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RELEASE OF POTASSIUM FERTILIZER COATED WITH POLYMER

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Abstract: Among the challenges faced in agricultural production, one of the main ones is the search for new means to achieve greater efficiency of inputs, with emphasis on fertilizers, since they are of great importance among the production factors. The line of research on fertilizers with added technologies emerges as one of the possible alternatives, with the physical coating of fertilizer granules being a relevant option to be studied. The objective was to study the release dynamics of controlled-release potassium fertilizer (coated), verifying the influence of percentages of coating applied to the fertilizer and its reflections on the time required for release. Identical experiments were conducted in a controlled environment (laboratory) and in a greenhouse. 5 percentages of polyurethane polymer were used for the potassium chloride (KCl) coating and one treatment without coating. Using porous bags, made with permeable screens, the fertilizers were allocated and these were buried in pots containing 1 kg of an Oxisol. Weekly collections of porous bags containing the fertilizer were carried out and the material was sent for chemical analysis. The results, analyzed by mean comparison test (Duncan at 5% significance) at the end of the experiment, showed that coatings greater than 6.75% (m/m) delay the release of KCl into the soil and, to the extent that that if the percentage of coverage increases, the release decreases, regardless of the place where the fertilizer is allocated. Thus, physical protection can be considered as an alternative to improving the use of this input.

Keywords: Potassium chloride; polyurethane; controlled release; release curve.

INTRODUCTION

The population increase results in the need to increase the production of food, fiber and energy, consequently, the demand for agricultural products grows, which, for their production, need the nutritional support provided by fertilizers.

Once highlighted that these inputs are of vital importance for the good development of agricultural activities, it becomes essential to develop alternatives that optimize the use of available inputs, avoiding losses and facilitating or enabling the development of new management strategies by the of the producer, resulting in possible improvements in the production system.

Potassium, in general terms, figures as the second macronutrient in content contained in plants, listed as the third element most likely to limit plant growth (Furlanetto et al., 2018). It is, after phosphorus, the nutrient most consumed as fertilizer by Brazilian agriculture (Raij, 1991; ANDA, 2018).

In the plant, it has the main functions of osmoregulation, enzyme activator, respiratory processes, performance in photosynthesis and, considered as one of the nutrients directly related to the quality of the agricultural products produced (Taiz and Zeiger, 2009). In its absence, it can present visual symptoms of generalized chlorosis, usually reaching the edges of the leaves and progressing to necrosis of plant tissues, starting symptoms in the lower portion of the plants (Malavolta, 2006; Taiz and Zeiger, 2009).

According to Troeh and Thompson (2007), plants absorb large amounts of potassium, all of it in the form of K+ ions. Ernani et al. (2007), explain that these fertilizers originate from the grinding of rocks from deposits formed by the evaporation of ancient seas and lakes. In terms of importance, potassium chloride stands out, the most used in the world among potassium fertilizers, due to its price, with a lower cost per unit of K, even in conditions of high price volatility in the last two years (2020 and 2021) (Global Fert, 2021; Osaki, 2021). However, potassium is a finite resource, with no substitute as a nutrient for plants, and deposits of this mineral are located in a few countries, notably Belarus, Canada, Russia and the United States of America (USGS, 2009; ANM, 2014).

Brazil imports practically all the potassium it uses, making the country's strategic situation delicate, values above 90% can illustrate the Brazilian dependence on this input (ANM, 2014; Silva et al., 2018).

In this context, strategies that increase the efficiency of this fertilizer have an important technical and strategic role on the world stage. Technologies such as coating fertilizers, to delay solubilization or control release, have been adopted by several countries, with market consumption projections of 7.5 million tons (Trenkel, 2010; Guelfi, 2017). The coating of the granules can be performed using wax, latex, polymers or others (Vitti and Heirinchs, 2007), in order to physically protect the raw material.

