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Urea coated with cellulose acetate-lignin composite presents lower loss by ammonia volatilization

Ureia revestida com compósito de acetato de celulose-lignina tem menor perda por volatilização

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Abstract
Urea is one of the main nitrogen sources used in plant nutrition. During its management, due to chemical, physical, and biological processes, part of N is volatilized in ammonia form, and negatively impacts the environment. When protected with renewable and biodegradable materials, such as lignin (Lig) and cellulose acetate (Ac), urea can reduce ammonia losses. Therefore, this work aimed to develop Lig and Ac composites to cover urea in order to reduce N-urea loss. The lignin was obtained by the acid precipitation of commercial kraft black liquor, corresponding to a 3-6 pH range. Film-forming solutions (Fs) were produced by combining Lig (0.3, 0.6, 0.9, and 1.2

%, w/w, based on Ac), and Ac (2 %, w/w, based on urea). In addition, two reference treatments were included: urea without coating (U) and urea coated only with Ac. In order to obtain the the coatings, the granules were placed in a dish-type granulator, equipped with shovels, sprayed with the Fs, kept in rotation (125 rpm), and dried under hot air flow (~100 ºC). Ammonia volatilization was evaluated in a static capture system (24 h), with 2% boric acid, followed by titration with sulfuric acid (0.005 mol/L). The results revealed that the granules with Ac coating, without and with Lig, reduced volatilization. For the coating without Lig, there was a U reduction of 33.2%. For the coating with Lig, the combination of Ac, 2%, and Lig, 0.9%, was the most effective, compared to urea without coating. The mean reduction in volatilization for this formulation was 58.4%. According to the visual and SEM image evaluations, the coating system developed was satisfactory and presented a thin and uniform layer. Satisfactory adhesion of the films was also observed, both with and without Lig, in the granule surfaces.
Keywords: Kraft lignin. Cellulose acetate. Urea. Coating. Nitrogen fertilizer. Biorefinery.

Resumo
Uma das principais fontes nitrogenadas utilizada em nutrição de plantas é a ureia. Durante o seu manejo, devido aos processos químicos, físicos e biológicos, parte do N é volatilizada na forma de amônia, impactando negativamente o ambiente. A ureia protegida com materiais renováveis e biodegradáveis como a lignina (Lig) e o acetato de celulose (Ac) pode contribuir para a redução das perdas de amônia. Dessa forma, este trabalho objetivou desenvolver compósitos de Lig e Ac para recobrir a ureia visando redução de perda de N. A lignina utilizada foi obtida por precipitação ácida do licor negro kraft comercial, correspondente à faixa de pH 3 a 6. Produziram-se soluções filmogênicas (Sfg) combinando Lig (0,3; 0,6; 0,9 e 1,2 %) em base mássica de Ac, e Ac (2 %) em base mássica de ureia. Ainda, foram incluídos dois tratamentos referências: a ureia sem recobrimento (U) e a ureia recoberta apenas com Ac. Para os recobrimentos, os grânulos foram dispostos em granulador tipo prato, munido de haletas, e pulverizados com as Sfg, mantido em rotação (125 rpm) e secagem sob fluxo de ar quente (~100 ºC). Avaliou-se a volatilização de amônia em sistema estático de captura (24 h), com ácido bórico 2% seguido de titulação com ácido sulfúrico. Os resultados mostraram que o recobrimento com Ac, sem e com Lig, reduziram a volatilização. Para o recobrimento sem Lig, houve uma redução de 33,2% em relação a U, e para o recobrimento com Lig, a combinação de Ac, 2 %, e Lig, 0,9 %, foi a mais eficaz. Se comparado à ureia sem recobrimento, houve redução média da volatilização para essa formulação em 58,4 %. De acordo com as avaliações visual e por imagens em MEV, o sistema de recobrimento desenvolvido atendeu de forma satisfatória apresentando uma camada fina e uniforme. Observou-se por imagem, também, que houve adesão satisfatória dos filmes, com e sem Lig, à superfície dos grânulos.
Palavras-chave: Lignina kraft. Acetato de celulose. Ureia. Revestimento. Fertilizante nitrogenado. Biorrefinaria.

