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Research Paper

Phosphate organomineral fertilizer based on banana peels and coffee ground waste

Fertilizante organomineral fosfatado a base de casca de banana e borra de café

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ABSTRACT: Population growth impacts all areas of society. Food production is one of the most pressing challenges resulting from population growth creating the need for optimized production and the application of innovative ideas in the agricultural sector to meet growing demands. A common method used to increase crop yields is the application of fertilizers. Aiming to reduce the impact of fertilizer application, specifically soil leaching, this study proposes the production of a slow-release organomineral fertilizer made from triple superphosphate. The proposed fertilizer was created via hand extrusion ensuring heterogeneity in the resulting fertilizer pellets. The sample F15 (9,2% of banana peel; 1,6% of starch; 57,3% of TSP and 32% of coffee waste) showed the slow-release time (1h for the release of 50% of the nutrients and 8h for the total release). Tests were then conducted seeking to analyze and improve their pyrolysis performance, biochar creation potential, and polymer coating in the soil. Test results enabled improvements to the fertilizer pellets via polymeric coating and thermal treatment. Both methods displayed good results, however, the thermal treatment method resulted in fertilizer loss due to unwanted reactions. Test results were analyzed using Weibull's kinetic model, which after great consideration, was deemed the most appropriate to analyze the properties of the proposed fertilizer. The development of pelleted and heat-treated organomineral fertilizers is promising because, in addition to saving the mineral fraction, it also provides an environmental benefit by reusing waste that would otherwise be thrown.

Keywords: phosphate fertilizer, slow release, thermal treatment, extrusion.

RESUMO: *Com o grande crescimento populacional, a agricultura precisa de uma maior eficiência cada vez mais e como forma de otimizar a produção, o uso de fertilizantes se tornou necessário. Para um melhor aproveitamento do fertilizante no solo, com o intuito de diminuir suas perdas, este trabalho propõe a produção de um fertilizante organomineral de liberação lenta a partir do superfosfato triplo. A partir disso, realizar análises de liberação e melhoramento em seu desempenho com pirólise, criando o biochar, e recobrimento com polímero. A criação dos fertilizantes foi realizada por extrusão manual, em que causou uma heterogeneidade nos pellets. A amostra F15 (9,2 de casca de banana, 1,6% de amido, 57,3% de TSP e 32% de borra de café) apresentou maior tempo de liberação (1h para liberar 50% odos nutrientes e 8h para liberação total). A partir desta amostra realizou-se um melhoramento com um recobrimento polimérico e tratamento térmico. Ambos os testes apresentaram um bom resultado, porém no tratamento térmico ocorreu perdas de fertilizante devido as reações indesejadas. O modelo cinético de Weibull foi o que mais se adequou para as análises de liberação. A obtenção de fertilizantes organominerais peletizados e submetidos a tratamento térmico é promissora, pois além da economia da fração mineral proporciona também um ganho ambiental devido ao reaproveitamento de resíduos que seriam descartados.*

Palavras-chave*: fertilizante fosfatado, liberação lenta, tratamento térmico, extrusão.*

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INTRODUCTION

The rise in the global population has resulted in the creation of large urban centers and technological development throughout human history. To meet increased demands in food production the agricultural sector underwent explosive growth in professionals in the field and innovations in farming techniques.

This rapid increase in technology and production capacity did not come without new challenges, such as the constant need for more fertile farmland, plagues that threaten crop yields, and soil damage. As a result, fertilizers were created to supplement crops with nutrients and to ensure maximum crop yields (JESUS; TEIXEIRA; SANTOS, 2019).

Brazil presents a very particular challenge when it comes to agriculture. The nation possesses ample farmland, and an ideal climate. However, the soil has a low phosphate content. Tests show that although the phosphate content is low, the soil has a great absorption capacity enabling the use of external phosphate sources. Phosphate is paramount in the growth cycle of crops, ensuring strong roots, healthy growth, and aiding photosynthesis (FREITAS et al. 2013; LOPES, 1998).

The surface runoff of rainwater, and erosion are natural processes that generate nutrient losses. In addition, adopted agricultural management practices, such as soil movement, and replacement of original vegetation by monoculture, end up attenuating the degree of soil degradation (SPADOTTO; GOMES, 2010). To combat nutrient loss strategies and technologies are in constant development to improve the use of nutrients by the soil in hopes of boosting the benefits of fertilizers and minimizing negative impacts. A promising solution is slow-release organomineral fertilizers. Organomineral fertilizers have a low reactive chemical potential compared to mineral fertilizers, however, their solubility is gradual throughout the development of a plantation, demonstrating a higher agronomic efficiency compared to the inorganic fertilizers (JESUS; TEIXEIRA; SANTOS, 2019).

Organomineral fertilizers release phosphate into the soil slowly, making its nutrients available to plant for longer periods of time. The transformed organic substance, rich in humic materials, can increase nutrient availability, especially for plant roots (KIEHL, 2008). The gradual solubility of phosphorus with organic matter is explained by the formation of phospho-humic complexes, absorbed more easily by plants; anion exchange of phosphate for the humate ion; coating of sesquioxide particles by humus, forming a protective layer, reducing the chances of phosphate fixation (TISDALE; NELSON, 1993).

