CAIO PEREIRA MOTA

BIOCHAR-NITROGEN COMPOSITES: SYNTHESIS, PROPERTIES AND USE AS FERTILIZER FOR MAIZE

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Dissertation presented to the Federal University of Lavras as part of the requirements of the Postgraduate Program in Soil Science, area of concentration in Recursos Ambientais e Uso da Terra, to obtain the Master's degree.

Supervisor: Prof. Dr. Carlos Alberto Silva.

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COMPÓSITOS DE BIOCARVÃO-NITROGÊNIO: SÍNTESE, PROPRIEDADES E USO COMO FERTILIZANTE PARA O MILHO

Dissertation presented to the Federal University of Lavras as part of the requirements of the Postgraduate Program in Soil Science, area of concentration in Recursos Ambientais e Uso da Terra, to obtain the Master's degree.

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Compósitos de biocarvão-nitrogênio: síntese, propriedades e uso como fertilizante para o milho

RESUMO

O nitrogênio é altamente reativo e propenso a ser facilmente perdido para o ar e água do solo. O biocarvão desempenha um papel crucial na mitigação das perdas de nitrogênio no sistema solo-planta, e os compósitos de nitrogênio-biocarvão-mineral têm se mostrado eficientes na nutrição do milho. A formulação de compósitos à base de nitrogênio com biocarvão exige cuidados, especialmente em termos de controle de pH, redução de perdas de N durante a formulação e garantia de níveis ótimos e disponibilidade de N no compósito final. Este estudo teve como objetivo sintetizar e avaliar as propriedades de compósitos de biocarvão-nitrogênio formulados com sulfato de amônio (SA), ureia e diamônio fosfato (DAP), bem como avaliar a eficiência agronômica destas fontes de N na nutrição e promoção do crescimento do milho. Os biocarvões foram produzidos a partir da pirólise a 300 ºC de duas biomassas contrastantes: esterco de galinha (N = 3,5%) e torta de leguminosas (N = 9%). O pH do biocarvão foi ajustado para ~6, utilizando-se, para isso, soluções ácidas antes da mistura desses biocarvões com SA, ureia e DAP, o que possibilitou a fomulação de seis compósitos de N-biocarvão. O milho foi cultivado por 50 dias em condições de casa de vegetação, com avaliação da matéria seca (MS) e nitrogênio na parte aérea. Os teores de nitrogênio mineral (amoniacal e nítrico) e nitrogênio residual de amostras de um latossolo vermelho-amarelo de textura média utilizado para o cultivo de milho também foram analisados. Amostras dos biocarvões e compósitos foram caracterizadas para atributos químicos e físico-químicos, bem como para espécies químicas e solubilidade do N nos compósitos e biocarvão. A dinâmica da liberação de N mineral (amoniacal e nítrica) dos compósitos e biocarvões originais foi avaliada simultaneamente ao longo do cultivo do milho, em função da amostragem sucessiva da solução do solo. Com a oferta de N em uma única dose (400 mg kg^{-1} de N), os compósitos mostraram-se tão eficazes quanto a ureia dividida em três aplicações no fornecimento de nitrogênio às plantas de milho. Além disso, os compósitos formulados com DAP e supridos em menor dose (270 mg kg^{-1} de N) produziram a mesma quantidade de matéria seca que outros compósitos nos quais o N foi fornecido às plantas na dose de 400 mg kg^{-1}. Os compósitos contendo SA foram muito eficazes na liberação da maior parte do N mineral na solução do solo, embora, ao final do cultivo do milho, não tenham sido observadas diferenças no nitrogênio residual no latossolo para as diversas fontes de N, incluindo a ureia. Os compósitos testados demonstraram eficiência agronômica comparável à ureia na promoção do crescimento do milho. A biomassa do milho foi menor para as plantas nutridas com biocarvões puros sem adição de N mineral, indicando que a disponibilidade de N das matrizes carbonizadas é reduzida e que o N não é liberado dentro do prazo requerido pelas plantas de milho.

Palavras-chave: N disponível em biocarvões. Nitrificação. Relação NH_4^+:NO_3^-. Volatilização de N. N aromático. Pirólise.

ABSTRACT

Nitrogen is highly reactive and prone to be easily lost into the air and soil water. Biochar plays a crucial role in mitigating nitrogen losses in the soil-plant system, and biochar-mineral nitrogen composites have proven to be efficient in nourishing maize. The formulation of nitrogen-based composites with biochar demands careful consideration, particularly in pH control, minimum loss of N during formulation, and ensuring optimal levels and available N in the final composite. This study aimed to synthesize and assess the properties of biochar-nitrogen composites formulated with the following synthetic fertilizers: ammonium sulfate (AS), urea, and diammonium phosphate (DAP), as well as evaluate the agronomic efficiency of N composites in nourishing and promoting the maize plentiful growth. Biochars were derived from two contrasting biomass: chicken manure (N = 3.5%) and leguminous cake (N = 9%) and pyrolyzed at 300°C. The biochar pH was adjusted to ~6 using acid solutions before they blended with AS, urea, and DAP, thus, it was formulated six composites. Maize was cultivated for 50 days in greenhouse conditions, with the evaluation of dry matter (DM) and nitrogen in the shoot. Mineral nitrogen content (ammonium and nitrate) and residual nitrogen in the Red-yellow Latosol medium-texture used for maize cultivation were also analyzed. Biochar and composite properties underwent scrutiny for chemical and physicochemical attributes, as well as for N chemical species, and their solubility in composites and biochars as well. The dynamics of mineral N (ammonium and nitrate) released from the composites and raw biochars were concurrently assessed throughout maize cultivation by successively sampling soil solution. With N supplied in a single dose (400 mg kg^{-1} N), composites proved to be as effective as urea - split in three applications - in providing nitrogen to maize plants. Additionally, composites formulated with DAP and provided at the dose of 270 mg kg^{-1} N yielded the same dry matter production as other composites in which N was furnished to plants at the rate of 400 mg kg^{-1}. Composites containing AS effectively released most mineral N into the soil solution, although, at the end of maize cultivation, no differences in residual nitrogen in the Oxisol were observed among the various N sources, including soil samples treated with N from urea. The formulated composites demonstrated comparable agronomic efficiency to urea in promoting plentiful maize growth. Maize biomass was lower for plants nourished with raw biochars without mineral N doping, indicating that the availability of N from the carbonized matrices is reduced, and N is not released within the required timeframe for maize plants.

Keywords: N pools in biochar. Nitrification. NH_4^+:NO_3^- ratio. N volatilization. Aromatic N. Pyrolysis.

List of abbreviation ad acronyms

N= Nitrogen;

C= Carbon;

DM= Dry matter;

ATR-FTIR= Fourier transform infrared spectroscopy with attenuated total reflection;

CEC= cation exchange capacity;

EC= Electrical conductivity;

AS= Ammonium sulfate;

DAP= Diammonium phosphate;

UR= Urea;

MAP= monoammonium phosphate;

LC= Leguminous cake;

CM= Chicken manure;

BLCAS = Biochar from leguminous cake + ammonium sulfate;

BCMAS = Biochar from chicken manure + ammonium sulfate;

BLCDAP = Biochar from leguminous cake + DAP**;**

BCMDAP = Biochar from chicken manure + DAP;

BLCUR = leguminous cake biochar + urea;

BCMUR = chicken manure biochar + urea;

BLC= Biochar from leguminous cake;

BCM= Biochar from chicken manure; **No N**= Negative control, no N added to soil;

DAP= days after maize planting.

SUMMARY

1. GENERAL INTRODUCTION

Despite accounting for almost half of the world's food production, Brazil is a country heavily dependent on mineral fertilizers. Approximately 80% of the fertilizers consumed in the country are imported (MAPA, 2022). The nitrogen added to highly weathered soils through the use of synthetic fertilizers not needed to be adequately used by crops (Szulc et al., 2016; Mendes, 2019; Szulc et al., 2020). While N can be used by crops with greater efficiency, N losses through volatilization, leaching, or denitrification should be reduced (Gastal et al., 2002). According to Modolo et al. (2018), these N soil loss processes explain the approximately 50% loss of the mineral fertilizer applied to the soil, considering that N is not fully uptake by plants. Nitrogen is a crucial nutrient to improve maize grain yield, playing a role in various biological processes, including the central function in the photosynthesis and as constituent of chlorophyll (Asibi et al., 2019). Enhancing the N use efficiency by crops is a pertinent challenge for many farmers and technicians. This is not an easy task, as nitrogen can be uptake by plants in both N-ammonium and N-nitrate forms, whose proportions are guided by the plant's nutritional requirement and crop tolerance to the prevalence of N as ammonium or N as nitrate in the growth media (Grzebisz et al., 2021). Therefore, alternatives are being sought to reduce N losses from soil to air and water bodies while avoiding pollution and improving N crop use efficiency.

