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Development and evaluation of slow-release organomineral phosphate fertilizer based on coffee waste

Desenvolvimento e avaliação de fertilizante organomineral fosfatado de liberação lenta à base de borra de café

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ABSTRACT

Slow-release fertilizers are sustainable alternatives to soil nutrition that can effectively enhance agricultural productivity. In this study, we formulated slow-release organomineral fertilizers using spent coffee grounds (SCG) impregnated with triple superphosphate (TSP). The effects of the composition of the fertilizer on pellet resistance and P release capacity were evaluated, along with heat treatment at different temperatures and times. The pellets with 10 g sugarcane molasses and 2.5 g TSP per gram of SCG, dried at 100 °C, presented the best mechanical resistance, releasing about 90% P in 13.8 h. The release kinetics of these pellets followed the Korsmeyer-Peppas model, controlled by Fickian diffusion. The fertilizer thermally treated at 400 °C for 30 min was classified as a slow-release fertilizer, as it released 90% P in 793.3 h. Thus, the partial carbonization of biomass promoted P adsorption to the surface of the porous matrix of the pellets, allowing the slow release of nutrients. Overall, we found that pelletized OMFs can be used as sustainable and inexpensive fertilizers derived from waste biomass; thus, their application can contribute to eco-friendly agricultural practices.

Index terms: Extrusion; release kinetics; thermal treatment; fickian diffusion; sustainable agriculture.

RESUMO

Os fertilizantes de liberação lenta podem ser usados como alternativa sustentável para a nutrição do solo e aumento da produtividade industrial. Este trabalho formulou fertilizantes organominerais de liberação lenta a partir de borra de café impregnado com superfosfato triplo. Nós avaliamos o efeito da composição de fertilizantes na resistência do pellet e capacidade de liberação de P e o tratamento térmico a diferentes temperaturas e tempos. Os pellets com 5 g de do ligante de melaço de cana e 2,5 g de TSP/g SC, secos a 100 ºC, apresentaram a melhor resistência mecânica, liberando 90% de P em 13,8 h. A cinética de liberação seguiu o modelo de Korsmeyer-Peppas, sendo controlada pela difusão Fickiana. O fertilizante tratado termicamente a 400 ºC por 30 min foi classificado como de liberação lenta, liberando 90% de P em 793,3 h. Assim, a carbonização parcial da biomassa promoveu a adsorção de P na matriz porosa dos pellets, permitindo a liberação lenta dos nutrientes. No geral, este estudo demonstra o potencial dos OMFs granulados como fertilizantes sustentáveis e de baixo custo derivados de biomassa residual, contribuindo para práticas agrícolas ambientalmente sustentáveis.

Termos para indexação: Extrusão; cinética de liberação; tratamento térmico; difusão Fickiana; agricultura sustentável.

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Introduction

The food crisis is a serious challenge, especially considering that the global population is projected to reach 8.6 billion by 2030 (Da Costa et al., 2019). To address this problem, the United Nations proposed the Sustainable Development Goal (SDG 2), which aims to eliminate hunger, ensure food security, improve nutrition, and promote sustainable agriculture by 2030 (Sim et al., 2021).

Soil fertilization is necessary for increasing agricultural yield, especially in areas where soil fertility is low (Alberto et al., 2022). Natural resources, such as phosphate, nitrates, and potassium, which are essential for producing fertilizers, are limited and can directly affect food production (Stoppe et al., 2023). A steady depletion of the reserves of phosphate rocks, coupled with an increase in demand, necessitates the development of innovative and efficient methods to produce phosphorus fertilizers. To address these challenges, researchers have investigated various strategies to develop alternative P fertilizers that optimize nutrient utilization, reduce losses, and minimize environmental impact.

In contrast, researchers have investigated whether the recycling of animal and vegetable waste is a feasible means to achieve a more natural production of agricultural products. Novel approaches are constantly being developed and tested, highlighting the possibility of adopting new methods to convert organic waste streams into value-added products like biochar (Silva et al., 2022), nitro-humic fertilizers (Sarlaki et al., 2023), and artificial humic acids, such as lignin-rich biogas digestate (Sarlaki et al., 2024).

Organomineral fertilizers (OMFs) are a promising alternative to conventional fertilizers (Carneiro et al., 2021). They help decrease nutrient leaching, improve water and air quality, and increase soil organic matter content (Wang et al., 2022). The development of organic and organomineral fertilizers has advanced significantly in recent years (see Table 1), conforming to sustainability and the concept of circular economy.

Thermal treatment techniques, such as co-pyrolysis, are used to produce slow-release organomineral fertilizers (Luo et al., 2021), transforming biomass into biochar (Santos et al., 2019). In these fertilizers, also known as biochar-based fertilizers (BBF), biochar enhances nutrient retention and slows down nutrient release, thus improving soil fertility and promoting sustainable agricultural practices.

The BBFs synthesized via the co-pyrolysis of biomass and mineral P sources often have considerable benefits, such as simplicity of synthesis, high P loading, and excellent slow-release function. Thus, the efficiency of the growing crops to absorb P may increase. Slow-release fertilizers can be used as an alternative to reduce the need for frequent fertilization and the associated labor costs. As they release nutrients at a slower rate than traditional fertilizers, they prolong the nutrient availability for plant uptake, decrease leaching into groundwater, and reduce crop production costs (Wang et al., 2022).

Furthermore, the disposal of spent coffee grounds (SCG), a byproduct of coffee consumption, is an environmental challenge. As coffee is commonly consumed around the world, the accumulation of SCG has become a significant global waste management issue (Colantoni et al., 2021).

Although OMFs have several benefits, their application faces several challenges associated with their formulation, mechanical properties, and nutrient release kinetics, necessitating the development of alternative fertilizers.

In this study, we proposed a novel approach to address these challenges by developing pelletized slow-release OMFs using spent coffee grounds (SCG) and triple superphosphate (TSP) as raw materials to create a sustainable and cost-effective fertilizer solution that conforms to the principles of circular economy and environmental management (Carneiro et al., 2021).