This study aims to produce a slow-release organomineral fertilizer from triple superphosphate, coffee ground waste, and banana peel pulp. Mixtures of different compositions were pelletized via extrusion. The samples were then evaluated via the release of nutrients in the water. The best formulation was subjected to polymer coating and thermal treatment (TT) in a muffle, for the pyrolysis of the biomass, creating biochar. The samples were submitted to a nutrient release test. The kinetic release of nutrients of all samples were investigated, in order to classify the fertilizers as being of slow-release.

LITERATURE REVIEW

Fertilizers

Fertilizers contribute to the growth, health, and photosynthesis in the life cycle of plants. The agricultural sector uses fertilizers in the expansion, and maintenance of crop production, restoring nutrients to the soil that were lost during the harvest (SILVA; LOPES, 2011). Fertilizers are paramount to increasing crop yields.

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There are several elements essential for the normal development of plants. These elements are utilized by plants in different amounts and can be sorted into two categories. The macronutrients are nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), magnesium (Mg), carbon, hydrogen, and oxygen. The micronutrients are iron (Fe), boron, chlorine, iron, copper, manganese, molybdenum, zinc, sodium, silicon, and cobalt.

However, only seven chemical elements would be necessary for the development of plants, the macronutrients being: nitrogen (N), phosphorus (P), potassium (K), sulfur (S), calcium (Ca), magnesium (Mg) and micronutrients such as iron (Fe), varying according to the plant's needs (CABRAL, 2016).

Phosphorus (P) as phosphate (PO_4^{-3}) is essential for plant metabolism. Within the cell, this element plays an essential role in energy transfer, respiration, and photosynthesis. The energy absorbed by chlorophyll during photosynthesis is transformed into triphosphate adhesin (ATP), which is the first energy source required in plant development. The limitation of phosphorus (P) supplementation in the initial phase of crop development can directly affect the optimization of final production, as it influences productivity in later stages (HANSEL, 2013).

Organomineral fertilizers are considered a promising option to provide better results and better production quality (ANDRADE et al., 2012). The justification for the addition of mineral nutrients to organic fertilizers is to reduce the mineralization, fixation, and leaching of nutrients. In addition, these organic fertilizers have the inconvenience of not having defined proportions of NPK, unlike commercial formulas of mineral fertilizers, in which the composition can be balanced according to the needs of the plant and the soil.

To ensure better crop yields, and production quality, the use of organomineral fertilization is an alternative. Organomineral fertilizers are defined as: “products resulting from the physical mixture or combination of mineral and organic fertilizers”. Organic fertilizers have low concentrations of N, P, and K, to be complemented with the addition of mineral nutrients, on the other hand, the plants can better use the nutrients through the synchronism of slow release during plant growth. Organic residues promote an increase in pH, maintaining adequate levels of P and K in the soil, and reducing the loss of nitrogen by leaching due to its slower solubility. When these are associated with chemical fertilizers that contain phosphorus, and potassium in their composition, which can be balanced according to the characteristics of the soil and the requirements of the plant (RUPPENTHAL; CONTE, 2005).

In summary, the combined use of the application of organomineral fertilizers can generate greater efficiency when compared with the exclusive use of organic and inorganic fertilizers. The absence of some nutrients essential for crop development can be complemented by the combined use of different fertilizers, which may contain greater amounts of the missing elements in the soil (ANDRADE et al., 2012).

For ecological, economic, and social reasons, the reuse of coffee ground waste has been a priority among countries with large coffee bean production. Several reuse strategies of these substrates have been tested through composting, the manufacture of organic fertilizers, biogas, the manufacture of animal feed, and mushroom production (OLIVEIRA; COSTA; LIMA, 2014).

The physical properties of coffee ground waste (small particle size and high specific surface area) make this waste product an attractive alternative to help with water management in soils with low cohesion, such as acidic soils, which are more susceptible to erosion (KASONGO et al., 2013).

In arid or semi-arid regions, where water is a scarce resource or its availability for harvesting is scarce, some practices can be used to improve water retention and therefore

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help with water management. In addition, in areas with the occurrence of sandy soils or with large particle aggregation and hydraulic conductivity, the small specific surface area associated with other properties leads to the adsorption of less water. Therefore, the use of soil conditioners, which are products of minerals, industrial or organic origin (for example, gypsum, synthetic polymers, pruning residues, and sewage sludge) is an option to decrease the evaporation surface and water percolation (YANGYUORU et al., 2006). These materials provide water absorption and increase retention capacity, and the capacity to modify the physical-hydraulic properties of the soil along the soil depth, such as infiltration and water storage, improving its availability to plants (VALE et al., 2006).

Slow-release fertilizers are characterized by a delay in the availability of nutrients for absorption and use by plants after application, or by extending their availability in the soil to the plant for a longer period of time than conventional fertilizers (NASCIMENTO, 2014). This release of nutrients occurs according to the needs of the plant. Slow release occurs when soluble fertilizers are coated with hydrophobic organic polymers or inorganic sulfur coatings (AZEEM et al., 2014). Resins and thermoplastic polymers are also used for coating.

State of the Art Organomineral Fertilizers

For the development of this study, research was carried out to form a theoretical basis. **Table 1** shows some of these works present in the literature.