1. Introduction

Fertilization is a practice widely used to increase agricultural production (Barberis *et al*., 2022) to meet the world population's growing demand for food (Jiao *et al*., 2018). In the current scenario, around 1.2% of the global energy consumption is dedicated annually to fertilizer production, of which 90% goes to nitrogen fertilizers. Due to the high rates of fertilization and the dynamics of N in the soil, the United Nations has set a target to reduce the loss of N forms to the environment by half by 2030 (Govers; Devuyst, 2022). Therefore, it is expected a reduction in the impacts that these forms of N generate, such as global warming, the destruction of the ozone layer, the intensification of acid rain, eutrophication, and water contamination (Vermoesen *et al*., 2023). To this end, we seek to reduce doses by improving fertilization management and promoting more sustainable agricultural practices (Gu *et al*., 2019).

Economically, urea has become one of the main nitrogen fertilizers (Yamamoto *et al*., 2016). This is justified by its high N content, which can range from 44 to 46%, and the physical characteristics favorable to fertilization management. However, this fertilizer presents high

solubility in water and is susceptible to enzymatic reactions triggered in the soil, which cause approximately 40 to 70% of nitrogen to be lost, mainly by ammonia volatilization (Jiao *et al*., 2018). In this context, controlled-release fertilizers (FLC) have demonstrated to be a viable alternative for a more efficient application of this nutrient, in addition to reducing the impacts caused to the environment (Jiao *et al*., 2018; Wei *et al*., 2021).

The application of FLC aims to reduce and control the rate of nitrogen release, according to the specificities of each crop (Andrade *et al*., 2021; Vermoesen *et al*., 2023). In general, the granules of these fertilizers are physically protected through the application of various materials (Lu *et al*., 2022; Trankel, 2010), which are usually non-renewable, such as paraffin, polyurethane, silicone polymers, polyamide, and polyacrylonitrile. However, many of them are of low degradability, accumulate in the soil, and cause negative effects, in addition to those already caused by the loss of N (Wei *et al*., 2021).

The lignocellulosic biomass, which is mainly composed of cellulose, hemicellulose, and lignin, emerges as a renewable and biodegradable alternative for coating materials (Chen *et al*., 2020). Brazil is the world's largest producer and exporter of bleached eucalyptus cellulosic pulp, and kraft pulping is the most implemented process in the individualization stage of the fibers (Figueiredo; Cohen, 2019). In any chemical pulping process, the goal is to remove enough lignin to separate the cellulosic fibers without causing significant yield losses (Abdelaziz; Hulteberg, 2017; Chakar; Ragauskas, 2004), which makes both cellulose (the main product) and lignin (a by-product present in black liquor) valuable for a variety of applications (Demuner *et al*., 2019).

Thus, biocomposites (mixture of two or more materials) of cellulose acetate (Ac), prepared by cellulose acetylation, and lignin, from the biorefining of the by-product of the kraft process, are applicable as fertilizer coatings, due to their favorable characteristics, such as biodegradability, biocompatibility, non-toxicity, and hydrophobicity (Fertahi *et al*., 2019; Pinto *et al*., 2022; Puls; Wilson; Hölter, 2011). This application provides better use of the lignin produced since only about 1 to 2% of this material is removed from the production process of the cellulosic pulp factories and used for other applications, while the rest is employed in the factory's energy matrix for steam generation (Demuner *et al*., 2019; Wei *et al*., 2021).

The expression of the FLC character depends on the nature and porosity of the coating material, the thickness of the coating layer, as well as the soil type, moisture level, pH, and microbial and enzymatic activity (Fertahi *et al*., 2019). Thus, this research aimed to evaluate the efficacy of coating urea granules with a lignin and Ac composite in reducing NH_3 volatilization.

2. Materials and methods

For the development of the research, it was used a fraction of lignin precipitated with sulfuric acid in the pH range of 3 to 6, extracted from a sample of black kraft liquor from the recovery system of a bleached eucalyptus pulp plant, according to the research of Meireles (2022). Cellulose acetate (GS = 2.5; MM = 2,024,000 $g.mol^{-1}$), provided by the Rhodia Solvay Group; acetone p.a. (Alphatec) 99.5%; sulfuric acid P.A. 98% (CRQ); boric acid p.a. (ISOFAR); granular urea 46% (Fertipar Sudeste) and distilled water were also employed.

