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CASTOR OIL-BASED POLYURETHANE MODIFIED WITH GEOPOLYMER FOR APPLICATION AS A CONTROLLED UREA RELEASE SYSTEM

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Abstract: The use of agricultural fertilizers is essential to sustain current productivity levels, but their efficiency is often compromised by losses, such as ammonia (NH_3) volatilization. To reduce these inefficiencies, a promising strategy is the application of barrier coatings that control the release of nutrients. These coatings must form a uniform and adhesive layer on the granule surface while also regulating the diffusion of soluble nutrients through their structure. The inclusion of internal diffusional barriers, such as finely dispersed geopolymers, can further reduce nutrient permeation and enhance performance. Thus, we proposed a system based on castor oil-derived polyurethane (PU), modified with geopolymer synthesized from expanded clay waste, to control fertilizer release via an ion-exchange mechanism. The incorporation of this cation-exchange material into the PU matrix effectively delayed N release from urea granules, reducing ammonia volatilization from 36.75% to 18.78% over a 28-day period of soil incubation. Our findings demonstrate that the PU-geopolymer system not only enhances nutrient retention but also enables the use of thinner coatings, maintaining effective control over N release. This advancement opens new avenues for developing more efficient and environmentally friendly controlled-release fertilizers tailored to sustainable agricultural systems.

Keywords: expanded clay, castor oil, urea, fertilizer, controlled release.

POLIURETANA À BASE DE ÓLEO DE MAMONA MODIFICADA COM GEOPOLÍMERO PARA APLICAÇÃO COMO SISTEMA DE LIBERAÇÃO CONTROLADA DE UREIA

Resumo: O uso de fertilizantes é essencial para manter os atuais níveis de produtividade agrícola, mas sua eficiência é comprometida por perdas como a volatilização de amônia (NH_3). Uma estratégia promissora para mitigar essas perdas é o uso de revestimentos de barreira que controlam a liberação de nutrientes. Esses revestimentos devem formar uma camada uniforme e aderente sobre os grânulos, além de regular a difusão de nutrientes solúveis. A adição de barreiras difusionais internas, como geopolímeros finamente dispersos, pode reduzir a permeação de nutrientes e melhorar o desempenho do sistema. Neste contexto, propõe-se um revestimento à base de poliuretana (PU) derivada de óleo de mamona, modificada com geopolímero obtido de resíduos de argila expandida, atuando por mecanismo de troca iônica. A incorporação desse material catiônico à matriz de PU retardou a liberação de nitrogênio (N) a partir de grânulos de ureia, reduzindo a volatilização de amônia de 36,75% para 18,78% após 28 dias de incubação no solo. Os resultados indicam que o uso de PU-geopolímero permite reduzir a espessura do revestimento sem perder eficiência no controle da liberação de N. Essa abordagem representa um avanço para o desenvolvimento de fertilizantes de liberação controlada mais eficientes e sustentáveis.

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

1. Introduction

Expanded clay is a lightweight, porous ceramic material widely used in construction. However, its production generates waste that requires proper disposal. Therefore, the recovery of this waste emerges as an alternative, transforming it into new materials with innovative applications. The versatility of expanded clay enables the development of advanced composites, such as geopolymers, which offer a promising alternative to conventional materials, contributing to the circular economy and reducing environmental impact (Kanagaraj et al., 2023). In this context, the geopolymerization process converts materials rich in aluminosilicates into an inorganic binder with cementitious properties, with potential applications in agriculture, such as the use of expanded clay manufacturing waste.

Lightweight expanded clay aggregates are already used as substrates in wetlands, demonstrating their ability to remove phosphate and support plant rooting (Mlih et al., 2020). Incorporating these geopolymers into agricultural formulations can enhance crop development and reduce the reliance on synthetic fertilizers. Furthermore, promoting a more efficient life cycle and reducing the carbon footprint significantly contribute to strengthening sustainability (Alves et al., 2024). On the other hand, global population growth has increased the demand for food, posing a challenge for agriculture to increase productivity efficiently and sustainably. In this scenario, the appropriate use of fertilizers is crucial, necessitating strategies that maximize nutrient availability to plants while minimizing environmental losses (Bortoletto-Santos et al., 2020). Urea stands out as the most widely used nitrogen fertilizer globally due to its high nitrogen content and low cost. However, it is highly susceptible to ammonia (NH_3) volatilization, which can result in the loss of up to 50% of the applied nitrogen. A promising alternative to mitigate this limitation is the use of polymeric coatings on urea granules, forming a physical barrier that slows the release of the nutrient. Previous studies have demonstrated that these coatings can be designed to control the rate of nitrogen release, thereby reducing losses and promoting greater crop efficiency.