Research related to slow-release fertilizers has been developed for some time, with a great focus on the speed of nutrient release into the soil. **Table 1** demonstrates test results related to the development of coating films, and improvement through TT.

MATERIAL AND METHODS

The biomass used to formulate the pellets was derived from coffee ground waste. The coffee ground waste was collected from the canteen of the Institute of Technological and Exact Sciences - Unit 2 of the Federal University of the Triângulo Mineiro, located in the city of Uberaba in the state of Minas Gerais in Brazil. After collection, the material was dried in an oven at a low temperature (60°C) for 48 hours to avoid the risk of degradation of the organic matter. The fertilizer used was triple superphosphate (TSP). To prepare the pellets, the fertilizer must be in powder form (dp<500mm), then the fertilizer was ground with water to reduce the abrasion between the particles. Banana peel was added to the formulation as part of the binding material, according to the proportion defined by the experimental design. The material was then blended with a low amount of water. After milling the paste, it was sieved, and a strainer was used in the 500 µm opening.

Fertilizer formulation

All formulation used a fertilizer mass MF=179.15 g and coffee ground waste mass of M_{BC}= 100 g. So, the proportion of fertilizer mass and coffee ground waste was fixed at 1.8:1. In this work we used a Central Composite Design (CCD) to evaluate the effect of additives on the pellets resistance and release rate of nutrients. The factors evaluated at this work were the amount of banana paste (M_B) and starch mass (M_A), according to **Table 2**. So, the mass fraction of each component was calculated and reported at **Table 2.** The components were weighted and homogenized according to its respective masses, thus creating a moist, firm mass, suitable for extrusion, enabling the formation of pellets. After that, all the 16 mixtures were extruded manually, with an extrusion diameter of 6 mm.

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Table 1. Previous research present in the literature

Author	Title	Research Details
Machado e Souza (2012)	Availability of phosphorus in soils with different textures after application of increasing doses of slow-release mono ammonium phosphate	P availability was evaluated in soils with different textures, from the incubation of increasing doses of slow-release mono ammonium phosphate (MAP).
Domingues (2015)	Immobilization of phosphates in polymeric microspheres containing biochar: preparation, characterization and slow release in aqueous systems	The slow release of phosphorus by polymeric alginate microspheres containing biochar (pyrolyzed organic matter) was prepared, characterized, and evaluated in an aqueous medium.
Figueiredo et al. (2012)	Polymer-coated phosphate fertilizer and liming in production and corn morphological parameters.	The effect of the application of polymer-coated phosphate fertilizer, associated with liming, on the production and morphological parameters of the corn crop was evaluated.
Guareschi et al. (2011)	Early fertilization in soybean with triple superphosphate and potassium chloride coated with polymers	Sources, times, and doses of application and triple superphosphate and potassium chloride coated or not by polymers were compared on the productive performance of soybean under edaphoclimatic conditions of the savanna regions.
Liu et al. (2010)	Multifunctional slow-release organic-inorganic compound fertilizer	An organic-inorganic compound fertilizer that has attractive slow-release properties was prepared and a type of coating material capable of improving degradability, absorption, and water retention properties was developed.
Matoso (2018)	Biochars enriched with natural soils and phosphate fertilizer: characterization and application in tropical soils	Different combinations of raw materials (organic and mineral) were evaluated for the composition of biochar, to obtain a product capable of transporting the phosphate ion in the soil, protecting it from precipitation and adsorption reactions.
Zoca et al. (2014)	Coffee processing residues as a soil potassium amendment	Five types of coffee processing residues were characterized, their value as fertilizer was evaluated and the release of nutrients after application to the soil was investigated.
Pogorzelski et al., (2020)	Powdered ground chips TT (BC) +TSP	T = 350°C and t = 1 h; β =10°C/min; Blends: 5, 15 and 25% (w/w) of biomass. They reported a P release of 82% in 1.5 h
Barbosa et al. (2022)	Pellets based on Spent coffee grounds and TSP with TT: T= 300ºC,400°C; t = 10, 30, 90 min	The pellets treated at 400°C for 30 min had the slow-release rate of nutrients, about 3 times less than TPS.
Gonçalves et al. (2022b)	Pyrolysis of cellulosic residue from wasted dippers +TSP	The release time of 75% of nutrients was improved from 1.8 h to 750h after the TT

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Table 2. Design of the experiments varying the biomass derived from banana peels (M_B) and starch (M_A), with fertilizer mass MF=179.15 g and biomass derived from coffee ground waste M_{BC}= 100 g, as well as the mass fractions of bananas (f_B), starch (f_A), fertilizer (f_F) and coffee ground waste (f_{BC}).