We first assessed the composition of the OMF using a 2^3 factorial design to investigate the effect of binder addition, TSP, the SCG mass ratio, and drying temperature on pellet integrity and phosphorus (P) release performance. Subsequently, the formulation that exhibited slower P-release characteristics underwent thermal treatment (TT) for biomass carbonization. The drop resistance tests and P-release tests in water were conducted on all samples. To elucidate the primary mechanisms associated with the release of P, the kinetic parameters of the Weibull and Korsmeyer-Peppas models were adjusted accordingly. Overall, the proposed solution might advance the field of sustainable agriculture by offering a viable alternative to conventional fertilizers.

Material and Methods

In this section, the procedures used to synthesize, analyze, and evaluate the pelletized OMF from SCG and TSP are outlined. We specifically described pellet formulation, characterization methods, such as proximate analysis and FTIR, mechanical testing, and nutrient release experiments, and a release kinetic study.

Biomass Characterization

The biomass used was spent coffee grounds (SCG) obtained from a local coffee shop in Uberaba City, Brazil (Batista Jr et al., 2017). The SCG was initially washed and then dried at 70 °C for 24 h. Finally, it was classified by sieving and exhibited a mean Sauter diameter of 0.2893 mm.

Elemental analysis was conducted using CHNS/O 2400 Perkin Elmer equipment, which estimates the percentage of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). The oxygen content (%O) was calculated by difference.

Proximate analysis was conducted in triplicate following ASTM standards. This included determining moisture on a wet basis (ASTM E871), extractives (ASTM D1105), volatile matter (ASTM E872-82), fixed carbon, and ash content (ASTM E1755-01). The main SCG functional groups were identified by Fourier-transform infrared spectroscopy (FT-IR) analysis using a spectrophotometer Platinun-atm/Alpha, Bruker at a range of 4000–400 cm^{-1}, with a resolution of 4 cm^{-1} and 32 scans.

Formulation of organomineral fertilizers

Spent coffee grounds were used as the organic source, triple superphosphate (TSP) as the phosphorus mineral source, and sugarcane molasses as the binding component. A 2^3 factorial design with three replicates at the center point was used to ascertain the optimal formulation of the organomineral fertilizer. The influence of three factors on the response to pellet quality was investigated; the three factors included the percentage of molasses (M), the mass ratio of TSP to SCG (R), and the drying temperature (T_s), as indicated by Equations 1, 2 and 3, respectively.

Table 1: Some published studies on the kinetics of nutrient release and the production and evaluation of BBFs.

Reference	Objective	Conclusion
Jamnongkan and Kaewpierom (2010)	NPK slow-release fertilizers were produced using glutaraldehyde, PVA, glycerin, and a binder solution.	Kinetics of P release were well represented by the KP Model (n < 0.5 quasi-Fickian release). The value of the K parameter was between 0.6016 and 0.6875.
Noppakundilograt et al. (2014)	OMF NPK was produced through chitosan impregnation	Release rate was lower when chitosan was present. The kinetics were represented by the Korsmeyer-Peppas model and governed by quasi-Fickian diffusion.
Gwenzi et al. (2017)	Granulated sawdust biochar was pyrolyzed at 500 °C for 1 h, with NPK fertilizer and starch-PVA binder.	Release patterns were obtained using the sequential leaching method with water. About 50% of the final P concentration was released by the fifth day, whereas 90% of the final P concentration was released by the 25th day.
Lustosa Filho et al. (2020)	Pyrolysis of chicken litter and TSP was catalyzed by H_3PO_4 and/or MgO, at 500 °C for 2 h at a heating rate of 10 °C.min^{-1}. The mass ratio between the P source and biomass was 0.5:1.	Results showed that after the first cultivation cycle, the BBF promoted a higher crop yield than TSP fertilization. The BBF also demonstrated the potential for the slow release of P.
Buss et al. (2020)	Pyrolysis of sewage sludge at 700 °C was performed after doping it with 5% potassium acetate.	Percentage of water-extractable total P content increased by 237 times compared to undoped biochar. Due to this easy and inexpensive modification, sewage sludge can generate a safe biochar fertilizer with customized P availability that also supplies K, which improves soil properties and C sequestration.
Luo et al. (2021)	A BBF was developed by the co-pyrolysis of corn straw doped with $MgCl_2$ and biogas effluent.	Limited solubility of Mg-P precipitates on the surface of biochar influenced the slow-release performance of P. Also, BBF considerably promoted the development of corn crops.
Carneiro et al. (2021)	A BBF was developed by co-pyrolysis of coffee husk (CH) and poultry litter (PL) doped with phosphoric acid and magnesium oxide at 500 °C for 2 h.	A total P release of 6.47% (CH) and 8.99% (PL) was recorded in 1 h, which characterized the sample as a slow-release fertilizer. Thus, the production of slow-release P fertilizers was possible. Initially, P availability was limited but later increased due to fertilizer dissolution.
Yan et al. (2021)	Contribution of BBFs to the restoration of karst-degraded soils was evaluated.	BBFs stimulated an increase in the quantity and variety of soil microbes. Thus, more keystone species in the soil microbial network participated in soil carbon resource management and nutrient cycling.
Lv et al. (2021)	Immobilization of Cd in soil was investigated using a BBF consisting of rice husk biochar, lime, and inorganic fertilizers.	BBF improved the heavy metal immobilization in soil, which decreased its bioavailability and mobility in the soil. This occurred due to the presence of active functional groups, high pH, and abundance of micro-porous structures in biochar. The application of BBF in crop production helped reduce soil Cd bioavailability, and hence, plant absorption in Cd-contaminated rice fields.
Teixeira and Santos (2023)	A slow-release BBF was developed by co-pyrolysis of coffee waste, triple superphosphate, banana peel, and starch.	The best formulation consisted of 9.2% banana peel, 1.6% starch, 57.3% TSP, and 32% coffee waste, treated at 300 °C for 10 min. The slow-release capacity was 24 times greater than powdered fertilizers and three times greater than the sample without heat treatment.
Wang et al. (2022)	BBFs were synthesized via co-pyrolysis of biomass and mineral P source	The method had considerable benefits, such as simplicity of synthesis, high P loading, and excellent slow-release function. Thus, the efficiency of the growing crops to absorb P may increase.