Coated fertilizers, classified as controlled, are products that release fertilizer more slowly into the environment, with release rate, pattern and time factors known and better controlled in the production process (Shaviv, 2005; Blaylock, 2007). Controlled release has, in addition to the technical advantage of slower release than traditional fertilizers and better control and planning of input use, an environmental advantage, enabling an increase in use efficiency and avoiding contamination of the environment (Shaviv, 2001).

Fertilizers coated with polymers can be purchased commercially, however their dynamics in soil is not yet fully known, in this context, the objective was to study the release dynamics of controlled release potassium fertilizers, verifying the influence of different percentages of coating applied to the fertilizer and its effects on the time required for release.

MATERIAL AND METHODS

The experiment was carried out in a controlled environment (25°C) and, simultaneously, in a greenhouse, using a clayey red-yellow Latosol, with the following chemical and textural characteristics:pH($CaCl_2$) = 5,6; M.O = 2,3 g dm^{-3}; P = 68 mg dm^{-3}; K = 2,1 mmolc dm^{-3}; Ca = 72 mmolc dm^{-3}; Mg = 34 mmolc dm^{-3}; H+Al = 28 mmolc dm^{-3}; CTC = 135 mmolc dm^{-3}; V% = 79; sand content = 533 g kg^{-1}; silt content = 83 g kg^{-1}; clay content = 383 g kg^{-1}. Pots with a capacity of 1 kg of soil were used, maintained at 80% of field capacity.

The experimental design was randomized blocks (DBC) with three replications, it must be noted that the experiment was designed by developing a system of destructive analysis of the samples, so the same sampling unit was composed of four observation units, composing the treatment. This system, in addition to allowing the analysis of the amount of fertilizer released, made it possible to trace the release curve of the treatments over time, that is, the tendency, speed and intensity of release from the interior of the covered treatments to the soil was observed.

In each pot, a porous bag was buried, produced using 18-thread and 40-mesh polyester fabric, measuring 6 x 6 cm, containing five grams of potassium chloride (KCl) covered with polyurethane polymer in different percentages of coating, constituting five treatments: KCl + 5.05% polymer (K1), KCl + 5.90% polymer (K2), KCl + 6.75% polymer (K3), KCl + 8.45% polymer (K4), KCl + 9.30% polymer (K5) and; a treatment without coating was also used. It must be noted that the process of applying the polymer on the fertilizer was carried out by spraying with a subsequent period of drying and curing of the applied product, with this spraying process being carried out more often, according to the need to increase the thickness of the coating capsule of the treatments. applied.

Weekly collections of porous bags were performed in both environments (laboratory and greenhouse), which were taken to the laboratory. After removing the residual fertilizer from the porous bags, the material was treated with 2 mL of concentrated sulfuric acid (H2SO4 18M), being left to stand for 30 minutes for the acid to act and for the dissolution of the coating, thus exposing the fertilizer. After this step, 25 mL of distilled water was added and the material was heated in a digester block for 45 minutes at 150°C, solubilizing KCl.

From the extract obtained, this was filtered through a Whatman filter n°42 and the resulting volume was completed to 50 mL and stored in a polypropylene bottle (falcon) with a capacity of 50 mL. Due to its concentration, the extract obtained was diluted and analyzed in a flame spectrophotometer, using a 10 ppm K standard for calibration.

Based on the results obtained, the fertilizer release time was estimated, that is, the period necessary for the entire content of the coating capsule to be available. The results were submitted to the F test ($p \leq 0.05$) to verify the occurrence of differences between the treatments and, in case of significance, the Duncan test was applied at 5% probability, using the SAS program (version 9.2).

RESULTS AND DISCUSSION

The samples collected at the end of the first week (7 days after installation - DAI) did not show significant differences between the controlled environment and the greenhouse. Analyzing the release data, 90% of the KCl was solubilized, leaving traces of its presence in the porous bags. Products K1 and K2 had released 75 to 80% of the potassium. Products K3, K4 and K5 had a release of approximately 67%, 42% and 33% of K, respectively (Figure 1).