Nitrogen plays a crucial role in various plant traits associated with its growth and development (Lyra et al., 2014). According to Quan et al. (2020), on average, 40% of the nitrogen accumulation in maize plants was derived from fertilizers, highlighting the significance of correct N fertilization in maize fields. Brazilian soils, in general, exhibit low to medium levels of organic matter. Thus, of the availability of N is reduced in the country's highly weathered Oxisols, making nitrogen fertilization essential to crops fully express their potential yield (Morais et al., 2018). Brazil's main available mineral N sources are urea, ammonium sulfate, ammonium nitrate, MAP, and DAP for NPK formulation. Urea is the most widely used worldwide N source due to its better price/nutrient unit ratio (Mota et al., 2015). In the tropical landscape, mineral N sources are prone to interact with soil organic matter, leach with the soil water, or evolve to the air in the form of ammonia and nitrous oxide, which explains the low efficiency of N fertilizers in Brazilian crop fields. In addition, these fertilizers demonstrate low efficiency due high reactivity, intensive dynamics, and the facility of stable N forms to be converted into N gaseous or readily soluble N forms prone to be lost by leaching. For instance, urea needs to undergo hydrolysis before it can be uptake by plants, making the amidic N form more susceptible to be volatilized in the NH_3 form (Scivittaro et al., 2010). N losses through leaching occur mainly for N-nitrate present in some N sources or formed through nitrification, especially in sandy soils, with a considerable potential to pollute soil groundwater and the air (Lacerda et al., 2018; Cancian, 2018). Over the years, various technologies have been developed to mitigate N losses and consequently enhance the use efficiency of N sources employed in the fertilization of crop fields. Stabilized, slow-release, and controlled-release fertilizers are some of the strategies that have become increasingly widespread (Silva et al., 2017). In this context, using N-biochar composites emerges as an alternative that can provide nitrogen to the plant while increasing N use efficiency.

A composite is any multiphase material with an adequate ratio of the phases mixed, in which the mixture, compared to the single use of its constituents, achieves a better combination of properties and technical performance (Callister et al., 2006). Thus, a nitrogen-biochar composite is produced through the mixture of a soluble N source with a tailored (adequate pH, pyrolysis conditions, feedstock, etc.) biochar sample, which may enhance the properties and the agronomic value of N supplied by the final composite over its single and not conjugated use with N synthetic fertilizers. Biochar is the result of thermal degradation of a renewable biomass in the absence or under limited supply of oxygen, a process known as pyrolysis (Saletnik et al., 2019). The properties of composites will vary primarily based on the choice and composition of feedstock and the pyrolysis conditions it undergoes (Xiao et al., 2018; Yuan et al., 2019). It is known that, concerning biochar-N composites, an increase in pyrolysis temperature can raise the total carbon content while decreasing the biochar yield and its N availability and content (El-Naggar et al., 2019). One of the primary nitrogen sources used in biochar production is manure. However, the nitrogen available as nitrate in its derived biochar is known to be very low (Ippolito et al., 2014). Nevertheless, it can still exhibit good nitrogen availability, influencing other soil processes, such as N cycle and enhancing N use efficiency, while reducing N losses (DeLuca et al., 2012; Dempster et al., 2012; Nelissen et al., 2012). Biochars produced at temperatures below 350°C have a high nitrogen mineralization rate, while those pyrolyzed at temperatures above 550°C have low total N content, besides reduced yield less labile and available N chemical species (Nelissen et al., 2012). Owing the production of a composite with higher N availability, the acidification of some feedstocks is a pre-pyrolysis recommended practice to reduce the biochar pH to the acid range, thereby minimizing N losses, notably through volatilization and flow of N in gaseous forms to the air. This acidification has the ability to keep the H^+ high enough to avoid N volatilization during the composite synthesis. It also increases the CEC of the charred matrices, increasing the capacity of biochars in adsorbing N in the ammonium form (Rasse et al., 2022).

Regarding the agronomic effectiveness of biochar-N composites, Puga et al. (2020) combined eucalyptus wood with ammonium nitrate and urea in the synthesis of biochar-based N fertilizers and use maize as a test-plant. The maize plants exhibited a yield of approximately 26% greater than plants exclusively fertilized with urea. Additionally, they verified a lower emission of N greenhouse gases in soil treated with Biochar-based N fertilizers over mineral soluble N fertilizers. In another study, Pino et al. (a) (2023) produced N composites by combining olive pruning wastes with ammonium sulfate and urea, with the pre-acidification of feedstocks and the mixture of N with biomasses previously performed to the pyrolysis process. A high amount of hydrolysable nitrogen was determined in the composites formulated with urea. Conversely, the composites with ammonium sulfate only showed a high nitrogen concentration when acidified before the pyrolysis. The use of composites of plant residues-derived biochars mixed with urea improved in 25% the maize shoot biomass and in 37% root dry matter over the exclusive use of urea (Shi et al., 2019). It was also noted that N-biochar composites controlled the kinetics of N release, preserving ammonium nitrogen in the soil for a longer period. At the same time, the N from the mineral fertilizer was lost, uptake by plants, or converted into nitrate-N in the first days after fertilization. In a similar study carried by Pino et al. (2023b), the combination of biochar from olive tree prunings with urea reduced in 32% the nitrous oxide emissions, compared to the single application of urea.

This study aimed to produce N-biochar composites by combining pre- acidified chicken manure and leguminous cake with phosphoric and sulfuric acids, along the mixture of the derived biochars with three synthetic N fertilizers (ammonium sulfate, DAP, and urea). We evaluated their effect on maize growth, soil N availability, as well as on the amount of mineral N released in Oxisol solution simultaneously to maize cultivation in greenhouse conditions.

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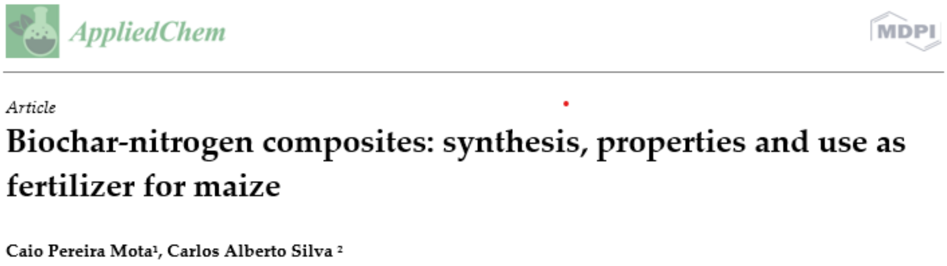

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Article

Biochar-nitrogen composites: synthesis, properties and use as fertilizer for maize

Caio Pereira Mota[1], Carlos Alberto Silva [2]

Abstract: Nitrogen (N) is highly reactive and prone to being easily lost into the air and soil water. Biochar-N composites have proven effective in nourishing and improving maize growth. The aim of this study was to synthesize and assess the properties of composites made from biochars (pyrolyzed at 300°C) derived from chicken manure (N=3.5%) and leguminous cake (N=9%) and enriched with ammonium sulfate (AS), urea, and diammonium phosphate (DAP). The biochar pH was adjusted to approximately 6 using sulfuric and phosphoric acids prior to formulating the six tested composites. Maize was cultivated for 50 days under greenhouse conditions, with evaluations of maize dry matter (DM) and N in the plant shoot. The biochar and composite properties underwent scrutiny for chemical and physicochemical attributes, as well as for N soluble in water and in an HCl solution. Throughout maize cultivation, it was successively assessed the release of N as ammonium and nitrate from the composites and pure biochars in the Oxisol solution. Composites formulated with DAP and supplied at a dose of 270 mg kg^{-1} N yielded the same maize dry matter as composites in which 400 mg kg^{-1} N was supplied to plants. Regardless of the N source, at the end of maize cultivation, the residual N in the Oxisol was reduced and inadequate for a new cultivation, even in soils treated with urea. Notably, the biochar-N composites, particularly those formulated with DAP, were as effective as urea in nourishing and promoting robust maize growth. In contrast, maize biomass was lower for plants fertilized with pure biochars, indicating that the N from the carbonized matrices was insufficient for optimal biomass production.

2. INTRODUCTION

The challenge of producing more food worldwide is increasingly difficult to attain, given a scenario of intensified climate change and scarce, expensive inputs, such as nitrogenous fertilizers, extensively imported by Brazil from other countries. Nitrogen (N) is highly reactive and can be lost to the air and soil water, thereby increasing fertilization costs and reducing the use efficiency of N by plants, with the potential for environmental pollution in crop fields. As one of the world's major food producers, Brazil surpassed historical records in fertilizer imports in 2021 (Conab, 2022), notably nitrogen mineral fertilizers. Approximately 85% of the nitrogen fertilizer used to fertilize our crops is imported (StoneX, 2022), with, on average, 50% of the N from these fertilizers applied to the soil being lost, notably through ammonia volatilization, denitrification (N_2O emission) and leaching (Beig et al., 2010). Barbosa (2017) observed that N rates exceeding 150 kg ha^{-1} N favor the leaf area index and increase corn yield. Additionally, Lyra et al. (2014) noted that yields exceeding 5.5 t ha^{-1} of corn were produced for doses greater than 200 kg ha^{-1} of N, highlighting the high demand for N in maize fields. Besides increasing the rate of N added to soils, it is crucial to enhance the nutrient use efficiency by crops. Therefore, understanding the characteristics of each nitrogen fertilizer is necessary, along with exploring new technologies, matrices, wastes and synthesis routes for renewable and efficient N fertilizers to achieve more efficient N use in Brazilian cropland areas.