This study aimed to develop a coating system that combines ion exchange properties with the physical protective effect of the polymer, thereby optimizing the nutrient release profile of fertilizers. To this end, we propose incorporating the geopolymer obtained from expanded clay waste into a biodegradable polyurethane (PU) matrix and applying it as a coating for urea granules. Thus, PU coatings containing geopolymer were prepared, which effectively acted as a diffusion barrier, promoting the controlled release of fertilizer into the soil and reducing ammonia volatilization.

2. Materials and Methods

The geopolymer synthesis consisted of weighing 136.36 g of expanded clay waste and 45.45 g of metakaolin and adding them to a mixer. Next, 118.18 g of an alkaline solution composed of potassium hydroxide and potassium silicate was added, and the mixture was homogenized at low speed for 1 minute. The mixture was stirred for an additional 10 minutes, then the speed was increased to optimize dispersion and promote the reaction of the constituents. In the subsequent step, 4.9 g of 2% hydrogen peroxide was added, and the mixture was maintained at high speed for an additional 5 minutes to promote expansion and uniform incorporation of the foaming agent. The resulting paste was molded into cubic specimens, which were left in the molds for 24 hours to undergo initial curing. After this period, the specimens were demolded and kept immersed in water for 24 hours to verify the material's stability and confirm the formation of the geopolymer. After confirming structural integrity, the resulting material was ground in a hammer and ball mill for later application.

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 geopolymer percentage dispersed in the polymer matrix varied between 5 and 10 wt% on a urea weight basis.

The materials were characterized by X-ray diffraction (XRD, Shimadzu 6000, Japan) with Cu Kα radiation (λ=1.54178 Å), scan speed of 2º min^{-1}, and in a range 2θ of 5 to 60º, as well as X-ray Fluorescence (XRF, Malvern Panalytical miniPal4, United Kingdom) was used for obtaining mineralogical and chemical composition of the material. Moreover, the external surface area of geopolymer was determined according to Brunauer–Emmet–Teller (BET) method from the N_2 adsorption-desorption isotherms using an ASAP (Micromeritics Corporation 2020, United States America), as well as the determination of the residual surface charge was obtained at different pH levels using the Zetasizer Advance Series equipment from Malvern Instruments, Ultra model (Red Label).

The release experiments in soil were carried out with an Oxisol collected from the surface layer (30-40 cm) of an agricultural area in São Carlos, São Paulo State, Brazil (22º 01' S, 47º 54' W; 856 m above sea level). The soil (particle size < 2 mm) had the following characteristics: 587 g kg^{-1} sand, 76 g kg^{-1} silt, and 337 g kg^{-1} clay, according to textural analysis by the pipette method; water holding capacity (WHC) of 200 g kg^{-1}; pH (H_2O) 6.0, measured with a glass electrode; organic C content of 21.0 g kg^{-1}, cation exchange capacity (CEC) of 4.7 $cmol_c$ kg^{-1}, and phosphorus content of 2.3 mg kg^{-1}. The treatments were incubated in soil samples (10 g) to compare the release and dynamics of all nutrients. Urea granules with or without coating were incubated using a N/soil ratio of 1:1000 (g g_{soil}^{-1}). First, the soil was placed in 80 mL polyethylene screw-cap bottles, followed by the addition and homogenization of each sample. For the N determinations, a 5 mL acid trap containing 4% boric acid was attached to the polyethylene bottles to capture the ammonia (N-NH_3) volatilized during incubation (Bortoletto-Santos et al., 2020). After the complete incorporation of the granules, the soil moisture was adjusted to 80% of the water-holding capacity (WHC) and maintained at this level during the incubation period, with the addition of groundwater as needed.

The samples were incubated at a controlled temperature of 25 °C for 3, 7, 14, 28, and 42 days. After each incubation period, the remaining granules were removed, and the soil was air-dried at 100 ºC. The ammonia ($N\text{-}NH_3$) volatilized was determined by boric acid titration using HCl (0.01 mol L^{-1}).

