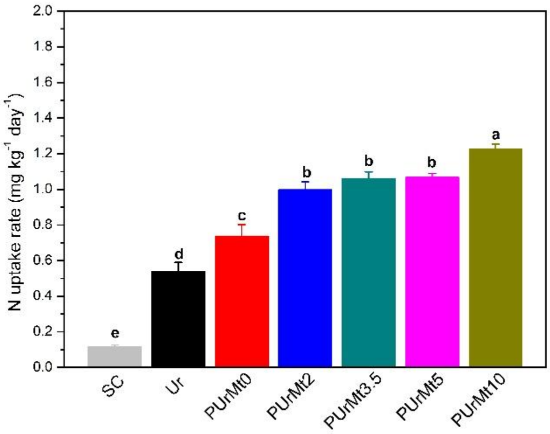

Figure 3. Nitrogen uptake rate for each treatment. The values of the bars with the same letter do not differ significantly (Tukey's test; $P < 0.05$).

4. Conclusions

Our results confirm that the structural modification of polymeric coatings can play an important 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. It highlights the advantages of the coating strategy and the importance of microstructure design (i.e., nanocomposite structure) in enhancing performance.

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