The production of mineral-N biochar-based fertilizers, hereafter named composites, is an alternative to enhance crops use efficiency of nitrogen (N) (Puga et al., 2020; Pino et al., 2023). Biochar is a product obtained through the thermal degradation of renewable biomass in the absence of O_2; apart from optimizing several N transformation processes in the soil, it alters soil properties and serves as a nitrogen source for crops, although pools, availability and kinetics release of N by carbonized matrices are not yet fully understood. In this direction, N associated with charred matrices and biochars is limited in the short term to crops (Joseph et al., 2021; Melo et al., 2022; Paiva et al., 2024). When it comes to N-doped biochars, the formulated fertilizers exhibit a characteristic of having contrasting N pools, both slow release and N pools that were gradually supplied throughout the crop cycle, reducing N losses to the air and water, while increasing the use efficiency of N by plants (Pino et al., 2023; Jia et al., 2021). Mandal et al. (2018) observed that, due to its capacity to adsorb ammonium N, biochar can retain N in soil for more extended period, preventing N losses through volatilization at pH levels above 6.3. The nitrate physical adsorption in carbonized matrices could be a mechanism to prevent nitrate leaching in soils treated with biochar (Zheng et al., 2017). Therefore, the diffusion of nitrate into micro and nano-pores of biochars could be a suitable strategy to reduce N losses in the soil-plant system (Shi et al., 2019). The use of biochar-nitrogen composites increased the nutrient use efficiency by corn by 44% compared to the N-urea supply (Zheng et al., 2017). In the phase of composite formulation, the correct choice of biomass, pyrolysis conditions, mineral N sources, and synthesis medium conditions (pH, minimal N volatilization, full interaction of N with the biochar organic matrix through weak bonds, etc.) are crucial. Some biochar matrices have a high capacity to sorb nutrients or are prone to strongly interact with different N chemical species, thus, they are illegible as raw materials to produce N composites. By growing maize in two contrasting soils, Banik et al. (2013) verified that the mixtures of biochar with urea in variable ratios and the use of slow-release biochar-based urea, urea ammonium nitrate, and S-coated urea decrease the release and loss of N from conventional urea, reduced nitrate leaching and increased the dry matter of maize shoot (1%–34%), root (0%–23%) biomass, N-recovery efficiency (17%–50%), and soil potential mineralizable-N over raw urea and S-coated urea. Activation (H_2O_2, HNO_3, and ultrasonication) and N-doping of biochar-based fertilizers lead to new surface carboxylic functional groups that increase the interaction of charred matrices with N from urea, and the urea-treated biochars had 14.5 % of total N soluble in water; the N chemical species from HNO_3 activation represented up to 60% of the total N, showing that BBFs enriched with urea gradually release N for plants, acting as true slow-release fertilizers (Pino et al., 2023).

To maximize pyrolysis, feedstocks must be dried before pyrolysis, and differences in cellulose, hemicellulose, and lignin content of feedstocks are also important in the biochar synthesis (El-Gamal et al., 2017). It has been reported that biomass rich in lignin and poor in N can produce biochars with higher yield but lower N content over feedstocks enriched in N (Novotny et al., 2015). Pyrolysis is the thermal processing of converting different feedstocks into biochar (Tomczyk et al., 2020). Slow pyrolysis involves the use of low temperatures over a longer residence time, where as fast pyrolysis operates at higher temperatures over a shorter residence time, which implies in less N in the final biochar (Sohi et al., 2009). Therefore, slow pyrolysis increases biochar yield and contributes to preserving N in the final biochar (Paiva et al., 2024). In its fast version, pyrolysis is supposed to increase the production of bio-oil and gas (Chatterjee et al., 2020), although nitrogen losses through volatilization are elevated, requiring more mineral N in composite production because the charred matrices are impoverished in recalcitrant and heterocyclic N forms (Paiva et al., 2024). However, there is still limited information regarding N pools present in charred matrices and the right conditions and biochar properties to be employed in the synthesis of N composites. Thus, it is necessary to add more information regarding the composite production processes and the kinetics of N release by the carbonized matrices used in the formulation of composites. The use of biochar not doped with N in field conditions is not a suitable practice to fertilize crops due to the high cost of elevated biochar rates added to soil. However, the doping of biochar with mineral N fertilizers can enhance the agronomic efficiency of novel N sources, leading to the generation of biochar-based nitrogen composites with improved capacity to supply N to crops at low rates (Shi et al., 2020; Puga et al., 2020; Pino et al., 2021). Several feedstocks have been employed in the production of nitrogen-rich biochar, including the mixture of biochar with chicken litter (Steiner et al., 2010), swine manure (Zhou et al., 2021), crop and post-harvest wastes, slaughterhouse wastes, and remnants of non-commercial wastes from meatpacking industrial plants. The adjustment of pH and the chemical functionalization of biochars through acid solutions can control the pH, facilitate the interaction of N with the biochar organic matrix, and create new organic functional groups in the biochar surface, thus elevating the agronomic efficiency of composite. Functionalization of biochar with the use of inorganic acids increase cation exchange capacity (CEC), adjust the pH of alkaline nature feedstocks or biochars, and enhance nitrogen retention in more labile forms during pyrolysis, resulting in higher availability of nitrogen in the final biochar (Wang et al., 2020; Pino et al., 2023). Acid-treated biochar, besides exhibiting increased yield over non-treated biochar, maintains the characteristics and improves biochar's capacity to sorb nutrients and interact with mineral N. This approach has the potential to reduce or partially replace the use of conventional mineral N fertilizers, contributing to environmental preservation by minimizing nutrient losses and promoting a more balanced and continuous supply of N for crops (Li et al., 2018; Pokharel et al., 2020; Sun et al., 2021).

The hypotheses of this study are as follows: i) Composites based on DAP and AS are more efficient than urea in providing nitrogen for corn. ii) Nitrogen supplied by raw biochars is insufficient to meet the maize N nutritional demand. iii) Composite production is an effective way to increase the use efficiency of mineral N fertilizers, thus, an adequate source of N for maize plants. The aims of this study were: i) Identify synthesis routes and evaluate the properties of nitrogen composites (DAP, ammonium sulfate, and urea) based on biochars derived from chicken manure and leguminous cake with contrasting nitrogen pools and total N content and pyrolyzed at 300°C. ii) Assess the efficiency of composites in supplying nitrogen for corn and simultaneously examine the kinetics of ammonium and nitrate nitrogen release in the Oxisol solution. iii) Determine the agronomic effectiveness of composites in supplying nitrogen and ensuring the plentiful maize growth over urea.

3. MATERIAL AND METHODS

3.1 Soil, biomass and mineral fertilizers

The study was carried out at the Laboratory of Soil Organic Matter Studies (LEMOS), Department of Soil Science, Federal University of Lavras, in the municipality of Lavras, Minas Gerais state (MG), Brazil. Two contrasting feedstocks were used for biochar production: chicken manure (4.38% N) and leguminous cake (9.09% N). Synthetic fertilizers, such as ammonium sulfate (AS), diammonium phosphate (DAP), and urea (UR), were mixed with the aforementioned biochars to produce the composites. The soil used in the experiment was collected in Itumirim, MG, and it is classified as a medium texture Red-Yellow Latosol (Oxisol), and its main attributes are shown in Table 1. Before maize cultivation, the soil was amended with carbonates to achieve a pH of ~6.0, with an adequate supply of Ca and Mg using analytical grade reagents to ensure optimal maize growth. The ammonium-N and nitrate-N content in the Oxisol were quantified, with values of 55 mg kg $^{-1}$ and 35 mg kg $^{-1}$, respectively; the total N content of Oxisol was 1.5 mg kg $^{-1}$.

Table 1 – The main chemical and physicochemical properties of the Oxisol (Itumirim soil) used to grow maize.

Soil	**pH**	**K**	**P**	**Ca**	**Mg**	**Al**	**H + Al**	**SB***	**t**
		(mg dm^{-3})		**(cmolc dm^{-3})**					
Medium texture Oxisol	4.7	226	0.1	0.9	0.39	0.35	2.80	1.87	2.22

T (cmolc dm^{-3})	**BS**	**m**	**C**	**P-Rem**	**Zn**	**Fe**	**Mn**	**Cu**	**B**	**S**
	(%)			**(mgdm^{3})**	**(mg dm^{-3})**					
4.67	40	16	1.66	36.6	0.2	36	3.5	0.1	0.1	1.2

*BS, base saturation; m, aluminum saturation; T, CEC at pH 7; t, effective CEC at soil natural pH; SB, sum of bases; P-Rem, remaining phosphorus.