3. Results and Discussion

Analysis of the expanded clay residue revealed a majority composition of silicon oxides (63.46% SiO_2), aluminum (18.74% Al_2O_3), and iron (7.61% Fe_2O_3), as shown in Table 1. X-ray diffraction (XRD) analysis revealed that mullite, quartz, and hematite were the predominant crystalline phases, characteristic minerals of materials subjected to thermal expansion processes, along with the presence of an amorphous fraction, as indicated by the diffuse halo at low angles. The specific surface area, determined by the BET method, was 0.5935 $m^2\ g^{-1}$. Moreover, zeta potential analysis revealed a negative surface charge throughout the evaluated pH range (2-9), a behavior typical of clayey materials, which ensures colloidal stability and potential applications in adsorption processes. After the geopolymerization process using expanded clay residue, XRD analyses revealed no significant changes, as the crystallographic peaks observed in the original sample were maintained, and the zeta potential behavior remained unchanged. However, a significant increase in the specific surface area was observed, reaching 59.9924 $m^2\ g^{-1}$ - approximately 101 times higher than the initial value - evidencing a substantial gain in the area available for surface interactions.

Table 1. Compositional analysis for expanded clay waste from X-ray Fluorescence.

Element	%
SiO_2	63.46
Al_2O_3	18.74
K_2O	4.82
Na_2O	0.62
Fe_2O_3	7.61
TiO_2	0.87
CaO	0.63
MgO	2.72
Mn_2O_3	0.09
P_2O_5	0.18

The ammonia volatilization ($N\text{-}NH_3$) curves were constructed (Figure 1) to investigate the N loss from the fertilizers. The $N\text{-}NH_3$ volatilization from urea increased up to 7 days of incubation, reaching a loss of 52.92% of the total N applied to the soil in the form of $N\text{-}NH_3$. This rapid loss can be attributed to the rapid solubilization of urea and increased hydrolysis, which begins on the third day of incubation (30.63% of the applied N is lost as $N\text{-}NH_3$). Moreover, the high conversion of urea to $N\text{-}NH_3$ was favored by the high urea hydrolysis rate in low CEC soils and low acidity buffering capacity. However, the control on urea release provided by the polymer coating was effective in reducing N loss by $N\text{-}NH_3$ volatilization, showing $N\text{-}NH_3$ emission nearly zero until 3 and 7 days of incubation for UrPU and UrPUGEO5%, respectively. The $N\text{-}NH_3$ volatilization rate for treatment without geopolymer (UrPU) increased on day 14, resulting in a loss of 51.35% of the applied N over the 42-day incubation period. On the other hand, the presence of geopolymer in the coating significantly reduced the $N\text{-}NH_3$ volatilization, and the volatilization rate increased after 14 d to UrPUGEO5% (3.45%). It is worth noting that the treatment containing 10% geopolymer (UrPUGEO10%) exhibited a release profile similar to UrPU, as the high amount of geopolymeric material likely led to the opening of pores and channels in the coating, thereby compromising its performance.

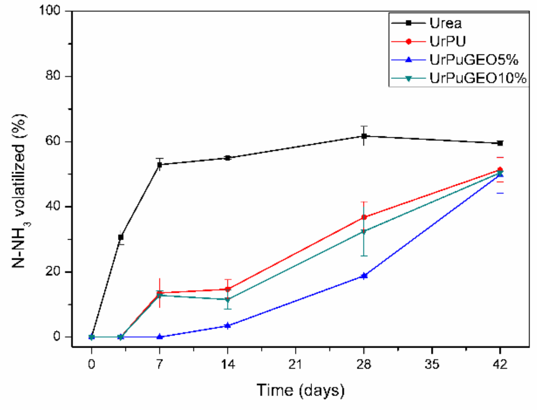

Figure 1. Average curves of N-NH_3 volatilized during the aerobic incubation in soil of uncoated and coated urea granules. Vertical bars are standard deviations.

4. Conclusions

Our results showed that the addition of geopolymer in PU coatings effectively controls the nutrient release process in granular fertilizers by promoting internal diffusion barriers. This feature was revealed by the fact that particles with affinity towards cations are efficient in controlling nitrogen diffusion. This strategy confirmed that controlled release can reduce N volatilization, as well as have a positive economic impact, since this filler (geopolymer) is cheaper than the PU components and is prepared from clay waste, thereby reducing the technology cost by allowing thinner coatings to be applied on granular nutrient sources.

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