2.1 Preparation of the film-forming formulation

The lignin in the form of a powder with a particle size of approximately 75 μm was dispersed in acetone, at room temperature, for 4 hours, under magnetic agitation. The proportions of lignin were 0.3; 0,6; 0,9; and 1.2%. Subsequently, Ac was dissolved in 2% acetone p.a., fertilizer mass base, under agitation, for 24 hours, in a hermetically sealed flask. Then, the treatments were identified as Ac2L0.3, Ac2L0.6, AcL0.9 and Ac2L1.2. Two reference treatments were also included: urea without coating (U) and urea with coating only with Ac 2%, i.e., without lignin addition (Ac2L0).

2.2 Coating of the Beads

A disc-type granulator was set up to coat the fertilizers, with the capacity to operate batches of 50 to 100 g of fertilizer (Figure 1). The granulator, mounted inside an exhaust hood, was composed of a rotating disc (effectively a tray), tilted at 40º and driven by an agitator that provided a rotation of 125 rpm. To obtain greater homogeneity in granule circulation, a radial shovel was installed on the disc to interrupt the continuous circular flow of the granules. A spraying system consisting of a micro spray and a peristaltic pump was used to spray the granules with the film-forming solution. Laboratory tests were carried out with 100 grams of urea granules, with a size range of 2.36 - 3.35 mm. During the coating process, a disc was heated with a hot air gun regulated between 100 and 120 ºC. The solvent evaporated, and the film was formed on the granule, thus eliminating the need for additional drying. Following this coating, the granules were stored in a moisture-free place, at room temperature, around 25°C (Ribeiro *et al*., 2020).

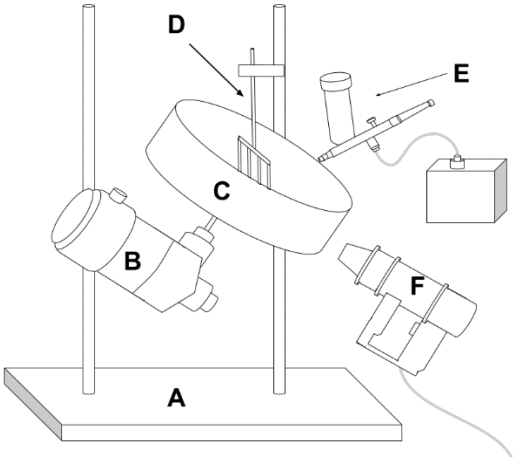

Figure 1 - Plate (or disc) granulator used for coatings A: Bracket; B: mechanical agitator; C: rotating disc; D: radial shovel; E: Micro spray with compressor; and F: heat blower.

2.3 Evaluation of NH_3 volatilization

The test to evaluate the ammonium volatilized from urea with the different coating treatments was conducted in static systems, consisting of closed incubation chambers (glass pot) and an internal container (plastic beaker) for placing the NH_3 collecting solution (Figure 2). About 80 g of soil with 22% (w/w) moisture content were placed in each. The fertilizer granules were weighed so that the fertilizer mass corresponded to 200 mg of nitrogen. This fertilizer amount was applied to the surface of the soil. Next, the plastic beaker containing 10 mL of the boric acid solution, 2%, with methyl red and bromocresol green indicators (collector solution), was positioned on the soil in the center of each incubation chamber, and then the chambers were closed. The tests were carried out in triplicate. After 24 h of incubation, the collectors were removed, and the captured NH_3 was measured.

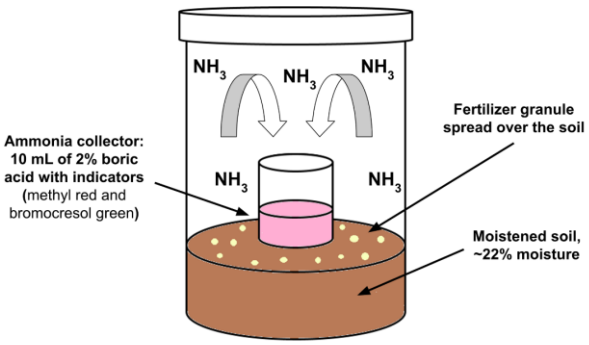

Figure 2 - Static system to evaluate NH_3 volatilization, consisting of the incubation chamber and the collection vessel.