3.2 Pre-acidification of biomass and synthesis of composites

Four biochars were formulated from two feedstocks (chicken manure and leguminous cake) pyrolyzed at 300°C. This lower temperature was chosen because it increases biochar yield as well as nitrogen retention (Paiva et al., 2024). Chicken manure was collected, pre-milled in a ball mill, and subsequently ground and passed in a 25-mesh sieve. This material underwent acidification with *pure analysis* sulfuric and phosphoric acids before pyrolysis. Acidification was performed owing to a targeted pH range (5-6) for the biochars in a previous of their mixing with mineral N sources. Sulfuric acid at 0.3 mol L^{-1} and phosphoric acid at the concentration of 0.5 mol L^{-1} were sprayed on 100 grams of chicken manure, which was, in sequence, dried. Naturally, the leguminous cake had a pH appropriate to produce the respective biochars; therefore, the material was mixed with N mineral sources without the acidification step. A single biochar was also produced from chicken manure without acidification. The material was weighed, and pyrolysis was carried out at 300°C with a residence time of 30 minutes with an increase of 10°C per minute, using a muffle furnace with a stainless-steel sealed chamber to carry out the pyrolysis process. Four biochars were produced, one form chicken manure biochar acidified with sulfuric acid, one chicken manure biochar acidified with phosphoric acid, one leguminous cake biochar without acidification, and three different analytical-grade mineral N sources were mixed: Ammonium Sulfate (21% N), Diammonium Phosphate (18% N), and Urea (46% N) mixied with CM and LC-derived biochars, thus, resulting in the production of six contrasting biochar-N composites.

Two composites were produced with DAP through its mixture with chicken manure (CM) and leguminous cake (LC) biochars, aiming at a final total N content of 10% in the respective composites. Two composites were also created with ammonium sulfate with 15% of N in the final composite, and another two with urea, whose composites have a target N level of 20% N (Table 2). The biochars and minerals were physically mixed in the appropriate proportions and mixed with water. With this, freeze-drying was carried out to dry the composite produced. Composites and the variable levels of total N were formulated by mixing varying proportions of mineral N sources and biochars, based on the following equation:

$$\text{N in composite (\%)} = [(1 - \text{a})\ \text{x}\ (\text{N in biochar})] + [(\text{a})\text{x}\ (\text{N in the mineral souce})]$$

Where "a" represents the mass of mineral N fertilizer used in the mixture and synthesis of composites.

Table 2 - Biochar/mineral proportions and the composite total N content.

Treatment	Proportion of biochar/N-synthetic fertilizer (%)	Composite total N content (%)
BLCAS*	32 – Biochar 68 – Mineral N	15
BCMAS	8 – Biochar 92 – Mineral N	15
BLCDAP	32 – Biochar 68 – Mineral	10
BCMDAP	8 – Biochar 92 – Mineral	10
BLCUR	31 – Biochar 69 – Mineral	20
BCMUR	13 – Biochar 87 – Mineral	20

*The composites refer to: BLCAS = Biochar from leguminous cake + ammonium sulfate; BCMAS = Biochar from chicken manure + ammonium sulfate; BLCDAP = Biochar from leguminous cake + DAP; BCMDAP = Biochar from chicken manure + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea.

3.3 Biochar and composites characterization

The pH and electrical conductivity of the samples were determined in distilled water at a ratio of 1:10 (0.5 g of biochar-composite/5 ml of water) through the shaking of the suspension at 100 rpm for 1 hour in a Toledo digital pH meter (Mettler-Toledo AG, Schwerzenbach, Switzerland) (Singh et al., 2017). After the digestion of the biochar in sulfuric acid, the total nitrogen content in biochars and composites was determined using the *Kjeldahl* method (Phares et al., 2020). The following formula calculated the yield of the biochars:

$$Biochar\ yield\ (\%) = \left(\frac{biochar\ mass}{feedstock\ mass +\ additive\ mass}\right) x100$$

Where the weight of the additive corresponds to the mass of the acid sprayed on the feedstocks used to produce the biochars.

Total carbon content was determined using an automatic analyzer (dry combustion) with the sample heating at 950°C in an Elementar analyzer, model Vario TOC Cube. Regarding ash analysis, the ASTM D1762-84 (2021) protocol was adopted, and samples were previously dried at 105°C in an oven until a constant weight was achieved. After this step, the samples were burned at 650°C for 8 hours. The ratio between the mass of burnt material and the mass of material dried at 105° C only was then calculated to determine the biochar/composite ash content.

3.4 Nitrogen release in soil solution

Throughout the maize growth cycle, the soil solution was collected using solution samplers (*Suolo Acqua*®) (Carmo et al., 2016) inserted in all pots to assess ammonium (N-ammonium) and nitrate (N-nitrate) levels in the soil solution. An aliquot of each soil solution was initially distilled with 0.2 g of magnesium oxide to create an alkaline condition to convert ammonium into NH_3. The distillation was followed by titration to determine each sample's ammonium nitrogen (N-ammonium) content. Subsequently, 0.2 g of Devarda's alloy was added to the same digested sample, creating an environment capable of converting NO_3^- into NH_3. The NH_3 was collected in a boric acid solution, with the subsequent titration of ammonium borate with a 0,07143 mol l^{-1} HCl solution to determine N as ammonium and nitrate in the soil solution (Singh et al., 2017).

3.5 Infrared spectroscopy

Four biochars and the six composites produced had their spectral signatures evaluated in the middle-infrared region (ATR-FTIR). The main peaks and bands observed in the spectra were identified. To identify primary linkages, organic functional groups, and spectroscopic signatures of each material produced in the range of 3500 to 600 cm^{-1} the FTIR spectra and their bands were interpreted based on the libraries available elsewhere (Lin-Vien et al., 1991; Parikh et al., 2014; Gautam et al., 2015; Boguta et al., 2016).

3.6 Maize cultivation conditions

The agronomic efficiency of the composites, two biochars without N doping, and two controls (positive control with urea and negative control with no N fertilization) was assessed by growing maize for 50 days in a 1 kg pot filled with samples of an Oxisol. Ten seeds were planted in each pot, and thinning was performed, remaining only two plants per pot after germination. The experiment was set up and carried out in greenhouse conditions, in a complete randomized block design, aiming to evaluate the agronomic efficiency of the composites in supplying nitrogen to maize. Soil solution samplers used to extract mineral N in soil solution were installed on the first day of the study, with five solution sampling times performed throughout the maize cultivation cycle. In total, 10 treatments were evaluated, with 4 replicates per treatment, totaling 40 experimental units. Fertilization was performed aiming to add 400 mg kg^{-1} N, 600 mg kg^{-1} P, and 400 mg kg^{-1} K. Regarding composites formulated with DAP, a lower N dose (compared with 400 mg kg^{-1} N added in other treatments) was provided to maize plants, with the addition of 270 mg kg^{-1} N to each pot. Micronutrient fertilization with Zn, Cu, Mn, and B at the concentrations of 4, 2.50, 2.65 and 1.1 mg kg^{-1}, respectively, was also performed with the addition of *pure per analysis* diluted micronutrient sulfate salts and boric acid added to all pot (Morais et al., 2022). Fertilization was performed one day before maize planting, which took place on 28/03/2023. The N from urea was split into 3 applications, with the first two initial fertilization of 150 mg kg^{-1} N each, and the last one with the addition of 100 mg kg^{-1} N as urea. On the planting day, soil sampling was carried out in each pot to quantify the content of N-ammonium and N-nitrate in the whole Oxisol, simultaneously with maize sowing. At the end of the experiment, the shoot and root biomass were removed from each pot, dried, and weighed to determine maize dry matter production. The dried biomass was ground to determine total N and assess the N accumulated in maize shoot. Soil samples were stored to further determine the residual mineral N at the end of maize cultivation.

3.7 Hydrolysable N in composites and biochars

To assess the solubility of N chemical species in the composites and biochars, both a water and an acid solution (HCl 6 mol l^{-1}) was used in the analysis of hydrolysable N (Wang et al., 2012). To evaluate the water-soluble N, 1 g of the material was added to 20 ml of water, and this solution was shaken for two hours. Subsequently, the material was centrifuged at 4000 rpm for 15 minutes, filtered, and the obtained sample was analyzed according to the protocols previously described for determining ammonium-N and nitrate-N content. The analysis of N solubility in an HCl solution was performed by adding 0.5 g of the material to 25 ml of a 6 mol l^{-1} HCl solution, which was digested in a aluminium block for 24 hours at 105°C. Later, the residual material was topped up with distilled water as needed to reach 15 ml and filtered for the determination of the total N content, following the protocol described in Wang et al. (2020).