Factors			Mass Fractions			
Sample	M_B [g]	M_A [g]	f_B	f_A	f_F	f_{BC}
1	8.379	1.464	0.029	0.005	0.620	0.346
2	8.379	8.536	0.028	0.029	0.605	0.338
3	48.866	1.464	0.148	0.004	0.544	0.304
4	48.866	8.536	0.145	0.025	0.532	0.297
5	0.000	5.000	0.000	0.018	0.630	0.352
6	57.245	5.000	0.168	0.015	0.525	0.293
7	28.622	0.000	0.093	0.000	0.582	0.325
8	28.622	10.000	0.090	0.031	0.564	0.315
9	28.622	5.000	0.092	0.016	0.573	0.320
10	28.622	5.000	0.092	0.016	0.573	0.320
11	28.622	5.000	0.092	0.016	0.573	0.320
12	28.622	5.000	0.092	0.016	0.573	0.320
13	28.622	5.000	0.092	0.016	0.573	0.320
14	28.622	5.000	0.092	0.016	0.573	0.320
15	28.622	5.000	0.092	0.016	0.573	0.320
16	28.622	5.000	0.092	0.016	0.573	0.320

Physical characterization of the pellets

Characterization of the size and shape of the pellets was carried out using the ImageJ software to determine the roundness, elongation, and perimeter (BONTEMPO et al, 2020).

A drop test was performed to assess their integrity. According to Carvalho and Brink (2010), this type of test aims to simulate the briquette transport handling conditions. The impact strength of the briquettes was analyzed by a drop test under the following conditions: briquettes not submitted to TT were dropped from a height of 0.3 meters; briquettes submitted to TT were dropped from a height of 1.5 meters.

Impact resistance is determined by the number of drops the briquette can withstand, breaking up only to the point where it loses at least 5% of its initial mass. The briquette is released from its respective height until it collides with a concrete bulkhead. The procedure is repeated successively until it has lost 5% of its initial mass.

The drop test was performed in triplicate, with each test covering falls from heights of 100 and 150 cm, for each of the samples produced.

Water release test

Water release analyses followed the method proposed by Pereira (2014). An apparatus was assembled in which the masses of 3 pellets with an average of 1.196 ± 0.178 g. were placed in a beaker immersed in an aqueous medium under agitation external to the beaker in 5 L of water for 24 hours. The proposed form of agitation is based on ensuring that the content of the active component measured in the liquid medium corresponds to the diffusion into the medium and not the mechanical action of the agitator.

Tests were performed at neutral pH, and at room temperature. The release was measured utilizing the electrical conductivity of the solution. A Vernier conductivity meter

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was used, and the data was read by the Logger Lite software every second for 3 hours. After this time, the material was disintegrated and stirred until the electrical conductivity remained constant. To obtain the final conductivity data all the fertilizer was released.

The data of electrical conductivity from the release test were analyzed using Excel Software. The fraction of release of nutrients along time can be defined by **Equation 1.**

$$X_N = \frac{\sigma_N}{\sigma_F} \quad (1)$$

where N is the sample point, σn is the electrical conductivity at point n, and σf is the final conductivity. After this data treatment, the nutrient liberation curves were obtained, which are proportional to the electrical conductivity of the solution.

Fertilizer Improvement Methods

Thermal treatment: The pyrolysis process was carried out in a muffle, at temperatures of 300ºC and 400ºC, and different TT times: 10, 20, 30, and 90 min for the sample with the shortest release time. About 15 g of pellets were weighed before and after each thermal treatment to assess weight loss. Then, these samples were submitted to a release test in a 5L agitated tank for 24 h, using the same method previously described (GONÇALVES et al, 2022b).

The use of this TT brings two benefits to fertilizers: the formation of biochar and the adsorption of phosphate in the pores of this charcoal. Carrying out the TT increases the number of active sites in the material, which favors the P adsorption of and provides its slow release in the soil.

Coating: The sample with the shortest release time was submitted to a coating process. This process was carried out with a polymer suitable for coating fertilizers, provided by the company *Paraíba Fertilizantes*. The coating process was carried out by immersion and placed in an oven at 60°C for 24 h.

Nutrient release kinetics in water

To understand the phenomena taking place during the release of P in water, two kinetic models used in release tests were adjusted, namely the Weibull Model **(Equation 2)** and the Korsmeyer-Peppas Model **(Equation 3)**.

$$X = \frac{M_i}{M_\infty} = 1 - \exp\left(-A \cdot t^b\right) \quad (2)$$

$$X = \frac{M_i}{M_\infty} = K \cdot t^n \quad (3)$$

where X is the ratio between the mass of fertilizer released at the time I (M_i) and the total mass of fertilizer in the pellet M_∞); A is a parameter of the Weibull model that defines the time scale of the process, b is an exponent that characterizes the curve as exponential (b=1, case I of diffusion), sigmoid curve, with ascending curvature followed by a return point (b>1, diffusion case II), or parabolic (b<1) (GONÇALVES et al, 2022a).

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RESULTS AND DISCUSSION

Physical characterization of the pellets

The pellets morphological analysis was performed using the ImageJ software, in order to determine some of their characteristics, such as elongation (1.207) and roundness (0.707). Thus, we can say that the sample is not long, like a cylinder, as obtained by Barbosa et al. (2022).

Table 3 presents the mean values of the number of falls and standard deviation for each sample. After the statistical analysis, it was not possible to verify the effect of the addition of starch and banana paste on the material resistance. The high value of the standard deviation of the samples referring to the central point (replications) indicates the heterogeneity of the material. The way of manual extrusion may have influenced the structure of the pellets, as well as the irregular shape of the pellets.

The organomineral fertilizer developed by Barbosa et al (2022), showed a maximum number of drops of 92 and 32 drops for heights of 100 cm and 150 cm, respectively. That is, the authors obtained a more resistant fertilizer than the one found in this study, which can be explained by the differences in the extrusion method, which used compaction forces of the extrudate.