$$X_1 = \frac{M - 5\%}{5\%} \quad (1)$$

$$X_2 = \frac{R - 2.0}{0.5} \quad (2)$$

$$X_3 = \frac{T_s - 80°C}{20°C} \quad (3)$$

Each formulation consisted of a mixture weighing 30 g, in which the mass fractions of molasses, TSP paste, and biomass were predetermined according to the parameters of the experimental design. The mixtures were agitated and homogenized for 5 min to ensure uniformity. Subsequently, the homogeneous mixtures were manually extruded to form pellets, with an average height of 1.2 ±0.124 cm and a diameter of 0.6 cm. Following extrusion, the pellets were weighed and dried at temperatures specified in the experimental design to achieve the desired characteristics.

The initial moisture content of the pellets was determined by the gravimetric analysis conducted in an oven at 105 °C for 24 h, according to Equation (4):

$$U_{bu} = \frac{M_0 - M_s}{M_0} \quad (4)$$

Here, U_{bu} indicates the wet basis moisture of the pellet, M_0 indicates the original pellet mass, and M_s indicates the dry pellet mass.

The drop test and nutrient release in water were conducted on all formulations. The acquired experimental data were statistically analyzed in order to evaluate the effect of fertilizer composition on the responses. This analysis involved the utilization of a hypothesis test utilizing Student's t-distribution at a significance level of 5% ($p < 0.05$).

Drop Resistance Test

In the drop test, five pellets were dropped from each sample from starting heights of 100 cm and 150 cm, until the sample lost more than 5% of its initial mass. The method proposed by Carvalho and Brinck (2010), according to which 10 drops is the maximum number of drops for briquettes exposed to heat treatments, was implemented in this test.

Nutrient release in water

A previously described method was used to assess nutrient release in an aqueous medium. Briefly, a pellet was placed in a 50 mL beaker, which was immersed in a 5 L vessel under vigorous agitation. The quantity of nutrients released over time was measured by the electrical conductivity of the fluid, using a Vernier conductivity meter. The data were collected online using the Logger Lite software every second for 3 h. Next, the conductivity was monitored until the release was complete and the conductivity reached a constant value.

From the collected data, the standard conductivity (C) was calculated using Equation (5), where C_n indicates the recorded conductivity and C_0 indicates the initial conductivity of distilled water.

$$C = C_n - C_0 \quad (5)$$

We assumed that the rate of phosphorus release at time *i* (*X*) was proportional to the release of total nutrients, estimated by Equation (6), where C_i indicated the conductivity along C_∞ (final conductivity).

$$X = \frac{C_i}{C_\infty} \quad (6)$$

The release test was performed on different formulations and the best formulation was subjected to subsequent heat treatment. From these release data, the responses of release times at 15%, 50%, 75%, and 90% were obtained, which were used to evaluate and classify the fertilizers and determine the nutrient release kinetics. The criterion for classifying the fertilizer as slow-release was defined by the European Committee for Standardization (CEN). As per the criterion, a maximum release of 15% within 24 h ($t_{15\%}$> 24 h) and 75% within 28 days ($t_{75\%}$> 28 days) is considered to indicate slow release (Trenkel, 2010).

Kinetics and Mechanisms of Nutrient Release

To describe the release of fertilizer in water, Weibull and Korsmeyer-Peppas (KP Model) kinetic models were adjusted, represented by Equations (7) and (8), respectively (Jamnongkan & Kaewpirom, 2010).

$$X = \frac{C_i}{C_\infty} = \frac{M_i}{M_\infty} = 1 - \exp\left(-A \cdot t^b\right) \quad (7)$$

$$X = \frac{C_i}{C_\infty} = \frac{M_i}{M_\infty} = K \cdot t^n \quad (8)$$

Here, M_i represents the weight of nutrients released at time *I*, M_∞ represents the total weight of the released nutrients at equilibrium, and *t* represents time.

The parameter 'A' of the Weibull Model defines the timescale of the process. According to Papadopoulou et al. (2006), the parameter 'b' indicates the transport mechanism of a substance through a particle matrix. When $b \leq 0.75$, Fickian diffusion occurs; when $0.75 < b < 1$, a combined mechanism occurs, associating Fickian diffusion with the swelling/relaxation of the solid matrix (or release upon erosion), involving the transition from a semi-rigid state to a more flexible one, known as Case-II transport (Lopes et al., 2005).

According to Siepmann and Peppas (2000), the exponent ‘n’ of the Korsmeyer-Peppas model also indicates the release mechanism. For a cylindrical particle, $n < 0.45$ indicates a quasi-Fickian type of release characterized by the dispersed flux in concentration along the particle; $n = 0.5$ represents a Fickian diffusion release mechanism. For $0.5 < n < 0.89$, an anomalous or combined transport occurs. Finally, when $n = 0.89$, it indicates Case II transport. The K parameter represents the release speed.

Thermal Treatment

The formulation with the lowest release rate underwent thermal treatment (TT). Tests were conducted in triplicate at 300 and 400 °C, with TT durations of 10, 20, 30, and 90 min. Approximately three pellets were placed in ceramic crucibles with lids and heated to the specified temperature for a set duration in the muffle furnace. The samples were weighed before and after each TT to assess mass loss resulting from the thermal decomposition of the biomass in the sample. As the atmosphere in the muffle furnace was not inert, combustion and pyrolysis reactions occurred, leading to a loss of mass of the material.

Pellets that were heat-treated also underwent the drop test and the nutrient release test under aqueous conditions, as previously mentioned. However, due to the slower rate of nutrient release, the conductivity monitoring time was 816 h (34 days). The kinetics of nutrient release from these pellets were also investigated using the previously described method.

Results and Discussion

In the Results section, the findings are discussed considering relevant published studies, and a comprehensive analysis of the obtained results is provided.