It was observed that, in subsequent weeks, there was a reduction in the velocity of material released in all treatments and environments, observed by the lower slope of the release curve.

At the end of the 14 DAI, the control treatment was practically exhausted, with more than 99% of K released, a similar dynamic was found for the K1 and K2 products, with an average accumulated content of 94%. Products K3, K4 and K5 released 84%, 60% and 30% of K, respectively (Figure 1).

Analyzing the total nutrient released in the period, 21 DAI, we concluded that the K1 and K2 products did not differ, at 95% confidence, from the control treatment. The K3 product showed a reduction in release, both weekly and cumulatively, reaching the end of the test with about 94% release, however this product showed inferior performance to the K4 and K5 treatments. The K4 product resulted in a final accumulated total of around 65% release and K5 of 35%, the latter with the best performance, however when considering the percentage of coating, a significant amount of polymer applied 9.30% was observed (mass/mass ratio - m/m) (Table 1) (Figure 1).

The release of the treatments in the experiments in the greenhouse and in the controlled environment did not differ significantly, leading to the inference that the environmental parameters temperature and air humidity were not determinant for the solubilization of the fertilizers. Thus, the preponderant factor in solubilization, therefore, was soil moisture, responsible for hydration, solubilization and rupture of the polymeric capsule and, consequently, release of the fertilizer, as consolidated since Trenkel (1997).

It must be noted that up to 6.75% of polymer, which includes products K1, K2 and K3, most of the polymeric coating capsules were completely ruptured at the time of sample preparation, which reflects