Table 3. Means and standard deviation of sample drop tests

	Height – 1 meter		Height – 1.5 meters	
Sample	Average	Standard Deviation	Average	Standard Deviation
1	2.33	1.15	2.67	1.53
2	4.67	1.15	4.00	1.00
3	3.33	1.53	2.00	1.00
4	5.00	1.00	3.00	1.00
5	7.00	1.00	4.00	2.00
6	3.33	0.58	4.67	1.53
7	8.67	4.16	7.33	1.53
8	4.67	1.15	3.33	0.58
9	6.67	1.15	5.00	1.00
10	5.67	2.31	4.33	1.32
11	3.33	0.58	3.33	1.53
12	3.00	1.00	2.33	1.53
13	2.00	1.00	2.33	0.58
14	3.00	1.00	3.67	1.53
15	3.00	0.00	2.67	0.58
16	6.33	1.15	4.56	1.53

Release Test of P by Pallets in Aqueous Mediums

From the analysis of the data, the release curves of the 16 formulations were obtained. It was observed that formulation F15 presented the slowest release of nutrients under the test conditions, taking about 1h for the release of 50% of the nutrients and 8h for the total release. Samples F9 to F16 have the same composition, however, the same release rates were not obtained. This fact can be explained by the manual extrusion method.

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Manual extrusion cannot exert constant compression, force producing heterogeneous compaction pellets with empty spaces in their cores. Pellets with voids end up forming air bubbles in their core and the moment they are immersed in water, the bubbles tend to come out causing the breakdown of the pellet structure and releasing the fertilizer more quickly (BARBOSA et al., 2022). Sample F15 displayed the best results under the test conditions and was chosen for coating and TT.

Thermal treatment

Figure 1 shows the sample mass loss fraction curve with the thermal treatment time, at temperatures of 300°C and 400°C. The data shows that devolatilization occurs more quickly at the highest temperature, making the final mass of the samples under these conditions smaller. Thus, after 90 min at 400°C, there was a reduction of 41.2% in the initial mass of the pellets, with the initial percentage of organic matter in the pellet corresponding to 42.7% of the total mass. According to Barbosa et al (2022), the pellets thermally treated for 90 min were not suitable for transport and handling due its fragile mechanical structure.

During TT, the organic matter undergoes pyrolysis due to an oxygen-poor atmosphere, and a small loss of mass may also occur due to the combustion of part of the sample. It is believed that part of the fertilizer may be lost during this process as the fertilizer may be reacting with volatile byproducts emitted by sample during the TT (BARBOSA et al, 2022). Consequently, the samples were submitted to a release test to evaluate the release of phosphorus (P) in an aqueous medium.

Figure 1. Fraction of loss of mass (Mf/M0) of sample F15 after pyrolysis at 300°C and 400°C, in thermal treatment times of 10, 20, 30, and 90 min.

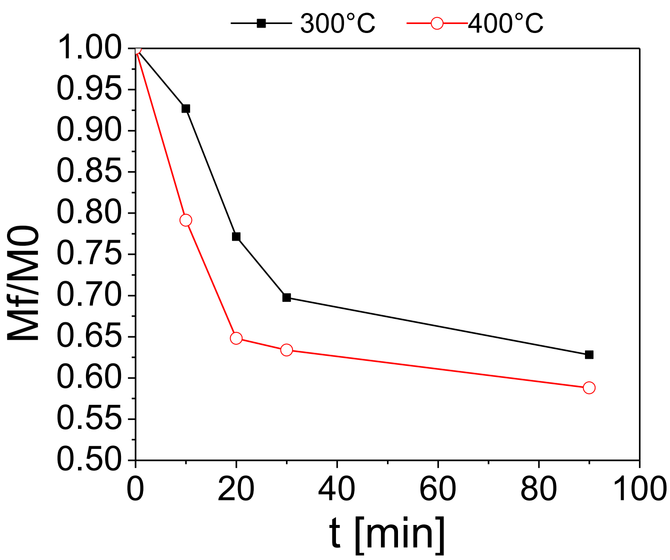

Table 4 presents the initial mass of the 3 pellets used in each of the release tests, before and after pyrolysis, as well as the value of the electrical conductivity of the solution measured experimentally at the end of the experiment (Co_{Exp} [μSc]) and the expected conductivity (Co_{Calc}), calculated from the mass of fertilizer present in the sample if all the fertilizer remained in the sample after TT.