Biomass Characterization

The results of Elemental and Proximate Analysis are presented in Table 2. The SCG mainly consisted of significant concentrations of carbon (C) and oxygen (O). The high H/C atomic ratio of 0.14 suggested a high potential degree of carbonization and aromaticity within the biomass organic matrix. Additionally, the O/C atomic ratio of 0.74 indicated a higher abundance of carbon compared to that of oxygen, with lower ratios indicating higher hydrophobicity and stability of the material (Batista Jr et al., 2023). The C/N ratio of 17.13 suggested that pure biomass can be used as a soil conditioner and can enhance plant nutrient absorption (Tangmankongworakoon, 2019).

The results of the Proximate Analysis showed that the ash content was 3%, while the content of volatile material (77.06%) and fixed carbon (10.18%) suggested a significant potential for devolatilization of the biomass (Silva et al., 2022).

Table 2: Elemental and Proximate Analysis and Functional groups determined by the FT-IR analysis of SCG.

Elemental analysis							
%C	%H	%N	%S	%O	H/C	O/C	C/N
49.00	7.02	2.86	1.43	36.69	0.14	0.74	17.13
Proximate analysis							
Moisture	9.76	Volatile	77.06	Ash	3.00	Fixed carbon	10.18

The infrared region was investigated using a spectroscope to gain a better understanding of the organic structures present in the SCG (Figure 1). A broad band between 3,650 and 3,200 cm^{-1} was detected, which represented the O-H bond found in cellulose, hemicellulose, and lignin. This bond was derived from alcohols, phenols, or the moisture content of the material. In the region from 3,000 to 2,800 cm^{-1}, $-CH_2$ and $-CH_3$ groups were detected, which are commonly found in various organic compounds containing hydrocarbon radicals. For example, these groups are present in cellulose and hemicellulose.

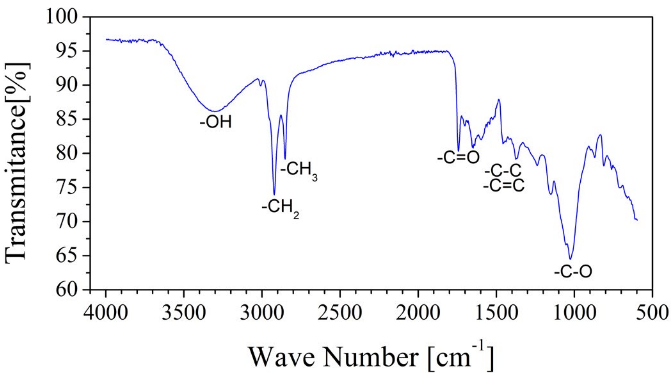


Figure 1: The FT-IR spectra of biomass.

Physical characteristics of organomineral fertilizers

The pellets had an average height of 1.75 cm and a diameter of 1.25 cm. During the drying process, the loss of moisture from the pellets ranged from 14.6% to 29.3%, with the highest moisture content observed in pellets containing 2.5 g of fertilizer per gram of SCG. Subsequently, the pellets were tested for resistance to impact and release in aqueous environments.

Effect of fertilizer formulation on drop resistance

Drop tests from various heights are commonly performed to assess the resistance of pellets during handling and storage. The information obtained can be used to prevent the development of brittle formulations. The number of falls from 100 cm (NQ [100 cm]) and 150 cm (NQ [150 cm]) is presented in Table 3. Based on the criteria established by Carvalho and Brinck (2010), only samples F7 and F8 met the requirements for impact resistance (NQ>10). The higher resistance of samples F7 and F8 could be attributed to a higher binder content in their composition, resulting in greater cohesion among SCG particles.

The effect of significant factors on drop test results is presented in Table 4. Irrespective of the drop height, the variables with the strongest influence on pellet strength were the addition of molasses (X_1) and the mass ratio of fertilizer to SCG (X2). Increasing the values of X_1 and X_2 increased pellet resistance. Additionally, the interaction between X_1 and X_2 was significant and positive, suggesting that higher levels of molasses and a greater fertilizer-to-biomass ratio led to an increase in pellet strength. The curvature parameter was also significant, which indicated that the quadratic factors were important.

Table 3: Experimental design conditions and responses of drop resistance test and P releasing test for fertilizers that did not undergo TT.

Sample	Factors			Responses					
				Drop resistance		Release test			
	M [%] (X_1)	R [g.g^{-1}] (X_2)	T_s [ºC] (X_3)	$N_{Q[100\ cm]}$	$N_{Q[150\ cm]}$	$t_{15\%}$ [h]	$t_{50\%}$ [h]	$t_{75\%}$ [h]	$t_{90\%}$ [h]
F1	0.0 (-1)	1.5 (-1)	60.0 (-1)	2.0	2.0	0.037	0.081	0.139	0.367
F2	0.0 (-1)	1.5 (-1)	100.0 (+1)	1.8	1.4	0.076	0.152	0.260	0.637
F3	0.0 (-1)	2.5 (+1)	60.0 (-1)	8.2	9.0	0.060	0.183	0.399	0.986
F4	0.0 (-1)	2.5 (+1)	100.0 (+1)	13.8	6.6	0.100	1.042	2.307	3.057
F5	10.0 (+1)	1.5 (-1)	60.0 (-1)	1.0	1.2	0.091	0.312	0.647	1.545
F6	10.0 (+1)	1.5 (-1)	100.0 (+1)	1.4	1.2	0.036	0.111	0.258	1.133
F7	10.0 (+1)	2.5 (+1)	60.0 (-1)	90.6	37.0	0.271	1.009	1.895	7.780
F8	10.0 (+1)	2.5 (+1)	100.0 (+1)	91.8	32.0	0.294	1.639	5.920	13.800
F9	5.0 (0)	2.0 (0)	80.0 (0)	7.0	4.0	0.127	0.381	0.730	3.078
F10	5.0 (0)	2.0 (0)	80.0 (0)	7.0	4.0	0.090	0.505	1.053	2.156
F11	5.0 (0)	2.0 (0)	80.0 (0)	7.0	4.0	0.114	0.341	0.661	3.057
F_{POW}	-	-	-	-	-	0.021	0.090	0.800	2.969

Table 4: Analysis of the effects of the factors on the number of drops from 100 cm and 150 cm, the half-life time ($t_{50\%}$ [h]), and the time in which 90% of P was released ($t_{90\%}$ [h]) for samples that underwent TT.