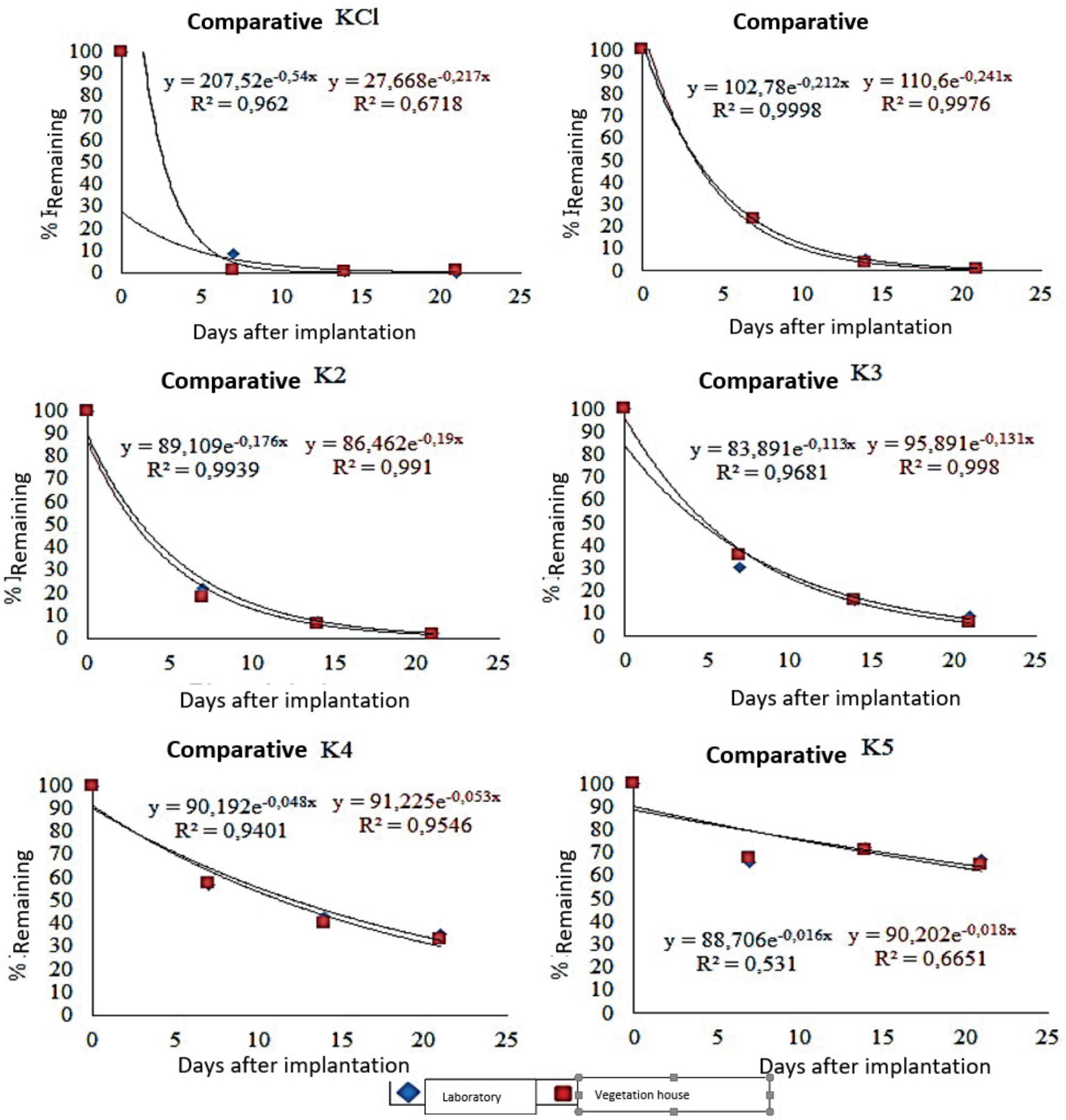

Figure 1. Release dynamics of treatments with and without coating during the evaluation period of the experiment

Treatment	Polymer	Release AC [1]*	Release CV [2] *
		---%---	
KCl	0,00	100,0 a	99,2 a
K1	5,05	98,8 a	99,3 a
K2	5,90	97,6 a	98,3 a
K3	6,75	91,1 b	93,9 b
K4	8,45	64,6 c	67,2 c
K5	9,30	32,7 d	35,0 d

Environments for carrying out the experiments: (1)AC = controlled environment (25°C); (2) CV = vegetation House; * means followed by the same letter, lowercase, in the column (within each environment) do not differ from each other by Duncan's test ($p<0.05$).

Table 1: Release percentages of coated fertilizers at the end of the experiment.

the loss of physical protection and the release pattern found, which did not occur with the K4 and K5 products, where the percentage of polymers was at least 8.45% (m/m) (Figure 1).

By observing the release pattern of the treatments, it was observed that the KCl output from the coating capsules showed exponential dynamics, that is, a greater portion of the fertilizer was released in the first collection of the experiment.

Treatments K1, K2 and K3 had values greater than 60% of release in the first collection performed and, although treatments K4 and K5 had a more controlled release of KCl, with values lower than 40% of the total released, the better release pattern adjusted the obtained curve, it was also the exponential (Figure 1).

The exponential release pattern allowed estimating the total period for capsule release. The estimate was performed by calculating the percentage release, called Average Velocity (Vm), characterized by an index that used data from the average of all release values and their standard deviations, thus verifying the daily percentage of release and the time necessary to provide 100% of the KCL (Table 2).