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Table 4. Thermal Treatment conditions applied to sample F15: weight loss data during thermal treatment (**Mf/M0**) and electrical conductivity results from the release test

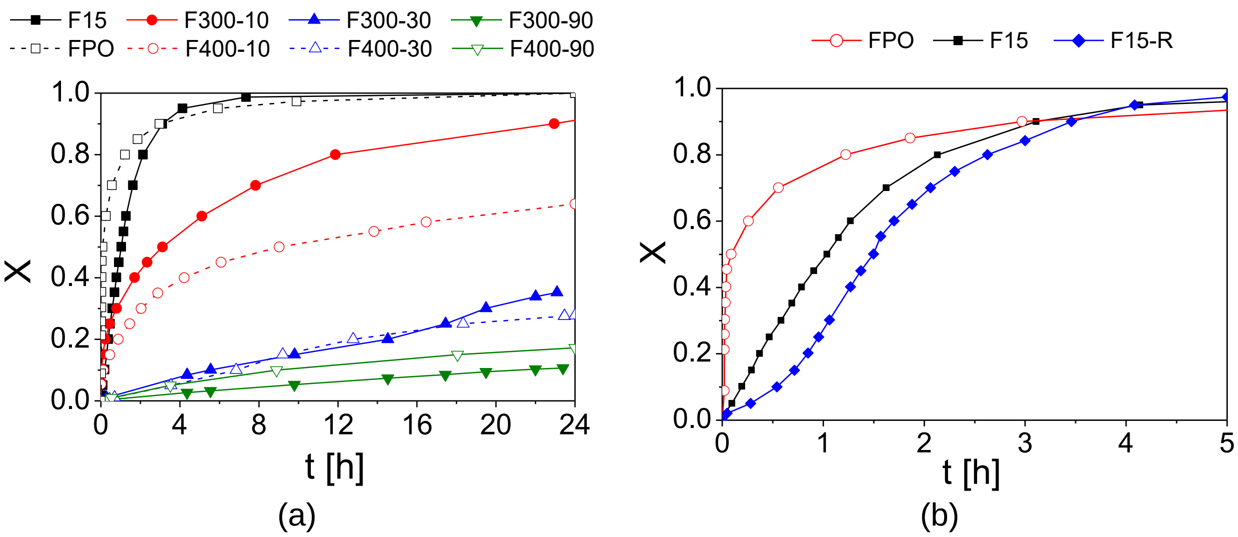
Sample	Factors		Thermal Treatment			Release Test	
	T [ºC]	t [min]	M0 [g]	Mf [g]	Mf/M0	Co_{Exp} [µSc]	Co_{Calc} [µSc]
F-300-10	300	10	1.658	1.537	0.927	123.8	135.1
F-300-30	300	30	1.271	0.887	0.697	62.3	105.2
F-300-90	300	90	1.248	0.784	0.628	25.1	103.4
F-400-10	400	10	1.543	1.221	0.791	73.3	126.1
F-400-30	400	30	1.844	1.169	0.634	89.6	149.5
F-400-90	400	90	1.333	0.784	0.588	41.2	110.0

The experimental electrical conductivity values were low for TT with longer exposure and higher temperature as well. Fertilizer loss can be observed, but the experiments should have a longer evaluation time to obtain certainty about the amounts lost. During a 90-min period, the conductivities are very low, indicating a very strong adoption of mineral fertilizer at this condition.

Barbosa et al (2022) studied the effect of time and temperature of thermal treatment over the nutrients release. The pellets submitted to the thermal treatment at 400 ºC for 30 min presented an increasing the half-life liberation time (t 50%), which was classified as slow release according to Trenkel's (2010) criteria (t15%> 24 h and t75%> 28 days). This demonstrated the significant potential of thermal treatment in the modification of particulate matrix.

Figure 2 shows the curves of the P release fraction of the samples from the TT. The fraction of P released during the TT was obtained using the calculated total electrical conductivity as a reference. The data shows that all heat-treated samples displayed a slower release of P than the F15 sample, confirming that the thermal treatment alters the particle structure so that the pellet does not disintegrate at the beginning of the release, as occurred with the F15 sample. It is noteworthy that higher temperatures and longer exposure times seem to lead to fertilizer losses.

Figure 2. Comparison of the phosphorus (X) release fraction of Sample 15 and powdered fertilizer with: (a) heat-treated samples at 300°C and 400°C; (b) coated F15 sample



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As the shape of the release curves changes, it is estimated that a change in the release of P mechanism in the samples may occur, which can be better evaluated by studying the Kinetic releases.

Gonçalves et al. (2022b) evaluated the composition of organomineral fertilizer based on cellulosic waste and TSP reporting a small reduction (20%) in the total P2O5 content after TT of the pellets.

Coating

Sample 15 was coated in preparation for the P-release tests. **Figure 2b** shows the release curves of the powdered fertilizer, Sample 15, and the coated sample (F15-R), where it is possible to verify that the coated sample releases slower than the pure powdered fertilizer and the F15 sample pellet.

Fertilizer Kinetic Release

Table 5 shows the parameters of the Weibull and Korsmeyer-Peppas (or Low Power) models estimated by non-linear regression using the Least Squares method, for all fertilizers examined in this study. In all cases, the Weibull model best represented the kinetic release of P in water. However, the best fit of this model may indicate a smaller contribution from diffusion and a greater contribution from dilution (SCHAFFAZICK; GUTERRES, 2002).

Most fertilizers pelleted by manual extrusion, according to the Central composite design (CCD) shown in Table 1, had the parameter $b>1$. According to Papadopoulou et al. (2006), the parameter b is an indicator of the transport mechanism of a substance through a particle-matrix, where $b \leq 0.75$ indicates Fickian diffusion. When $0.75<b<1$, a combined mechanism occurs, associating Fickian transport with Case-II transport, resulting from swelling/relaxation of the solid matrix (or release upon erosion), which involves the transition from a semi-rigid state to a more flexible one (LOPES et al, 2005).