Drop test					Release Test				
Response	Factor	Effect	Deviation	p-level	Response	Factor	Effect	Deviation	p-level
$N_{Q[100cm]}$ (R^2=0.995)	Média	26.325	1.004	0.000	$t_{50\%}$ [h] (R^2=0.959)	Média	0.523	0.043	0.000
	Curvatura	-38.650	3.237	0.000		X_1	0.403	0.100	0.010
	X_1	39.750	2.008	0.000		X_2	0.804	0.100	0.001
	X_2	49.550	2.008	0.000		X_3	0.340	0.100	0.019
	X_1X_2	40.450	2.008	0.000		X_1X_2	0.308	0.100	0.027
$N_{Q[150cm]}$ (R^2=0.990)	Média	11.300	0.512	0.000		X_2X_3	0.405	0.1000	0.010
	Curvatura	-13.400	1.650	0.000	$t_{90\%}$ [h] (R^2=0.961)	Média	3.418	0.34	0.000
	X_1	13.100	1.023	0.000		X_1	4.803	0.796	0.002
	X_2	19.700	1.023	0.000		X_2	5.485	0.796	0.001
	X_1X_2	13.600	1.023	0.000		X_3	1.987	0.796	0.055
						X_1X_2	3.966	0.796	0.004
						X_2X_3	2.058	0.796	0.049

The response surface for NQ $_{[100cm]}$ is shown in Figure 2; we found that the F8 formulation produced pellets with better resistance to falling (10% M, R = 2.5 (g fertilizer). (g SCG)$^{-1}$, and T = 100 °C). The temperature variations examined did not significantly affect the drop resistance of the pellet, possibly due to the narrow range of the temperatures at which the tests were conducted.

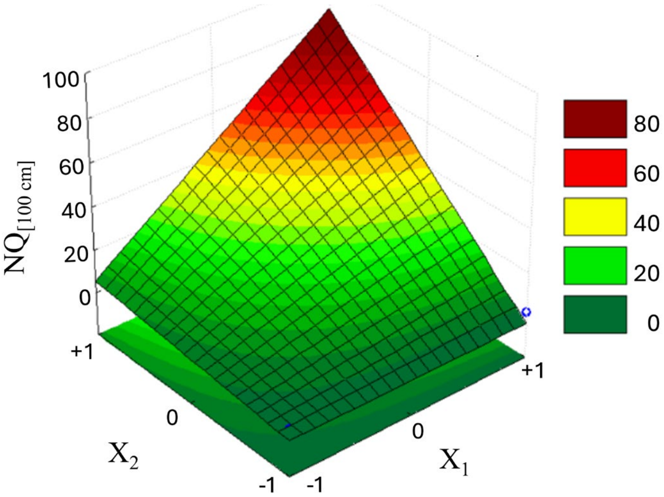


Figure 2: Response surface analysis of factors X_1 and X_2 on the NQ (number of falls from a height of 100 cm).

Effect of fertilizer formulation on the nutrient release kinetics in water

The release profiles of the 11 pelletized OMF formulations are depicted in Figure 3, with the corresponding release timings of 15%, 50%, 75%, and 90% presented in Table 3. As per the criteria outlined by Lustosa Filho et al. (2017), samples F1 and F2 displayed a release pattern similar to that of pure powdered TSP (FPO); in these samples, approximately 95% of all nutrients were released within 1 h. This rapid release can be attributed to the absence of a binder, which resulted in brittle samples with minimal compaction.

Oliveira & Martins (2003) stated that the binder plays a crucial role in providing the cohesive force necessary for particle agglomeration. This force is influenced by the capacity of the particle to absorb the binder, thus enhancing the mechanical strength of the pellet. While molasses was found to act as an effective binder for biomass agglomeration, the fertilizer paste also acted as a binder between particles, imparting mechanical integrity to the pellets.

All samples exhibited slower nutrient release than the FPOW sample (Table 3), due to the larger particle size obtained after pelleting. Among the pelleted samples, F4, F7, and F8 exhibited the slowest release rates. Particularly, sample F8 had the longest half-life ($t_{50\%}$ = 1.639 h), representing an approximately 18-fold increase in half-life compared to the half-life of the FPOW sample.

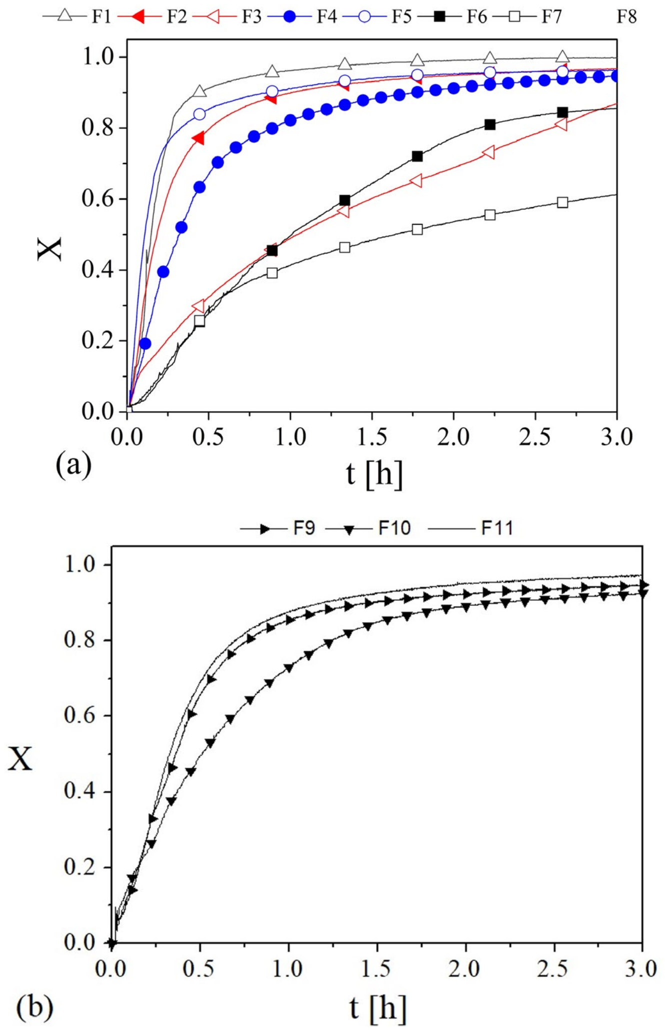


Figure 3: P release fraction curves over time from samples that did not undergo TT: (a) F1 to F8; (b) F9 to F11 All experiments were conducted in triplicate.