2.4 Captured NH_3 dosage

After the incubation time, the contents of each collection cup were quantitatively transferred to an Erlenmeyer flask, washed twice with 2 mL of distilled water each, and titrated with standard 0.0005 mmol.L^{-1} sulfuric acid solution. The amount of ammonia released by the fertilizer samples was calculated according to Equation 1.

$$ML = \frac{\left[2 * C * \left(V_g - V_b\right) * M_m\right]}{M} \quad (1)$$

Where ML = ammonia mass released per mass of fertilizer used, in mg.g^{-1}; Vg = mean volume of spent sulfuric acid solution, in mL; Vb = volume of sulfuric acid solution spent with blank sample, in mL; C = molar concentration of standardized sulfuric acid, 0.0005 mol.L^{-1}; Mm = ammonia molar mass, 17 g.mol^{-1}, and M = mass of the base fertilizer sample, N, in g.

The results were submitted to analysis of variance (ANOVA), and the treatment mean effects were compared by Tukey's test, at 5% probability.

2.5 Fertilizer granule coating evaluation by scanning electron microscope

The coating evaluation was performed based on the images obtained from a scanning electron microscope (SEM) model JEOL-JSM-6010LA, operated at an acceleration voltage of 10 kV. In order to obtain the SEM images, the fertilizer samples were coated in gold, using the Quorum Q150R metallizer. The images allowed the granules to be observed in greater detail in the coating. Thus, the images of the random coated granules and "empty" coatings, i.e., after the ammonia volatilization test (Topic 2.3), were obtained for each treatment. A cut was made with a scalpel blade to observe the cross-section of the coated granules.

3. Results and discussion

3.1 Coatings

Initially, aiming to test the coating system, pre-tests were carried out with the addition of blue and green food colorants to visually evaluate the coating efficiency and adjust the granulator operation (Figure 3). For this purpose, the same base formulation of Ac 2% was used, following the same factors presented in Topic 2.2, regarding drying temperature, urea mass, rotation in revolutions per minute, and disc tilt. In Figures 3B and 3C, a uniform staining of the granules can be observed when compared with the image of the uncoated granules (Figure 3A). The coating efficiency can also be observed when comparing the SEM images of the granules without coating (Figure 4A) and with coating (Figure 4B).

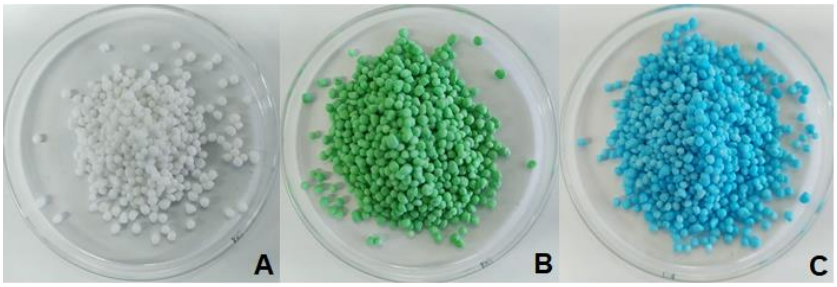

Figure 3 - Uncoated urea granule (A) and coated with 2% cellulose acetate dyed in green (B) and blue (A), to demonstrate the uniformity of the coating.

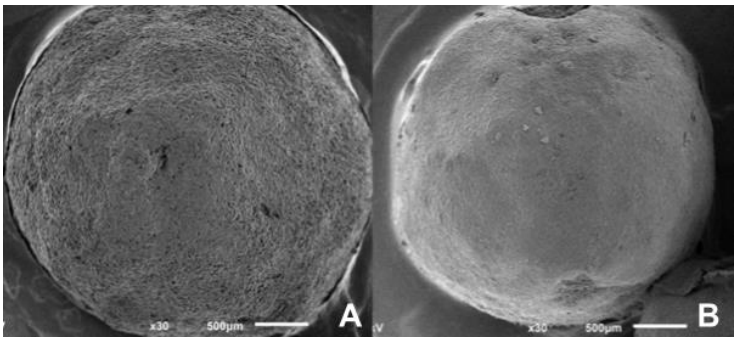

Figure 4 - SEM images of urea granules without coating (A) and with coating (B)

With the coating process properly adjusted, the film-forming solutions with and without lignin were prepared to coat the granules for the volatilization test. Figure 5 shows the urea granules without coating, reference, and the granules coated for the different levels of proportions of 0.3, 0.6, 0.9, and 1.2% and only with cellulose acetate AcL0. As found by Meireles (2022), the AcL0 coating was transparent and colorless (Figure 5B) and, as the proportion of lignin increased, the milky staining of the granules intensified (Figures 5C, 5D, 5E, and 5F).