3.8 Statistical analysis

All statistical procedures were performed using the Sisvar software, and data were previously submitted to analysis of variance. In sequence, the means of the treatments were compared by the Tukey test at $p<0.05$.

4. RESULTS AND DISCUSSION

4.1 Biochar properties

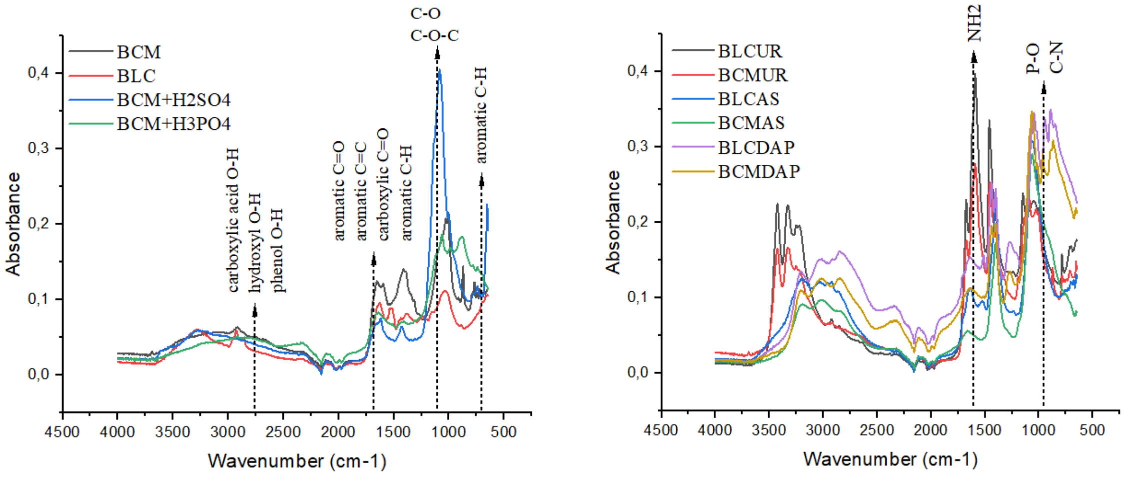
Chemical activation of chicken manure with sulfuric and phosphoric acids reduced the pH of its derived biochars (Table 3). The chicken manure-derived biochar (with no acid addition) had a pH equal to 8.5. For the other composites produced with chicken manure biochars, acid was used before mixing the biochar with the synthetic N sources. In the case of leguminous cake, the acidification process was not necessary, as the non-acidified biochar already had a pH within the optimal range (pH: 5-6) for the synthesis of N composites. It was noted that leguminous cake had a lower ash content than chicken manure, which had a lower N total content than LC biochars. The low C content, and high ash content as well as a lower N content than LC biochars demanded a greater mass of chicken manure biochar in the synthesis of CM biochar-N composites. During pyrolysis, a large portion of the feedstock organic matter matrix is converted into gas, resulting in an enrichment of inorganic compounds in the ash, consequently causing a higher pH and ash content in the chicken manure-derived biochars over low ash feedstocks (Bachmann et al., 2016). As chicken manure has a lower C content than LC, its biochars have a higher ash content and higher pH compared to the carbonized matrices derived from the leguminous cake. It is important to emphasize that, regarding biochars, a high pH does not necessarily imply in a high liming value of the charred matrix, as the biochar liming value depends on properties of the feedstock pyrolyzed, such as ash content, chemical nature, and soil acidity neutralization equivalence of inorganic and organic constituents found in the biochar (Domingues et al., 2017). It is also observed that, regarding EC, the two composites that stand out are those produced from the mixture of LC biochars with urea, which had a lower EC than the other composites. Materials that underwent acidification showed higher conductivity than those not acidified. Composites produced with urea were not acidified, which caused a lower EC of its derived composites. Thus, the urea composites are less prone to cause soil salinization or promote seed burning in the crop furrow. The quantity of soluble salts present in biochar is relevant for the N fertilization management because significant amounts of ions in the soil can negatively affect seed germination, soil solution EC, and plant growth (Joseph et al., 2009). It is noteworthy that biochars derived from chicken manure have a higher EC than those derived from leguminous cake. High values of EC of CM-derived biochars are in line with the data reported by Cantrell et al., (2012); Claoston et al. (2014); Rehrah et al. (2014); and Paiva et al. (2024) found that more lignified biomasses with a lower ash content generally produces biochars with lower EC values. An assessment of the CEC values of the materials produced was not made. The CEC of biochars depends on the composite production conditions and pyrolysis conditions, as well as the feedstock used to generate the biochar (Van Zwieten et al., 2010). Biochars from more lignified feedstocks, such as that from wood bark pyrolyzed at 350°C had a CEC between 90 and 130 mmol$_c$ dm^{-3} (Nguyen, Lehmann; 2009). Biochars from manure, such as the chicken manure used in this study, had CEC values between 290 and 510 mmol$_c$ dm^{-3} (Gundale & Deluca; 2007).

Table 3 – Biochar yield, carbon (C), nitrogen (N), ash content, electrical conductivity (EC) and pH of chicken manure (CM) and leguminous cake (LC) and biochars produced with the acidification of the feedstock with phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4).

N source	Yield, %	C, %	N, %	Ash, %h	EC, dS m^{-1}	pH in water
Biochar(CM) – H_3PO_4						
B – 0,5 mol/L	75	23	3.0	60	1.5	5.5
Biochar(CM) – H_2SO_4						
B – 0,3 mol/L	66	24	3.4	51	2.6	6.1
Biochars without acidification						
BCM	73	30	4.4	35	1.2	8.5
BLC	76	50	9.1	5	2.4	6.2
Composites						
BCMAS	-	9	15	15	65.0	5.1
BLCAS	-	17	15	9	50.2	5.5
BCMDAP	-	8	10	50	44.9	5.5
BLCDAP	-	16	10	35	41.5	5.9
BCMUR	-	23	20	44	8.1	6.3
BLCUR	-	36	20	10	8.3	5.2

The composites refer to: BLCAS = Biochar from leguminous cake + ammonium sulfate; BCMAS = Biochar from chicken manure + ammonium sulfate; BLCDAP = Biochar from leguminous cake + DAP; BCMDAP = Biochar from chicken manure + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea.

4.2 Infrared spectroscopy



(a) **(b)**

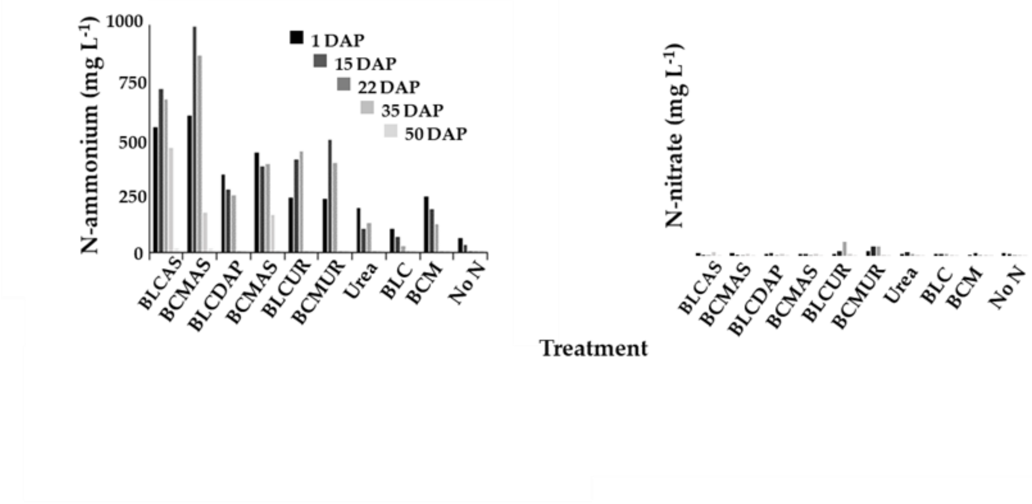
Figure 1 – (**a**) Spectral signature in the FTIR-ATR technique, including the region between 600 and 4000 cm^{-1} FTIR-ATR are displayed for chicken manure biochar, Chicken manure biochar with acidification and

leguminous cake biochar; (**b**) FTIR spectra in the region between 600 and 4000 cm^{-1} of infrared spectra of the composites produced. The composites refer to: BLCAS = Biochar from leguminous cake + ammonium sulfate; BCMAS = Chicken manure biochar + ammonium sulfate; BLCDAP = Leguminous cake biochar + DAP; BCMDAP = Chicken manure biochar + DAP; BLCUR = Leguminous cake biochar + urea; BCMUR = Chicken manure biochar + urea.