The response surfaces for the $t_{50\%}$ [h] and $t_{90\%}$ [h] release time responses are shown in Figure 4, while a statistical analysis of the influence of the variables on these responses is presented in Table 4. Since the curvature effect was not significative for these responses, the calculated linear model adequately explained the results.

All variables directly affected the $t_{50\%}$ and $t_{90\%}$ responses. The increase in $t_{50\%}$ was influenced by high levels of M, R, and Ts, indicating a stiffer and more agglomerated structure. Under the conditions of sample F8 (10% of M, R = 2.5 g.g^{-1}, and T = 100 °C), smaller internal pores were formed, which increased the resistance to mass transfer and restricted the diffusion of P from the particle interior to its surface. The ratio of fertilizer to SCG (X_2) emerged as the most critical factor, indicating that an increase in fertilizer concentration can promote biomass agglomeration by binding particles and infiltrating SCG pores to increase the diffusion impact of P release.

The parameters of the Weibull and Korsmeyer-Peppas kinetic models were calibrated based on the nutrient release curves, as outlined in Table 5. The Weibull model provided the most accurate representation of the kinetics of P release in water for all samples except sample F4. The b value for the kinetics of powdered fertilizer (FPO) was 0.379, indicating that Fickian diffusion was the primary mechanism, attributed to the absence of a matrix, which facilitated rapid diffusion into the fluid core. The high scale time value (A = 1.517) suggested swift diffusion under these conditions.

Regarding the estimated b values for replicates at the central point (samples F9 to F11), the extrusion method applied yielded homogeneous pellets. These samples exhibited a consistent combined transport mechanism ($0.75 < b < 1$), indicating the occurrence of swelling/relaxation within the solid matrix (or release by erosion).

For sample F7 (M = 10%; R = 2.5 $g.g^{-1}$; Ts = 60 °C), the value of b was 1.059, which indicated that the relaxation of the solid matrix probably influenced the release rate. The low scale time (A = 0.682) indicated that the disintegration of the particle required a long time, which in turn delayed the release. Moreover, the influence of the drying temperature on pellet fragility, as determined by the comparison between sample F7 dried at 60 °C and sample F8 dried at 100 °C.

In this study, we found that nutrient release rates decreased with scaling time, as determined by the slower release kinetics observed in sample F8, which had a short scale time (A = 0.494). The slower release kinetics of sample F8 can be attributed to its stiff matrix and Fickian diffusion-dominated release (b = 0.645), which matched the findings of Noppakundilograt et al. (2014) regarding the influence of matrix characteristics on nutrient release rates. These findings highlighted the intricate relationship among formulations, processing conditions, and matrix properties in regulating nutrient release dynamics from pelletized fertilizers. Thus, formulation F8 was used for high-temperature heat treatment in a muffle furnace.

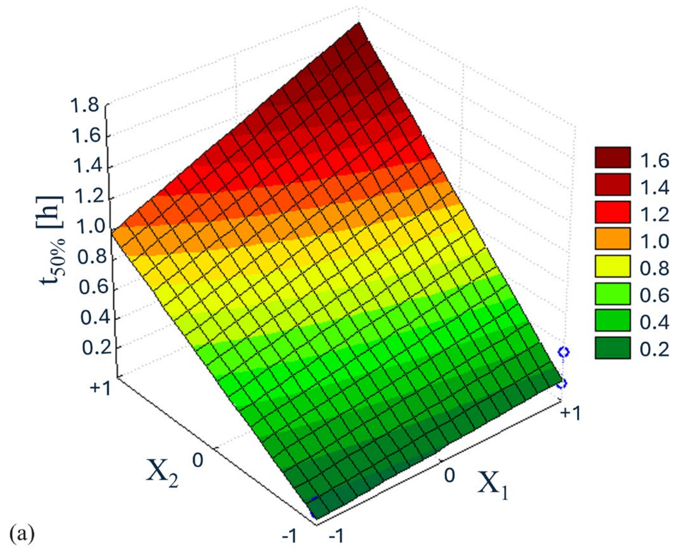
Evaluation of organomineral fertilizers with thermal treatment

In this section, we discussed the effects of heat treatment on the organomineral fertilizer (OMF) pellets. We treated the pellets at different temperatures and for specific durations to assess changes in their properties, particularly drop resistance and nutrient release kinetics.

Effect of temperature and time on pellet drop resistance

Table 6 shows the number of falls in the samples that underwent TT in contrast to the F8 sample that did not undergo TT. All heat-treated samples were mechanically weaker than sample F8.

Based on the criteria established by Carvalho and Brinck (2010), only samples F8-300-90 and F8-400-90 less than 10 falls before losing over 5% of their initial mass, indicating that the 90-minutes, suggesting that thermal treatment for 90 min yielded mechanically fragile pellets. However, the other samples remained viable for transportation and handling.