The parameter n in the Korsmeyer-Peppas model is also used to indicate the release mechanisms, and for cylindrical particles. $n<0.45$ indicates a quasi-Fickian type release, characterized by the dispersed flux of the concentration along the particle. $n=0.45$ indicates a Fickian diffusion release. The result $n=0.89$, as shown in Equation 3, corresponds to zero-order kinetics, in which the transport mechanism of Case II predominates. In the range $0.45<n<0.89$, combined or anomalous transport occurs, combining the diffusion and transport mechanisms of Case II.

Observing the estimated b and n values for fertilizer samples F9 to F16, it is possible to confirm that the form of extrusion applied produced heterogeneous pellets, with different release mechanisms, presenting b values between 0.847 and 1.491, which also suggests that there was particle erosion due to the swelling phenomenon, which was observed visually during the release test in an aqueous medium. The same was observed in the other fertilizer Samples (from F1 to F8), although it was not possible to evaluate the influence of the additives used in the formulation on the kinetics, due to the heterogeneity of the pellets.

Regarding the powdered fertilizer (FPO) kinetics, it is observed that $b=0.3788$ and $n=0.1185$, indicating that the predominant mechanism is Fickian diffusion, since there is no matrix holding the powder, it dissolves, and the P diffuses from the small Becker to the middle of the fluid. This result agrees with those reported by Barbosa et al. (2022) and Gonçalves et al. (2022a,b) for the same TSP fertilizer.

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Table 5. Parameters of the Weibull and Korsmeyer-Peppas models

	Weibull Model $X=\frac{M_i}{M_\infty}=1-\exp\left(-A\cdot t^b\right)$				Korsmeyer-Peppas Model $X=\frac{M_i}{M_\infty}=K\cdot t^n$			
	Parameters		Standard Deviation	R^2	Parameters		Standard Deviation	R^2
F1	A	1.0401	0.0005	0.9986	K	0.6081	0.0009	0.9634
	B	1.0017	0.0008		n	0.4752	0.0018	
F2	A	1.8044	0.0025	0.9925	K	0.7221	0.0012	0.8539
	B	1.3155	0.0023		n	0.3840	0.0021	
F3	A	1.2049	0.0013	0.9887	K	0.6477	0.0011	0.8473
	B	1.1789	0.0020		n	0.3492	0.0016	
F4	A	1.0719	0.0010	0.9956	K	0.6146	0.0011	0.9388
	B	1.0970	0.0016		n	0.4851	0.0023	
F5	A	1.1422	1.1422	0.9974	K	0.6278	0.0012	0.9335
	B	1.1571	1.1571		n	0.4919	0.0025	
F6	A	1.7246	0.0021	0.9961	K	0.7323	0.0014	0.8916
	B	1.1142	0.0018		n	0.3789	0.0025	
F7	A	1.5541	0.0016	0.9954	K	0.7154	0.0013	0.8930
	B	0.9812	0.0015		n	0.3449	0.0021	
F8	A	1.8627	0.0045	0.9903	K	0.7428	0.0021	0.8041
	B	1.0727	0.0034		n	0.2584	0.0026	
F9	A	1.1267	1.1267	0.9953	K	0.6165	0.0015	0.9259
	B	1.3801	1.3801		n	0.5524	0.0031	
F10	A	1.2253	0.0019	0.9938	K	0.6394	0.0016	0.9072
	B	1.4913	0.0033		n	0.5168	0.0032	
F11	A	1.6964	0.0008	0.9993	K	0.7324	0.0013	0.9144
	B	1.1271	0.0008		n	0.4008	0.0024	
F12	A	1.5049	0.0006	0.9994	K	0.7094	0.0010	0.9429
	B	1.0558	0.0006		n	0.4224	0.0020	
F13	A	1.2566	0.0029	0.9871	K	0.7022	0.0027	0.7223
	B	1.0766	0.0039		n	0.1876	0.0022	
F14	A	1.5476	0.0010	0.9975	K	0.7292	0.0009	0.9387
	B	0.8465	0.0009		n	0.3414	0.0016	
F15	A	0.6848	0.0008	0.9983	K	0.5420	0.0024	0.8888
	B	1.0803	0.0015		n	0.3554	0.0030	
F16	A	0.8657	0.0003	0.9991	K	0.5502	0.0009	0.9694
	B	1.1303	0.0006		n	0.5701	0.0019	
FPO	A	1.5166	0.0010	0.9869	K	0.7660	0.0006	0.9099
	B	0.3790	0.0005		n	0.1196	0.0005	
F15-R	A	0.3587	0.0009	0.9971	K	0.6009	0.0038	0.6550
	B	1.5568	0.0032		n	0.1942	0.0025	
F300-10	A	0.3733	0.0006	0.9957	K	0.3715	0.0007	0.9802
	B	0.5755	0.0006		n	0.2924	0.0007	
F300-30	A	0.0150	0.0001	0.9779	K	0.0173	0.0001	0.9831
	B	1.0511	0.0032		n	0.9476	0.0025	
F300-90	A	0.0079	0.0000	0.9994	K	0.0081	0.0000	0.9994
	B	0.8504	0.0004		n	0.8226	0.0004	
F400-10	A	0.2687	0.0003	0.9924	K	0.2465	0.0003	0.9833
	B	0.4223	0.0005		n	0.3110	0.0006	
F400-30	A	0.0249	0.0002	0.9729	K	0.0281	0.0002	0.9674
	B	0.8239	0.0026		n	0.7338	0.0025	
F400-90	A	0.0249	0.0002	0.9589	K	0.0257	0.0002	0.9573
	B	0.6438	0.0025		n	0.6061	0.0024	