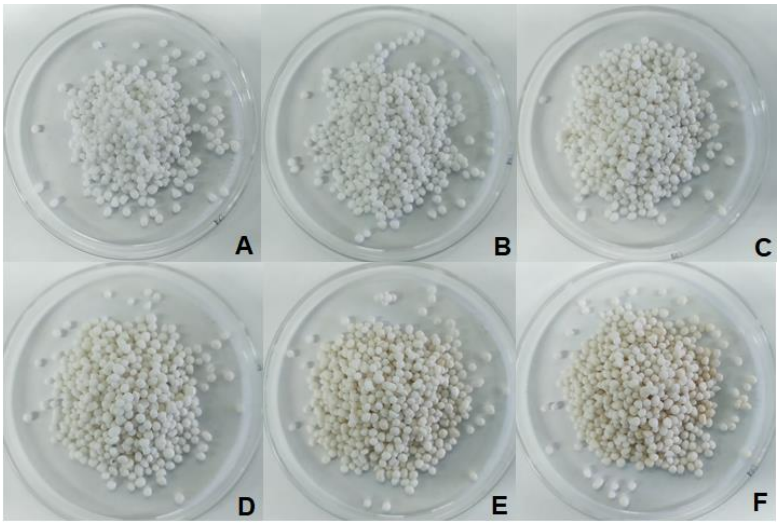

Figure 5 - Uncoated urea granules (A), coated with (B) cellulose acetate, 2% (AcL0), and the combination of 2% cellulose acetate with increasing proportions of lignin 0.3% (AcL0.3) (C), 0.6% (AcL0.6) (D), 0.9% (AcL0.9) (E), and 1.2% (AcL1.2) (F).

In the SEM images of the AcL0.6 treatment (Figures 6A and B), good interaction can be observed between the bead surface and the coating film. The images obtained with the other treatments revealed the same coating characteristics. This may be explained by the hydrophobic nature of both coating materials, as well as the presence of residual hydroxyls and acetyl groups of the Ac and hydroxyls of the lignin fragments. According to Glasser *et al*. (1998) and Schreiber *et al*. (2015), there is a strong interaction between lignin and cellulose derivatives, since it indicates the formation of hydrogen bonds between functional groups. In addition, they argue that the addition of lignin to cellulose derivatives benefits the interaction between these two materials by disrupting the polymer chains of cellulose. This interaction, which is a consequence of the drying of the layer, may have caused film contraction and, therefore, greater adhesion to the granule surface.

As described by Meireles *et al*. (2022), lignin precipitated in lower pH ranges (3 - 6) presents greater molecular fragmentation, and consequently, increased occurrence of hydroxyls, which may have intensified the hydrogen bonds between lignin and Ac.

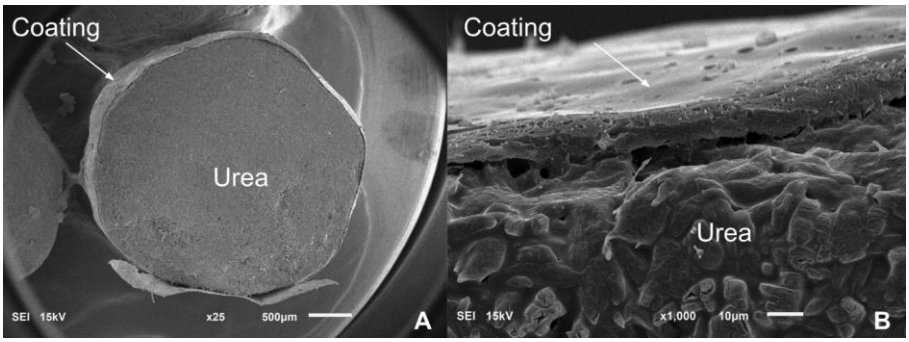

Figure 6 - SEM images of the (A) cross-section of the urea granule coated with the formulation AcL0.6, and (B) detail of the interaction of the coating film with the granule surface.