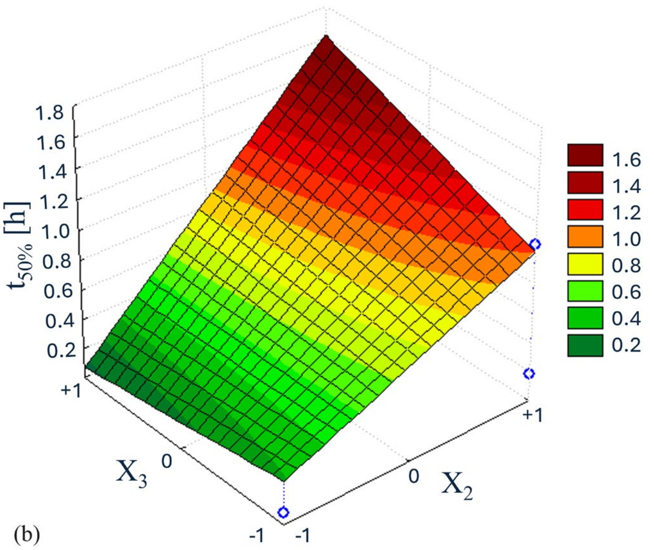


Figure 4: Response surfaces of the effect of the factors on the half-life ($t_{50\%}$) [h]: (a) X_1 and X_2 and (b) X_2 and X_3.

Table 5: Parameters of the Weibull and Korsmeyer-Peppas kinetic models for samples F1 to F11 (without TT) and for pure powder fertilizer (FPO)

	Weibull Model $X = \frac{M_i}{M_\infty} = 1 - \exp\left(-A \cdot t^b\right)$				Korsmeyer-Peppas Model $X = \frac{M_i}{M_\infty} = K \cdot t^n$			
Sample	Parameters		Deviation	R^2	Parameters		Deviation	R^2
F1	A	9.691	0.478	0.965	K	0.919	0.003	0.777
	b	1.057	0.024		n	0.112	0.004	
F2	A	7.042	0.018	0.988	K	0.895	0.004	0.829
	b	1.235	0.018		n	0.172	0.006	
F3	A	2.302	0.018	0.984	K	0.829	0.003	0.901
	b	0.700	0.008		n	0.209	0.005	
F4	A	0.680	0.002	0.997	K	0.476	0.001	0.999
	b	0.850	0.004		n	0.548	0.001	
F5	A	1.634	0.004	0.989	K	0.749	0.002	0.938
	b	0.734	0.003		n	0.288	0.003	
F6	A	3.789	0.046	0.974	K	1.018	0.003	0.960
	b	0.479	0.007		n	0.146	0.003	
F7	A	0.682	0.001	0.999	K	0.478	0.002	0.988
	b	1.059	0.003		n	0.619	0.005	
F8	A	0.494	0.002	0.987	K	0.383	0.002	0.978
	b	0.645	0.006		n	0.476	0.005	
F9	A	1.763	0.007	0.985	K	0.752	0.002	0.917
	b	0.878	0.005		n	0.302	0.003	
F10	A	1.261	0.002	0.997	K	0.672	0.002	0.965
	b	0.850	0.003		n	0.380	0.004	
F11	A	2.056	0.011	0.991	K	0.776	0.003	0.917
	b	0.967	0.006		n	0.295	0.005	
$_{FP}O$	A	1.517	0.001	0.987	K	0.766	0.001	0.910
	b	0.379	0.001		n	0.120	0.001	
Sample F8 after heat treatment								
F300-10	A	0.519	0.002	0.933	K	0.452	0.001	0.879
	b	0.279	0.001		n	0.141	0.001	
F300-30	A	0.015	0.000	0.942	K	0.050	0.001	0.885
	b	0.961	0.004		n	0.565	0.003	
F300-90	A	0.079	0.001	0.918	K	0.084	0.000	0.936
	b	0.448	0.002		n	0.374	0.001	
F400-10	A	0.007	0.000	0.989	K	0.010	0.000	0.996
	b	0.775	0.001		n	0.678	0.000	
F400-30	A	0.013	0.000	0.971	K	0.015	0.000	0.990
	b	0.667	0.002		n	0.592	0.002	
F400-90	A	0.005	0.000	0.995	K	0.010	0.000	0.977
	b	0.902	0.001		n	0.707	0.001	

Table 6: Experimental conditions and responses of drop resistance test and P releasing test after TT.

Sample	Factors		Drop resistance		Release time of %P [h]			
	T_{TT} (°C)	t_{TT} [min]	$N_{Q[100\ cm]}$	$N_{Q[150\ cm]}$	$t_{15\%}$	$t_{50\%}$	$t_{75\%}$	$t_{90\%}$
F8-300-10	300	10	33.3 ± 9.4	32.7 ± 9.7	0.07	4.0	37.3	223.2
F8-300-30	300	30	44.3 ± 6.8	17.7 ± 9.2	5.60	50.9	238.2	366.4
F8-300-90	300	90	18.3 ± 11.7	8.0 ± 4.3	0.04	87.75	289.2	505.6
F8-400-10	400	10	31.7 ± 4.6	21.7 ± 8.7	53.2	367.7	603.5	744.0
F8-400-30	400	30	28.3 ± 8.8	29.7 ± 14.4	49.53	391.0	689.4	793.3
F8-400-90	400	90	9.0 ± 6.5	30.7 ± 7.9	45.28	196.3	607.8	734.7
F8	-	-	91.8 ± 10.65	32.0 ± 10.654	0.294	1.639	5.920	13.8

Nutrient release kinetics in water

The nutrient release curves of the heat-treated samples are shown in Figure 5, while the time values corresponding to the release of 15%, 50%, 75%, and 90% of nutrients are presented in Table 6. The samples treated at 400 °C released nutrients at a slower rate. However, only the F8-400-30 sample met Trenkel (2010) requirements ($t_{15\%}$ > 24 h and $t_{75\%}$ > 28 days), and thus, may be classified as a slow-release fertilizer. The half-life ($t_{50\%}$) of the F8-400-30 sample increased by 3,078-fold compared to the FPO. The increase in sample F8 was around 30 times, demonstrating that thermal treatment substantially modified the particle matrix.

Gwenzi et al. (2017) used pyrolyzed sawdust biochar granules with NPK fertilizer and a starch–PVA binder and found that 90% of nutrients were released from their pyrolyzed biochar pellets within 25 days, using the sequential leaching method with water. Similarly, we found that F8-400-30 released 90% of nutrients within 33 days (793.3 h; see Table 6) and met the criteria for classification as a slow-release fertilizer. Although the materials, TT, and release methods were different between both studies, the results highlighted the potential of thermal treatment to modify the matrix of pellets, leading to slower nutrient release rates compared to untreated samples.