The spectral signature of the composites and biochars was obtained through infrared spectroscopy (ATR-FTIR). Analyzing the non-acidified biochars, the main band was observed at 1600 cm^{-1}, corresponding to O – H and aromatic C stretches. The acidified biochars had a predominant IR band in the range of 1300 cm^{-1}, which is assigned for carboxylic acid and ester group stretches. It is important to highlight that the treatment of biochars with an acid solution can cause the oxidation of aromatic C, increasing the number of oxygenated functional groups, which in turn, has the capacity to increase the matrix's binding sites (Li et al., 2014). Regarding the composites, the bands that predominated in the materials mixed with urea was assigned for the IR region between 1590 cm^{-1} and 1600 cm^{-1}, attributed to the formation of amide or amine groups. Bamdad et al., (2021) observed that the amide group peaks in biochar-N composites mixed with urea are much higher than the peaks in materials mixed with ammonium sulfate, corroborating the results reported in this study. Stretching of O – H was also observed in all composites in the range of 3200 cm^{-1} to 3500 cm^{-1}, with the main peaks at 3290 cm^{-1}, indicating the presence of alcohol or phenol stretches. Aliphatic C groups in the range of 2800 cm^{-1} to 3000 cm^{-1} were mainly observed in the DAP-composites. However, they also appeared in other composites, mainly due to C-H stretches of alkynes. Additionally, P – O groups were observed in the composites of DAP-biochar in the region of 1000 cm^{-1}. O – H stretches were assigned for all produced composites in the infrared region between 1500 cm^{-1} and 1700 cm^{-1}.

4.3 Nitrogen in Oxisol solution

Regarding readily available N in the Oxisol solution, after five samplings, it was possible to determine the dynamics of N release in the forms of NH_4^+ and NO_3^- over time in the Oxisol liquid phase. The highest levels of N-ammonium in the soil solution were observed in the first solution sampling, especially for soils treated with composites produced with ammonium sulfate. However, N-ammonium decreased during the maize growth, possibily explained due to the conversion of N-ammonium into N-nitrate, flow to the air as gaseous forms or N uptake by maize plants. As the cultivation time evolved, mineral N in soil solution reached values close to zero. This illustrates that, potentially, N-ammonium could be converted into nitrate, volatilized as ammonia, or uptake by maize plants (Figure 2). Regarding N-nitrate, the levels were lower than those of N-ammonium, indicating that the nitrification rate is reduced in the early days of maize cultivation, except for the composites with urea, whose N-nitrate levels in the solution were slightly higher than those of the other treatments (Figure 2). This could possibly be due to the great adsorption that biochar can provide to N in the ammonium form, causing a high rate of nitrification. Overall, almost N in the soil solution predominated in the form of N-ammonium. A high capacity to adsorb N-ammonium over N-nitrate is claimed for charred matrices (Borchard et al., 2019; Wang et al., 2019). Nitrogen-doped biochars are expected to reduce the nitrification rate, thus preserving N-ammonium in the growth media for a significantly longer period compared to urea (Shi et al., 2019). Low values of mineral N in both forms was verified for the treatment without the addition to soil of N (negative control). Thus, the soil available N was not adequately supplied to maize plants in soils not treated with biochars or composites.



(a) **(b)**

Figure 2 – (**a**) N-ammonium in the soil solution; (**b**) N-nitrate in the soil solution. DAP: days after maize planting.

4.4 Carbon in soil solution

Carbon in the Oxisol solution was determined for samples collected 15 and 22 days after maize planting for all ten treatments evaluated (Table 4). Carbon levels were greater for soil solution treated with DAP-biochar composites, urea, and treatments with biochars not mixed with N mineral sources. This trend becomes even more evident in the second sampling time, with higher carbon levels in soils fertilized with urea composites and biochars without N doping. It has been observed that biochar produced at lower temperatures has a higher solubility and capacity to release carbon into the soil solution over aromatic C matrices produced at high pyrolysis temperature (Saha et al., 2019; Han et al., 2020). Regarding the increase in the carbon level in the second over the first soil solution sampling time, the nitrogen release dynamics may have contributed to the water-soluble C content increase as the increased input of N into the soil via fertilizer contributes (Xu et al., 2020; Gao et al., 2021).

Table 4 – Water-soluble C content in Oxisol solution in the first two collections..

Treatment	C content – mg/L (first sampling)	C content – mg/L (second sampling)
BLCAS*	806	883
BCMAS	911	768
BLCDAP	1424	1393
BCMDAP	1261	986
BLCUR	1381	1419
BCMUR	532	1681
UREA	814	960
BLC	945	1140
BCM	1397	1272
No N	809	704

*The treatments refer to: BLCAS = Biochar from leguminous cake + ammonium sulfate; BCMAS = Biochar from chicken manure + ammonium sulfate; BLCDAP = Biochar from leguminous cake + DAP; BCMDAP = Biochar from chicken manure + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea; UREA = positive control; BLC = Biochar from leguminous cake; BCM = Biochar from chicken manure; No N = negative control

4.5 N availability in Oxisol

Regarding the N availability for maize plants, soil samples were taken from the pots immediately after maize sowing and at the end of maize cultivation (Figure 3). It was observed that none of the nitrogen sources was efficient in providing nitrogen after maize cultivation, considering that the extent of residual nitrogen would not be relevant for other crops grown in succession to maize. Thus, maize plants uptake the nitrogen, or it was partially lost through volatilization. It is relevant to discuss that part of the nitrogen in biochars and composites could have been strongly immobilized in the organic matrix of the carbonized materials. This refers to nitrogen in heterocyclic forms and high aromatic character, which are less susceptible to mineralization (Paiva et al., 2024). Therefore, the residual nitrogen content in the soil is reduced after 50 days of maize cultivation. It is also noted that biochars from chicken manure and leguminous cake furnished lower nitrogen than composites to maize plants, resulting in lower dry matter production than those verified for plants fertilized with composites combined with mineral fertilizers. Wang et al. (2020) also observed that mineral fertilizers supply nitrogen at a faster pace and in readily available forms in soils than non-modified biochars.

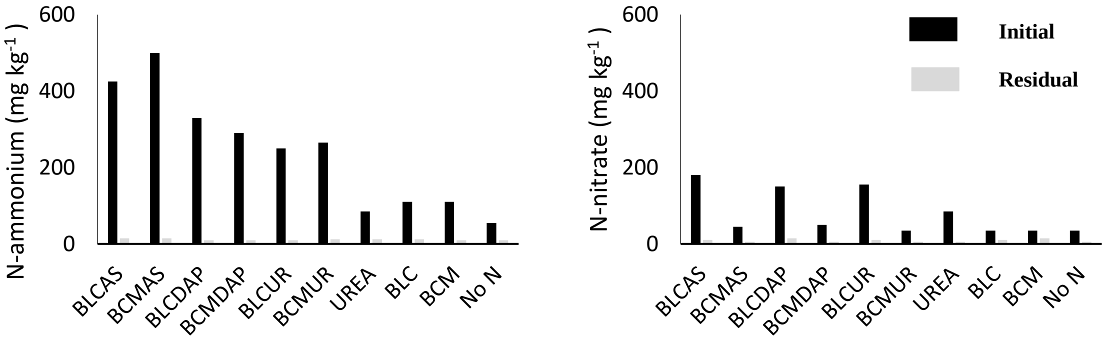


Figure 3 – Availability of mineral N in the whole Oxisol in the form of: (**a**) N-ammonium; (**b**) N-nitrate.

4.6 Hydrolyzable N in composites and biochars

After assessing the solubility of N in composites and biochars, it was noted that the N release dynamics in soil is closely related to N in maize shoot (Table 5). Firstly, it is noticeable that the composites formulated with ammonium sulfate (AS) and diammonium phosphate (DAP) showed higher levels of soluble nitrogen, both in water and in the 6 mol l^{-1} HCl solution, than the other N sources. It was also observed that the composites with chicken manure-derived biochars have higher levels of soluble nitrogen in both water and HCl solution. This is one of the possible explanations for the fact that the composites produced from chicken manure biochars contributed to a greater dry matter production of maize biomass than those synthesized with leguminous cake-derived biochars. Regarding biochars added to soil without N doping, it is possible to verify that these materials contain less soluble nitrogen, meaning that they have nitrogen in forms less soluble or not labile N chemical species. This explains the low maize dry matter production in soils fertilized only with biochar (CM and LC), without the addition of synthetic N fertilizers. Dong et al. (2021) found that the difference in fertilizer rate have changed the solubility of nitrogen, even though when the same nitrogen concentration was added to all treatments. The results obtained in this study are similar to those observed by Lin et al. (2018) and Zhang et al. (2020), who found that the use of biochars with no mineral nitrogen sources did not provide adequate N and plant growth, given that nitrogen in carbonized matrices has less soluble N pools than those present in N mineral fertilizers. Thus, when fertilizing plants exclusively with biochar, besides the total nitrogen content, it is necessary to observe the fraction of soluble and available nitrogen found in the charred matrix used to fertilize crops. Otherwise, maize growth will be limited by the scarce supply of readily available nitrogen in the biochar.