A urea granule coated with the formulation AcL0.9 indicates discontinuity, i.e., holes in the coating surface, which was observed with little intensity in all the coating formulations applied, as shown in Figure 7. This may have been due to the formation of acetone bubbles during evaporation, which caused film rupture. In addition, it is important to obtain uniformity in the temperature that the heat gun provides to the rotating disc, to avoid granule agglomeration, since, as the agglomerated granules pass through the radial shovel and tend to separate, the region in contact with the agglomerate forms fissures or cavities on the surface. Another factor causing the holes may be the contact points between granules caused by agglomeration, due to uneven evaporation. Therefore, the disc temperature must be constant and uniform to avoid granule agglomeration. According to Beig *et al*. (2020), to achieve a uniform and smooth coating on the fertilizer surface, the air used for heating must have a temperature higher than that required for film formation (acetone boiling temperature: 56ºC). In addition, the high temperature helps the evaporation process by reducing the formation of agglomerates. However, there is an upper limit, since the coating may dry out before coming into contact with urea. In this case, the admission may not be efficient.

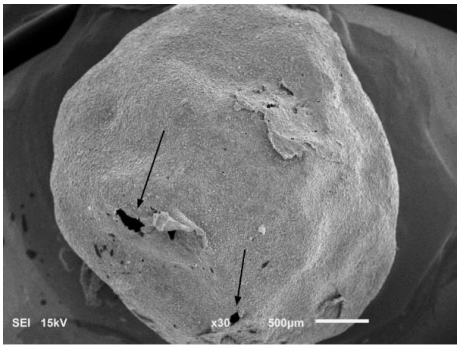

Figure 7 - Image of urea granule coated with the formulation AcL0.9, evidencing discontinuity in the covering film (and holes).

3.2 Ammonia volatilization tests

The evaluation results of the ammonia volatilization from urea with the different lignin coating treatments are shown in Figure 8. In this evaluation, granules with a small diameter range, 2.36 to 3.35 mm, were used, considering that the particle size can affect the volatilization intensity, as highlighted by Takahashi *et al*. (2018).

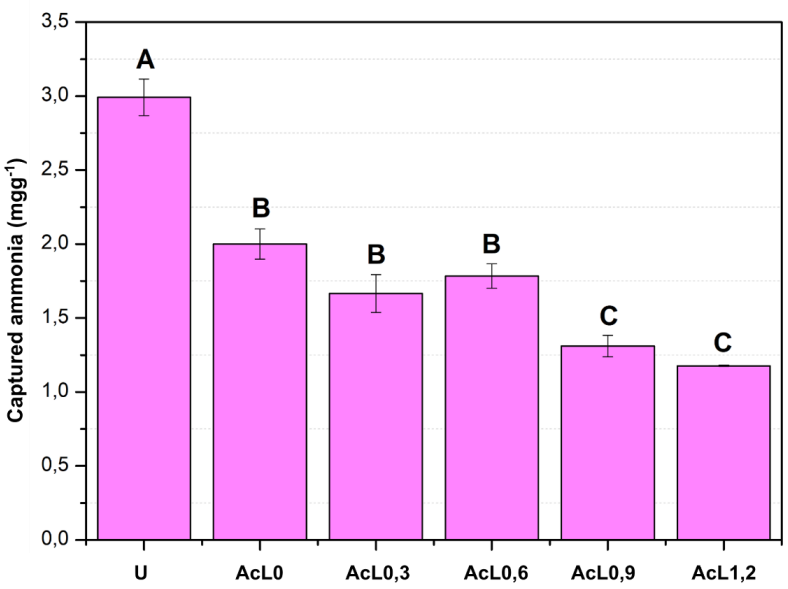

Figure 8 - Amount of ammonia captured per the amount of N applied as uncoated urea (U), coated with 2% cellulose acetate (AcL0), and with the combination of 2% cellulose acetate with increasing lignin proportions: 0.3 % (AcL0.3), 0.6 % (AcL0.6), 0.9 % (AcL0.9), and 1.42 % (AcL1.4).