The results of nutrient release kinetics in water for heat-treated pellets, along with the calculated parameters of the Weibull and Korsmeyer-Peppas models are presented in Table 5. The Weibull model provided the best fit for samples F300-10, F300-30, and F400-90, whereas the KP model better represented samples F300-90, F400-10, and F400-30.

According to the Weibull model, the release kinetics of the thermally treated samples exhibited time scale values on the A scale ranging from 0.005 to 0.519, and the values of b were <0.75 or 0.75 < b < 1. This finding suggested that the release mechanism followed Fickian diffusion, potentially associated with swelling/relaxation of the pellet matrix or release by erosion, as reported by Papadopoulou et al. (2006).

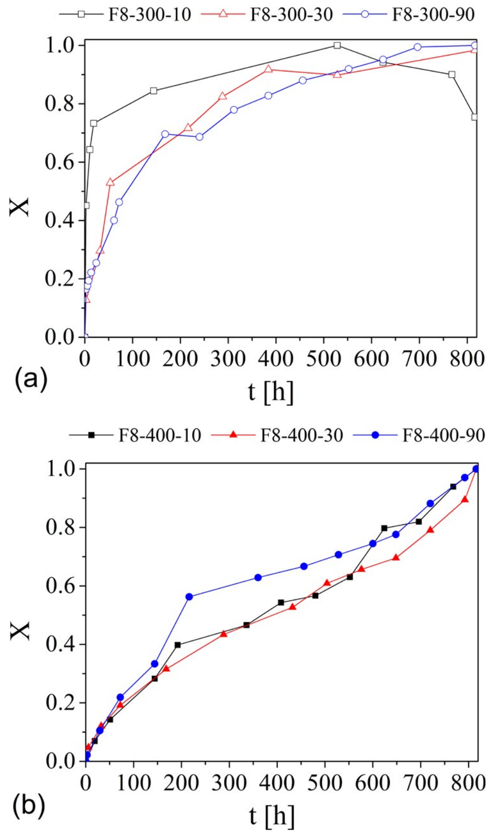


Figure 5: P release fraction curves over time from F8 samples after TT at (a) 300 °C for 10, 30, and 90 min; (b) 400 °C for 10, 30, and 90 min.

The pyrolyzed samples showed a decrease in parameter A compared to untreated samples, suggesting a reduction in the phosphorus release rate. Among the samples, F300-10 exhibited the fastest release, as determined by its high scale time (A = 0.519) and b = 0.279, indicating swift release via diffusion.

The samples that underwent TT at 300 °C had higher A values, indicating a greater release rate compared to those treated at 400 °C. The slowest releasing sample, F400-30, displayed a low scale time (A = 0.013), predominantly exhibiting diffusive release (b =0.667). This pellet fractured on the 29th day of the trial, leading to an increase in the release rate toward the end of the experiment.

By comparing the findings of Zhao et al. (2016), who investigated the co-pyrolysis of TSP fertilizer with sawdust and grass, with the results of our study, we found that the dissolution and diffusion mechanisms for releasing P were similar in both studies. According to Zhao et al. (2016), additional energy is required to break the bonds between C and P to release P into the solution. They found that around 90% of P was released within 20 h, whereas, in this study, we produced OMF samples that released 90% P between 223 and 793 h. Similarly, Lustosa Filho et al. (2017) studied biochar-based fertilizers (BBFs) produced through the co-pyrolysis of MgO and various P mineral sources with chicken litter. Their findings highlighted the regulation of water-soluble P release over time, with slow diffusion mechanisms governing P absorption or dissolution.

This study has several limitations. First, manual extrusion was performed to produce the pellets; however, mechanical extrusion would provide more consistent pellet dimensions and mechanical properties. Additionally, further testing of the release dynamics of the pelletized fertilizer in soil environments, including greenhouse and field trials, is necessary to validate its efficacy under real-world conditions. Moreover, this study focused on the physical and chemical characterization of the pelletized fertilizer; however, the agronomic performance and long-term effects of the fertilizer on soil health and crop productivity were not investigated. Future researchers should address these limitations by conducting comprehensive field trials and assessing the effect of pelletized fertilizer on the environment.

This study has several practical implications for the agricultural and environmental sectors. By developing pelletized organomineral fertilizers (OMFs) from waste biomass, such as spent coffee grounds (SCG), we provided a sustainable solution for waste management and fertilizer production. These OMFs can serve as inexpensive alternatives to conventional fertilizers, reducing the dependence on chemical inputs and promoting eco-friendly agricultural practices. Moreover, the slow-release characteristics of the formulated pellets can increase nutrient uptake efficiency, minimize nutrient leaching, and improve soil health over time. Overall, although this study provided valuable insights into the development of pelletized organomineral fertilizers, further research is needed to comprehensively evaluate their potential for sustainable agriculture.

Conclusions

This study developed and assessed a pelletized organomineral fertilizer using spent coffee and TSP. Thermal treatment enhanced pellet matrix, increased mass transfer resistance, altering nutrient release kinetics. Optimal formulation (10% molasses, TSP/SCG ratio of 2.5 g g^{-1}) dried at 100 °C, with thermal treatment at 400 °C for 30 min, showed optimal mechanical resistance and prolonged structural integrity in water, classifying it as a slow-release OMF. Further research, including life cycle assessment and field trials, is needed to enhance sustainability and agricultural efficacy.

Author Contribution

Conceptual idea: Santos, K.G.; Methodology design: Santos, K.G., Sousa, N.G.; Data collection: Barbosa, N.S., Santos, K.G., Sousa, N.G., Da Luz, M.S.; Data analysis and interpretation: Barbosa, N.S., Santos, K.G., Sousa, N.G., Da Luz, M.S.; and Writing and editing: Barbosa, N.S., Santos, K.G., Sousa, N.G..

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