Table 5 – Solubility of N in composites and fertilizers in water and in a 6 mol l^{-1} HCl solution.

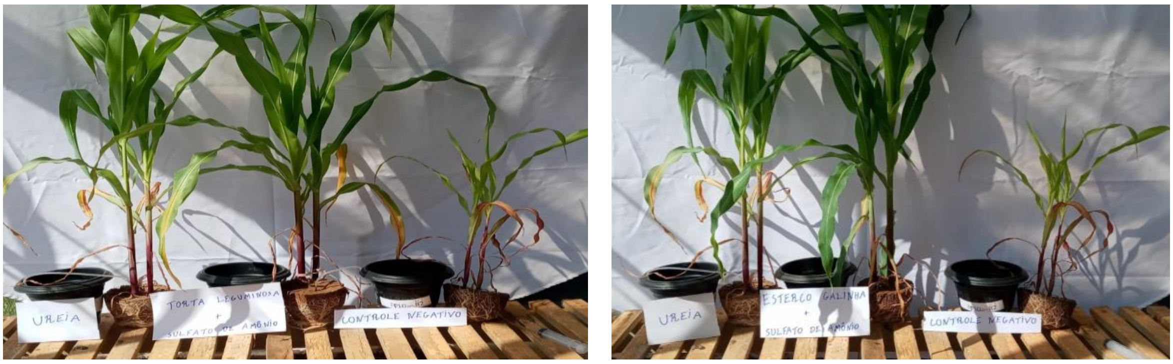
N source	N as ammonium soluble in water (%)	N solubility in HCl solution (%)
BLCAS*	6.72	10.45
BCMAS	8.57	14
BLCDAP	4.80	8.66
BCMDAP	6.07	9
BLCUR	0.19	4.55
BCMUR	0.22	7.57
UREA	0.43	-
BLC	0.01	0.65
BCM	0.01	1.24
AS	3.21	-
DAP	1.22	-
Biochar with H_3PO_4	0.09	0.69
Biochar with H_2SO_4	0.18	0.37

*BLCAS = Leguminous cake biochar + ammonium sulfate; BCMAS = Chicken manure biochar + ammonium sulfate; BLCDAP = Leguminous cake biochar + DAP; BCMDAP = Chicken manure biochar + DAP; BLCUR = Leguminous cake biochar + urea; BCMUR = Chicken manure biochar + urea; Urea = Positive Control; BTL = Leguminous cake biochar; BEG = Chicken manure biochar; SA = Ammonium sulfate; DAP = diammonium phosphate.

4.7 Agronomic effectiveness of composites

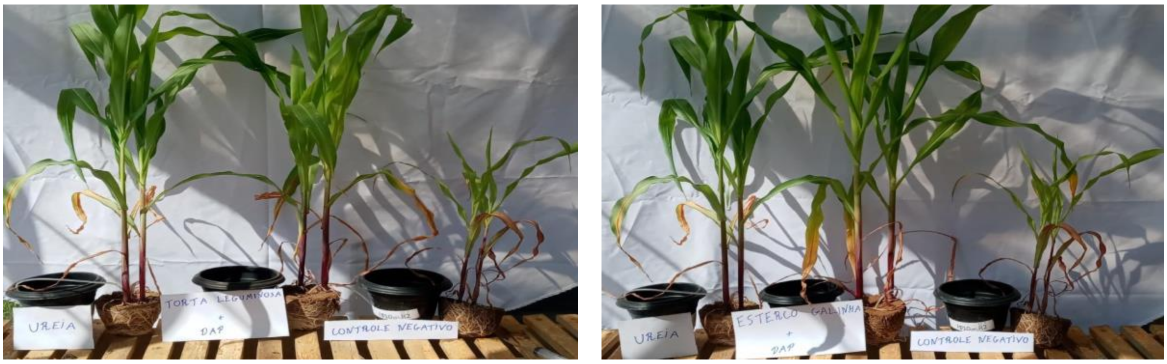
28/03 17/04 26/04 05/05 16/05

Figure 4 – Growth stages of maize plants throughout the experiment.



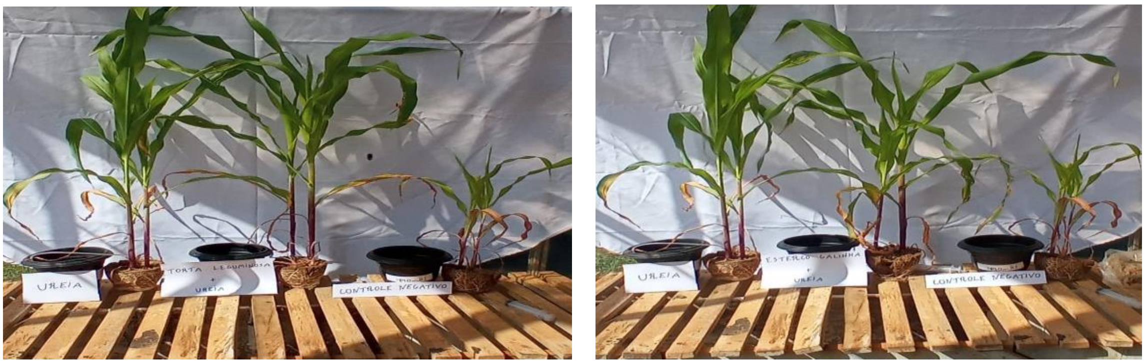
T1 - BLCAS

T2 - BCMAS



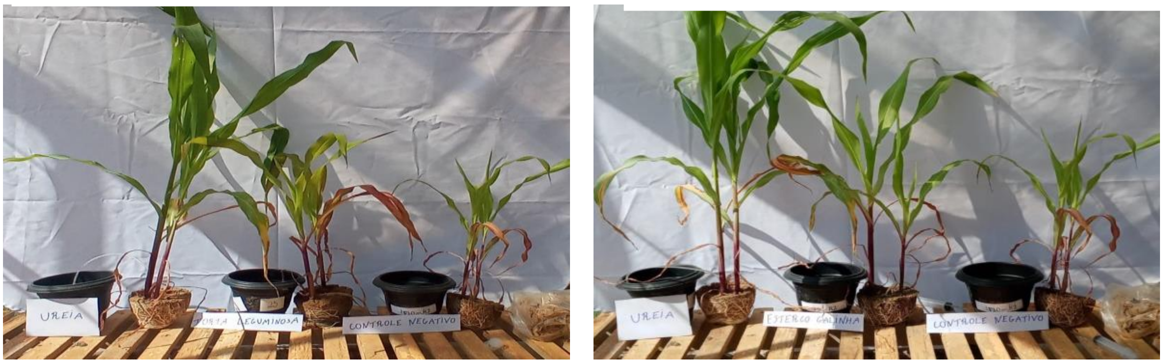
T3 - BLCDAP

T4 - BCMDAP



T5 - BLCUR

T6 - BCMUR



T8 - BLC

T9 - BCM

Figure 5 – Differences in growth among treatments and N sources. The plant on the left refers to the positive control (urea) and the one on the right refers to the negative control (without N).

After the entire experiment has been conducted (figures 4 and 5), the treatment means of maize shoot and root were compared using the Tukey test (*$p < 0.05$*), thus, the agronomic effectiveness of composites in nourishing plants was evaluated. It was observed that all composites did not differ regarding the dry matter production. Considering the maize growth, the biochar-N composites did not differ from the urea-N fertilized plants, despite urea-N being applied in three topdressing fertilizations, and the DAP-biochar composite added to soil only 270 mg kg^{-1} N. The composites have an advantage over the exclusive use of urea to fertilizer maize. They do not require splitting fertilization, unlike urea, which was divided into planting fertilization and two additional top-dressings fertilizations. Regarding DAP-biochar composites, the supply of 270 mg kg^{-1} N was enough to meet the maize nutritional requirement. Thus, at this dose, the similar dry matter was obtained with DAP-composites, compared to the other N sources, eliminating the need to add to soil 400 mg kg^{-1} N, which was supplied by the other N sources. Laird et al. (2010) and Liao et al. (2018) observed similar results, where an increase in the dose of nitrogen fertilizer increased N leaching, reducing N use efficiency by plants. Zheng et al. (2017) demonstrated that the N use efficiency by combining biochar with DAP was higher than the exclusive use of urea. All composites and the positive control (urea) statistically differed from treatments in which pure biochars without N doping were used to nourish maize plants, i.e., without adding mineral N. This implies that the pure biochars provided almost no readily soluble N to maize, meaning that the N chemical species in them are not available in the short term for plants, contrasting with the soluble synthetic N sources mixed with biochars. The exclusive use of biochar as an N source surpasses the maize dry matter production observed for the treatment where no N was added to Oxisol. The results reported in this study are in line with those published by Feng et al. (2021), who found that the use of N-enriched biochar, even at a lower dose, resulted in greater dry matter than of plants treated with biochar without N application (Figure 6).