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As for the coated fertilizer sample F15, the value of b=1.557 indicates a sigmoid-shaped curve, in which the swelling of the pellets controls the release of P. During the test, a gradual swelling of the particle and the dissolution of the internal part were visually observed, even if the outer membrane is not ruptured. At the end of the test, the internal solid matrix had already been dismantled. Despite this, the coating layer increased the release time of P.

Regarding heat-treated pellets, it is observed that there was a decrease in the A scale parameter when compared to untreated extruded fertilizers and FPO. The lower the A parameter, the lower the phosphorus release rate. As for the mechanism, it is observed that only the F300-30 presented b>1 and the others had values of b between 0.42 and 0.85, indicating that the treatment altered the matrix structure of the pellets, introducing the effect of Fickian diffusion, thus decreasing the fertilizer release rate in an aqueous medium. However, as previously mentioned, it is believed that the thermal treatment altered the amount of fertilizer present in the pellet, and it is more appropriate to work with low thermal treatment times, between 10 and 20 min, to reduce the possibility of unwanted reactions that cause the fertilizer loss.

Table 6 compares the releasing time of 50% of nutrients for the powder TSP sample (FPO), the F15 sample, The coated sample (F15-R) and the samples with thermal treatment.

Table 6. Comparison of the time in which there was a release of 50% of P ($t_{X=0,5}\ [h]$) present in powdered fertilizer (FPO), extruded F15 and coated fertilizer (F15-R), as well as heat-treated fertilizers

	FPO	F15	F15-R	F300-10	F300-30	F300-90	F400-10	F400-30	F400-90
$t_{X=0.5}\ [h]$	0.127	1.0115	1.527	3.12	38.41	194	9.03	56.6	174.9

The data demonstrates pellet sample 15, extruded by hand, took about 8 times longer to release 50% of its P content, when compared with the powdered fertilizer, showing that the extruded pellet has superior slow-release capabilities. As for the effect of the coating, sample F15-R released its nutrients 50% slower than the uncoated pellet. The heat-treated samples displayed the best slow-release capabilities, between 3 and 194 hours to release 50% of the fertilizer nutrients making them available for longer periods of time during the life cycle of plants.

Sample F300-10 slow-release capacity was 24 times greater than that of powdered fertilizers, and 3 times greater than sample F15 which was not heat-treated, demonstrating the potential of thermal treatment in altering the particle matrix of pelleted fertilizers, reducing the effects of the swelling mechanism, and providing a greater effect of release by the Fickian diffusive mechanism (GONÇALVES et al., 2022b).

The organomineral fertilizer with TT developed by Barbosa et al (2022), based on spent coffee grounds, showed the kinetics of nutrient release controlled by a Fickiano diffusion mechanism according to the Weibull Model (A= 0.013 and B=0.667). The value of A found by the authors is much lower than those found in this work, showing that they obtained longer release times.

Gonçalves et al (2022a) produced an organomineral fertilizer using a cellulosic residue from wasted diapers. The kinetic release of P from the pellets without TT followed the Weibull Model (A=0.014 and B = 0.512). Gonçalves et al. (2022b) performed the of the pellets at 500ºC for 10 min. The mean release mechanism still was the Fick diffusion, and the kinetics was described by Weibull Model (A = 3 x10^{-6} b = 0.940). So, the release time of 75% of nutrients was improved from 1.8 h to 750h, confirming the slow-release propriety.

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The fertilizers with TT have several advantages, including the ability to generate longer periods of nutrient release. These characteristics have an impact on reducing the fertilizers losses by leaching and enhancing nutrient bioavailability, which increases the crop growth.

CONCLUSION

Across 16 formulated fertilizer samples, the heterogeneity in the formation of the pellets was verified, which can be explained by the manual extrusion method utilized in the formation of the pellets. Given the heterogeneity of the pellets, it was not possible to analyze the influences of additives in the formulations made by planning the central compound.

Through the release tests carried out in aqueous mediums, it was possible to analyze the release curves of each sample, with sample F15 having the shortest release time.

The improvement tests of the organomineral fertilizer, applied to sample F15, showed greater efficiency in its performance. The sample coated with the polymer had a release time 8 times shorter than that of the uncoated sample F15.

The thermal treatment displayed greater improvements in the pellet matrix, however, tests demonstrated probable loss of fertilizer due to unwanted reactions with volatile byproducts emitted by the sample during the test. Thermal treatment with a short exposure time is recommended to mitigate this issue.

The Weibull model best described the kinetics of phosphorus release in aqueous mediums, having a greater contribution to dilution.

In future studies, the production of fertilizers through mechanical extrusion is recommended to ensure homogeneity across the samples; performing the release analysis for a longer time for heat-treated samples, until constant conductivity is obtained; testing other binders, such as lignin and sugarcane molasses.

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