In the bars, the means superscripted by the same letters are equal, by the Tukey test, at a 5% probability level.

The results presented in Figure 8 were submitted to analysis of variance (ANOVA), and corroborated that at least one of the formulations was significantly different at 5% level. According to the results presented in Figure 8, all formulations with coating significantly reduced urea without coating (U), which indicates that the coating helped to reduce nitrogen loss by ammonia volatilization. The Ac2L0 coating reduced ammonia release by 33.2%, which corroborates that only Ac would be sufficient to reduce nitrogen loss, since its mean result for ammonia release was statistically equal to the treatments with lower lignin contents (Ac2L0, statistically equal to Ac2L0.3 and Ac2L0.6). Regarding the evaluation of the effect of Ac coating with the different proportions of lignin, it was observed that the Ac2L0.9 treatment presented the lowest reduction in nitrogen loss by ammonia volatilization (37.8%), since its result was statistically equal to the Ac2L1.2 treatment. Also, if the result of the Ac2L0.9 treatment is compared to the mean result for urea without coating (U), the reduction achieved will be 58.4%.

Thus, the higher levels of lignin (Ac2L0.9 and Ac2L1.2) may have led to greater film densification, as proposed by Meireles *et al*. (2022). The lignin fraction precipitated at lower pH values (pH 3 to 6), such as the one used in this work, may have been characterized by greater amount of hydroxyl groups and smaller fragment size, which increases the amount of hydrogen bonds with the residual hydroxyl of Ac, also providing a higher density film. Consequently, the coating attenuated the urea solubilization and diffusion process and, consequently, the volatilization of ammonia (Alekhina *et al*., 2015; Meireles, 2022).

Figure 9 presents SEM images for comparing the surface of a coated urea bead and the remaining film after complete urea solubilization, both with the coating formulation AcL0.3. Film surface undulations were observed (Figure 9C, 30x magnification), which indicates that the coating is empty and in detail at 250x magnification (Figure 9D). However, this characteristic was not observed on the film surface, even when the urea granule was detected (Figures A and B), which suggests that the coating film interacted perfectly with the surface of the granule. These same characteristics were observed with granules of the other coating treatments.

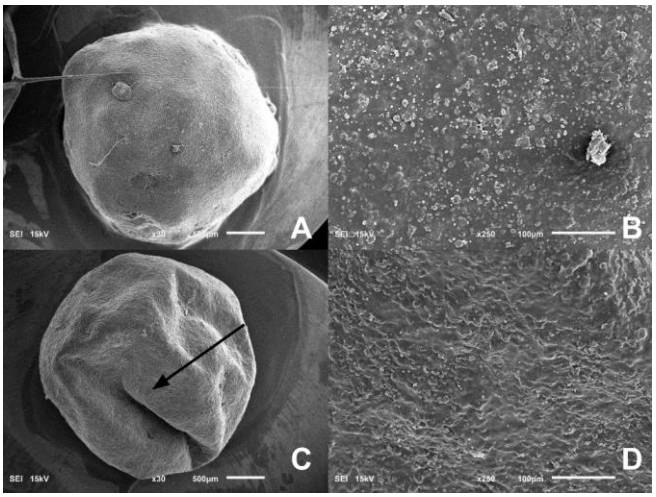

Figure 9 - Scanning electron microscopy images of urea granule coated (A, 30x and B, 250x) and of the remaining coating film after urea solubilization (C and D). Coating formulation AcL0.3.

4 Conclusions

The present work highlights the efficacy of the urea coating with cellulose acetate and lignin composite in reducing ammonia losses by volatilization. Based on the results obtained, the coating with cellulose acetate proved efficient, significantly reducing N losses by 33.2%. Cellulose acetate and lignin combination made the coating even more effective, since the lignin may have acted in the cellulose acetate film compaction contributing to the packaging of urea. The formulation of 2% cellulose acetate with 0.9% lignin provided an average reduction of 58.4% in ammonia volatilization compared to uncoated urea.

The scanning electron microscopy images revealed adequate coating of the urea granules, either with cellulose acetate alone or combined with lignin. This contributes to the reduction in ammonia volatilization.

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