Regarding root dry matter, it was observed that they did not statistically differ concerning the sources and the absence of N addition. The root:shoot dry matter ratio increased with the low and insufficient N supply to maize, i.e., in treatments with biochars and in soil not treated with N (negative control). Differences related to low nitrogen availability throughout the experiment were observed. Treatments with a low root/shoot ratio provided high maize dry matter production. In contrast, the treatments that increased this ratio had proportionally lower maize biomass (use of raw biochars and cultivation without N addition to Oxisol). In soil with reduced N availability, root proliferation prevails at the expense of shoot growth to increase the acquisition of less available N by plants in the growing medium. Thus, high proliferation of roots did not assure greater plant growth and yield (Figure 7). These results align with those reported by Chimento et al. (2015) and Somenahally et al. (2020), who reported an increased root proliferation in plants fertilized with biochar due to reduced N availability in the growing medium.

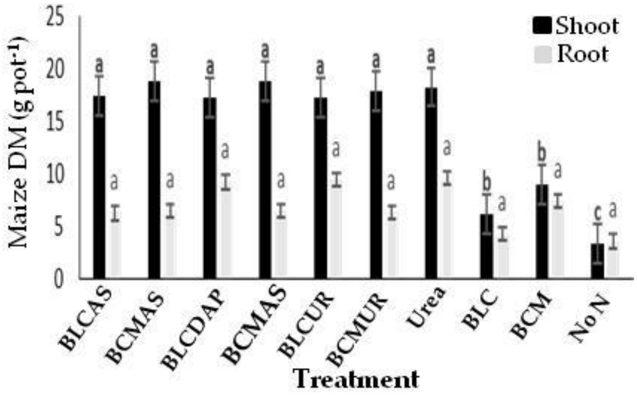


Figure 6 – Maize dry matter production (shoot and root) related to using raw biochar, urea and composites as sources of N to plants. Treatment means followed by the same letter did not differ statistically regarding dry matter production according to the Tukey test ($p < 0.05$). BLCAS = Legume cake biochar + ammonium sulfate; BCMAS = Chicken manure biochar + ammonium sulfate; BLCDAP = Legume cake biochar + DAP; BCMDAP = Chicken manure biochar + DAP; BLCUR = Legume cake biochar + urea; BCMUR = Chicken manure biochar + urea; UREA = Positive control; BLC = Legume cake biochar; BCM = Chicken manure biochar; NO N = Negative control.

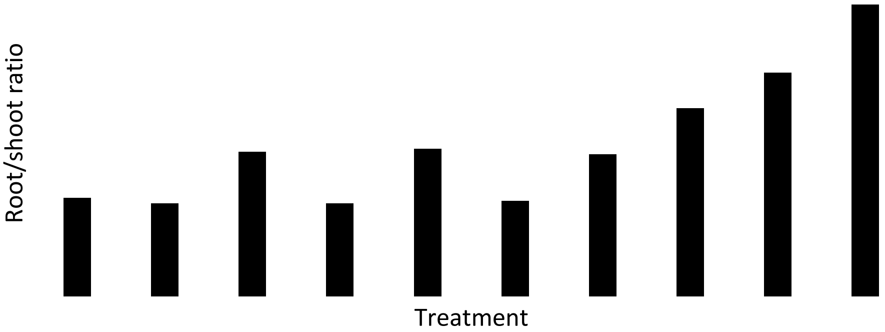


Figure 7 – Root/shoot dry matter ratio as a function of the use of urea, pure biochars and composites as N sources for maize plants. BLCAS = Legume cake biochar + ammonium sulfate; BCMAS = Chicken manure biochar + ammonium sulfate; BLCDAP = Legume cake biochar + DAP; BCMDAP = Chicken manure biochar + DAP; BLCUR = Legume cake biochar + urea; BCMUR = Chicken manure biochar + urea; UREA = Positive control; BLC = Legume cake biochar; BCM = Chicken manure biochar; NO N = Negative control.

4.8 N in maize shoot

Regarding the accumulation of N in the above-ground part of maize, it was observed that all composts had values between 0.17 and 0.25 g pot^{-1}, indicating that even in higher N rates (400 mg kg^{-1} instead of 270 mg kg^{-1}), the plants did not uptake the excessive levels of N added to Oxisol. A lower accumulation of N in maize plants fertilized with biochar without N doping, compared to other N sources (Table 6).

Table 6 – N accumulation in maize shoot.

Treatment	N in maize shoot (g/pot)
BLCAS*	0.25
BCMAS	0.24
BLCDAP	0.17
BCMDAP	0.23
BLCUR	0.21
BCMUR	0.23
UREA	0.18
BLC	0.03
BCM	0.08
No N	0.01

*Treatments refer to: BLCAS = Biochar from legume cake + ammonium sulfate; BCMAS = Biochar from chicken manure + ammonium sulfate; BLCDAP = Biochar from legume cake + DAP; BCMDAP = Biochar from chicken manure + DAP; BLCUR = legume cake biochar + urea; BCMUR = chicken manure biochar + urea; UREA = positive control; BLC = Biochar from legume cake; BCM = Biochar from chicken manure; No N = negative control.

5. CONCLUSIONS

The composites differ from pure biochars in terms of total nitrogen content, nitrogen solubility, and their ability to supply nitrogen to maize plants. These composites proved to be as efficient as urea in providing nitrogen and promoting robust maize growth. Relying solely on biochars without mineral nitrogen is not an effective strategy for ensuring vigorous maize growth. Maize dry matter produced using nitrogen from chicken manure and biochars derived from leguminous cake, or solely from the nitrogen available in Oxisol (the negative control), yielded only 32-40% of the total dry matter obtained when using composites and urea as nitrogen sources for maize. The accumulation of nitrogen in maize shoots serves as an index capable of predicting maize dry matter production. The advantages of using composites as nitrogen sources are associated with their application in a single dose, the cycling of organic residues, the prevalence of nitrogen in ammonium rather than nitrate form, and a greater presence of nitrogen soluble in water and HCl 6 mol l^{-1} compared to nitrogen chemical species prevalent in raw biochars. A lower dose of 270 mg kg^{-1} nitrogen for the chicken manure-DAP composite provided the same maize dry matter yield as 400 mg kg^{-1} nitrogen supplied by urea and other nitrogen-biochar-formulated composites. It is necessary to investigate the influence of carbon content and the dynamics of mineral nitrogen release by biochars in Oxisol solution on nutrition and maize growth, as well as the nitrogen use efficiency from composites by maize plants cultivated under field conditions.

6. FINAL REMARKS

Through the study in question, it was possible to observe both the behavior of biochar-N composites as fertilizers during maize cultivation and to gain a better understanding of the production process of biochars enriched with mineral nitrogen, the agronomic value of which remains relatively unknown. Regarding the use of composites as fertilizers, their advantage lies in their single application compared to conventional nitrogen fertilizers, such as urea. The kinetics of nitrogen release in the soil solution confirmed that biochars release nitrogen as nitrate and ammonium at a slower rate than mineral nitrogen fertilizers. Further studies in this direction would be beneficial, especially to assess nitrogen losses throughout the maize cycle, with a particular focus on the acidification process designed to reduce ammonia volatilization, as well as to better understand the ammonium/nitrate ratio for improved nitrogen use by the plant. A comprehensive field study across a complete crop cycle would also be valuable, particularly to observe if the nitrogen release kinetics over an extended period are linked to the plant's nutrient demand at different growth stages. It is also important to mention that phosphorus (P) and sulfur (S) were added to the pots at optimal levels. However, these nutrients are also present in the composites, and they may have influenced maize dry matter production. Further studies in this direction are necessary to explore the potential impact of these nutrients in the composites on maize growth.

Regarding the composite production process, the study revealed how different feedstocks and their derived biochars behave differently in terms of releasing nitrogen to plants, as well as the procedure of their acidification, appropriate concentrations of strong acids to obtain a final composite with an adequate pH range, nitrogen content, and pattern of nitrogen release coupled with the nitrogen required by maize plants. This study also discussed the effect of pre-acidification of feedstocks on other biochar properties (ash, yield, electrical conductivity, etc.). It is also important to highlight that since the carbon footprint of synthetic mineral fertilizers is very high, it is reasonable to synthesize nitrogen composites from biodigester slurry, wastewater, manure from intensive animal production systems, residues of animal origin rich in nitrogen, etc., so that the formulated fertilizers are categorized as bio-inputs and sources of organic and biologically-based nutrients. New combinations should be evaluated, including different acids, biomasses, and mineral fertilizers, aiming to produce composites that fulfill their purpose and contribute to the use of nitrogen in the soil-plant system with higher agronomic efficiency than synthetic nitrogen fertilizers. The present work has been submitted to the journal 'AppliedChem' for publication.

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