The arithmetic mean of the treatments was calculated and then the mean of one treatment was used to subtract the mean of a subsequent treatment, for example, mean of collection 2 subtracted from the mean of collection 1, for all collection times. The value obtained was divided by subtracting the DAI from the collections, in the same order used for the means (DAI collection 2 subtracted from the DAI collection 1). This same calculation procedure was performed for the standard deviation obtained from the treatments and, to calculate the daily Vm, the value of 100% was divided by the sum of all mean and standard deviation calculations (Equation 1 to 7).

$$\text{"Average treatment" ("by collection")} = \frac{\sum \text{Treatment}}{\text{number of treatments}} \qquad [1]$$

$$\frac{\Delta\text{"Average of treatments"}}{\Delta\text{Days}} = \frac{\text{"Average collection treatment 1 - Average collection treatment 2"}}{\text{"Collection Days 1 - Collection Days 2"}} \qquad [2]$$

$$\text{"Mean standard deviation of treatments (per collection)"} = \frac{\sum \text{"Standard deviations of treatments"}}{\text{number of standard deviations of treatments"}} \qquad [3]$$

$$\frac{\Delta\text{"Mean standard deviation of treatments"}}{\Delta\text{Days}} = \frac{\text{"Mean standard deviation of treatments collection 1-Mean standard deviation of treatments - collection 2"}}{\text{"}Collection\ Days\ 1 - Collection\ Days\ 2\text{"}} \qquad [4]$$

$$\text{"Overall average of treatments"} = \frac{\sum \frac{\Delta\text{"Average of treatments"}}{\Delta\text{Days}}}{\text{"}total\ number\ of\ collections\ performed\text{"}} \qquad [5]$$

$$\text{"Overall mean standard deviation of treatments"} = \frac{\sum \frac{\Delta\text{"Average standard deviation of treatments"}}{\Delta\text{Days}}}{\text{"}total\ number\ of\ collections\ performed\text{"}} \qquad [6]$$

$$\text{Average speed } (Vm) = \frac{-100}{\text{("Overall mean of treatments} \pm \text{Overall mean of standard deviation of treatments"}} \qquad [7]$$

Treatment	Number of days		
(Laboratory - AC)	Upper limit		Lower limit
KCl	28,1	--------	27,9
K 1	28,6	--------	28,3
K 2	29,2	--------	28,6
K 3	34,2	--------	29,7
K 4	55,2	--------	51,0
K 5	365,8	--------	216,0
Treatment	Number of days		
(Vegetation House - CV)	Upper limit		Lower limit
KCl	28,3	--------	28,3
K 1	28,4	--------	28,1
K 2	29,3	--------	28,1
K 3	31,3	--------	29,7
K 4	55,8	--------	44,9
K 5	256,5	--------	177,5

Table 2: Estimates of the days required for the total release of fertilizer from inside the coating capsules to the soil.

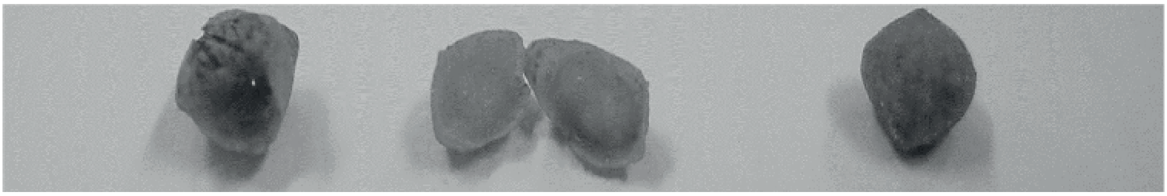

Figure 2: Example of fertilizer samples at the end of the experiment, after KCl release (thinner coatings – 5.05%, 5.90% and 6.75%)

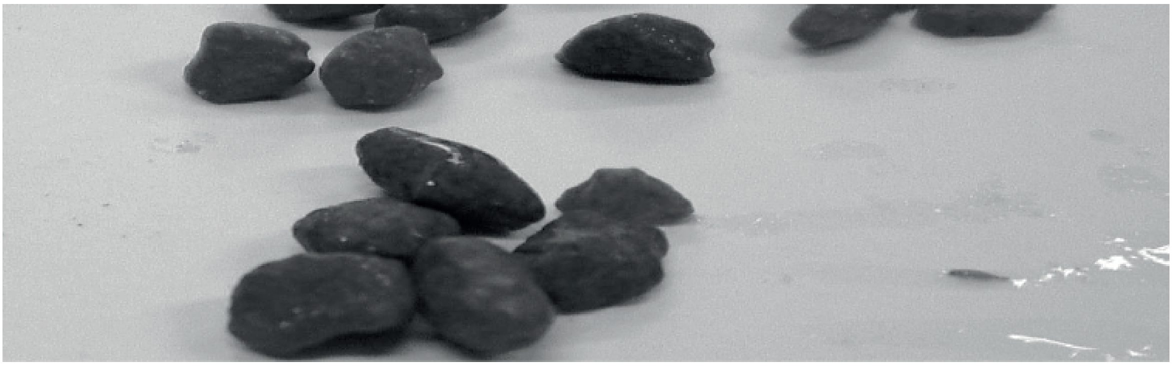

Figure 3: Example of fertilizer samples at the end of the experiment, after KCl release (thicker coatings – 8.45% and 9.30%)

The estimation of release days allowed estimating a release range between 28 and 35 days for treatments K1, K2 and K3, for both environments of the experiments (Table 2). The K4 treatment estimated a range of 45 to 56 days for release and, for the K5 treatment, between 177 and 365 days for the release of 100% of the fertilizer (Table 2).

It is important to emphasize that the highest values reached by the estimates were due to the exponential release dynamics, thus, most of the fertilizer was released in the first days of the experiment, with a small residual portion released in the last days of the estimated range (Figure 1). This point is essential to understand the dynamics obtained and carry out fertilization planning.

From the coverage percentages applied to the K4 treatment (8.45%), most of the capsules were intact, turgid and without apparent damage. These results show that, in fertilizers with lower percentages of polymer, the entry of water into the polymeric coating capsule, solubilizing the product through a possible osmotic effect, was accentuated in order to internally pressure the coating and, thus, rupture the capsule, exposing the fertilizer inside (Figures 2 and 3).

When considering the coating as a physical barrier for protection and release control, insufficient fertilizer coverage, as well as cracks or non-homogeneity in the coating, can lead to this type of breakage and, therefore, to the exposure of KCl (water-soluble), resulted in accelerated and intensified fertilizer release (Trenkel, 1997; Bognola, 2014).

KCl granules present variation in their particle size (0.8 to 3.4 mm in diameter), the smaller the particle, the greater the water permeation area, with a rough surface with edges and sharp points, high porosity and, low resistance to abrasion, making the coating an improvement in its mechanical property (Nascimento, 2014). However, given these morphological aspects, once the coating is broken, there is an accelerated release of KCl.

When considering the fertilizer under study, an input that presents great heterogeneity of the granules, a high number of edges and sharp points in its morphology, the possibility of non-uniformity in the coating could have been greater, with the aforementioned rupture of the capsule occurring (Figure 2). Therefore, such fertilizer granule morphology required a more rigid coating membrane and, if there was no rupture, the fertilizer was preserved inside the granules, which made the release more controlled and with greater longevity (release time) (figure 3). Greater contact between materials engineering professionals and agronomic engineering professionals is necessary, and the use of microscopic methods for better visualization of the dynamics of the capsules can increase the understanding of the release and the efficiency of the coating process, since, as it is of physical protection, flaws or cracks compromise technology concept.

Finally, more studies are necessary, since the literature has investigated aspects of reflections on the productivity of the application of coated products, but studies such as the one presented have not been developed, even though they are of fundamental importance for the knowledge and use of the technologies that arise every day on the market.

CONCLUSIONS

The physical coating of the fertilizer using polyurethane polymer, from 6.75% onwards, reduced the release of fertilizer over time and, as the percentage of coating increased, both in a greenhouse and in a controlled environment, it decreased up the release.

Fertilizer release met exponential dynamics, with a larger portion of the fertilizer released at greater intensity and speed at the beginning of the release process, and a small release at the end of the release estimate.

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